



Strasbourg (France)

E-MRS Spring Meeting 2002
June 18 - 21, 2002

SYMPOSIUM L

Crystal Chemistry of Functional Materials II

Symposium Organizers:

Peter Majewski, MPI Stuttgart, Germany

Amparo Fuertes, CSIC, Barcelona, Spain

Rudi Cloots, University Liege, Belgium

Papers will be published in *Crystal Engineering*

SYMPOSIUM L

E-MRS 2002 SPRING MEETING

SYMPOSIUM L

Tuesday, June 18, 2002

Mardi 18 juin 2002

Morning

Matin

Session I

- L-I.1** 9:00 THE DIFFERENT ROUTES TO FERROMAGNETISM AND METALLICITY IN MANGANITES
B. Raveau, C. Martin, A. Maignan, S. Hebert and M. Hervieu, Laboratoire CRISMAT, ISMRA/CNRS, UMR 6508, 6 Boulevard du Maréchal Juin, 14050 Caen cedex 4, France
 Ferromagnetism and/or metallic conductivity can be induced in perovskite manganites, either by A-site or by Mn-site substitutions. Two examples of very recent studies of Mn site doping open new routes for the development of such properties.
 The first example deals with the substitution of different M cations for Mn in LaMnO_3 ($M = \text{Li, Zn, Ni, Co, Ga, Rh}$). It shows that ferromagnetism can be induced in this structure, but not metallicity by replacing Mn^{3+} by cations with a smaller valency (valency effect), whatever their electronic configuration. A similar effect is described by introducing a manganese deficiency in the structure. The second example concerns the doping of the charge ordered CE-type antiferromagnet $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with different elements, showing that two classes of materials can be generated. The first class corresponds to the formation of spin glass insulators and is obtained for dopants without d orbitals or with d^0 or d^{10} orbitals ($M = \text{Al}^{3+}, \text{Mg}^{2+}, \text{Sc}^{3+}, \text{Ti}^{4+}, \text{Ga}^{3+}, \text{In}^{3+}, \text{Sn}^{4+}$). In this class, the doping element destroys the long range charge ordering but does not participate to the ferromagnetic coupling. The second class is obtained for magnetic cations with partially occupied d orbitals ($\text{Cr}^{3+}, \text{Rh}^{3+}, \text{Ru}^{4+}$, or $\text{Ru}^{5+}, \text{Ni}^{2+}, \text{Co}^{2+}$). In these oxides the dopant participates to the band formation, broadening the bandwidth so that both, metallic conductivity and ferromagnetism are induced. It results in a dramatic modification of the magnetic phase diagrams of different systems, $\text{LnMnO}_3 - \text{CaMnO}_3$ ($\text{Ln} = \text{La, Pr, Sm}$). A particular behavior is observed for Fe^{3+} , which in spite of its d^5 configuration belongs to the first class, certainly due to the great stability of its high spin $t_{2g}^3 e_g^2$ configuration.
- L-I.2** 9:40 PHYSICAL PHENOMENA AT THE CROSSOVER FROM LOCALIZED TO ITINERANT ELECTRONIC BEHAVIOR
J. Goodenough, Texas Materials Institute, ETC9.102, University of Texas, Austin TX 78712, USA
 The transition from localized to itinerant electronic behavior is first-order. Where phase segregation occurs at too low a temperature for atomic diffusion, it may manifest itself in an oxide by cooperative atomic displacements. In single-valent compounds, these displacements may become long-range cooperative in a static charge-density wave or they may fluctuate with only short-range cooperative displacements. In a mixed-valent 2D system, a spinodal phase segregation at high temperature may order into hole-rich itinerant-electron stripes that alternate with hole-poor localized-electron stripes; in a 3D system, alternating hole-rich and hole-poor planes are encountered. Strong-correlation fluctuations in an itinerant-electron matrix account for the transition from Pauli to Curie-Weiss paramagnetism and mobile stripes appear to be responsible for the high-temperature superconductivity of the copper oxides. A dynamic phase segregation gives rise to an even richer display of phenomena in the manganese oxoperovskites where the localized to itinerant electronic transition occurs for π -bonding electrons in the presence of localized σ -bonding electrons and local Jahn-Teller site distortions may be either long-range ordered or only short-range cooperative and fluctuating in the localized-electron phase. In perovskite-related structures, modulation of the M-O-M bond angle also plays a critical role.
- 10:20 **BREAK**
- L-I.3** 10:40 MICROSTRUCTURE AND PROPERTIES OF HIGH QUALITY $\text{Sr}_2\text{FeMoO}_6$ THIN FILMS FABRICATED BY ULTRASONIC SPRAY PYROLYSIS
 J. Rager (a,c), A. Sharma(a), A. Berenov(a), L.F. Cohen(b), P. Majewski(c), **J.L. MacManus-Driscoll**(a), (a)Dept. of Materials, Imperial College, Prince Consort Rd., London, SW7 2BP, U.K., (b)Dept. of Physics, Imperial College, Prince Consort Rd., London, SW7 2AZ, U.K., (c)Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium Heisenbergstr. 5, 70569 Stuttgart, Germany
 $\text{Sr}_2\text{FeMoO}_6$ (SFMO) is a conducting ferrimagnet with an ordered double perovskite structure and a T_c of 420K. A high spin-polarisation of carriers is beneficial for the potential application of tunneling magnetoresistance. SFMO is not straightforward to fabricate since, in its ordered form, it is stable within only a narrow range of reducing conditions. There are relatively few studies of high quality thin film samples. In this work, we report on the structure, microstructure and magnetoresistive properties of thin films made, for the first time, by ultrasonic spray pyrolysis.

SYMPOSIUM L

- L-I.4** 11:20 IMPURITIES AND NON STOICHIOMETRIES IN MAGNETORESISTIVE Sr₂FeMoO₆ DOUBLE PEROVSKITES
B. Jurca, P. Berthet, J. Berthon, P. Decorse, N. Dragoë, LPCES-UMR8648, Bât.414, E. Foy and A.M. Haghiri-Gosnet, IEF-UMR 8622, Bât.220, Université Paris Sud, 91405 Orsay, France
Sr₂FeMoO₆ (SFMO) exhibits extrinsic magnetoresistance in low magnetic fields and its Curie temperature is higher than 410K, both properties which make it a promising material for magnetic sensors and spin electronics devices. The preparation of this compound must be carried out under a strongly reducing atmosphere which is generally obtained by an argon-hydrogen mixture. This technique is efficient but it does not correspond to a thermodynamical equilibrium, moreover the prepared samples often contain small amounts of impurities such as SrMoO₄ or metallic iron. The presence of these impurities may modify the magnetic and transport properties of polycrystalline samples in several ways. For example, thin SrMoO₄ precipitates at the grain boundaries constitute an insulating barrier which modifies electron tunneling between SFMO grains. On the other hand, the presence of impurities is accommodated by modifications of the cation stoichiometries with Fe/Mo ratios which become different from 1. Taking into account these observations, samples with modified Fe/Mo ratios were prepared and characterized by magnetic and transport measurements. The SFMO stability and its oxygen stoichiometry have also been studied by annealing samples under controlled oxygen partial pressure.
- L-I.5** 11:40 CRYSTAL CHEMISTRY OF Sr(Fe,Mo)O₃
P. Majewski(a), J. MacManus Driscoll(b), J. Rager(a,b), F. Aldinger(b), (a)Max-Planck-Institut f. Metallforschung, Stuttgart, Germany, (b)Imperial College, London, UK
Recently, it has been reported that the ordered double perovskite SrFe_{0.5}Mo_{0.5}O₃ exhibits a large low-field room temperature magnetoresistance with a quite high Curie temperature of about 425 °C. At 1200 °C in air, the solid solubility of Mo in Sr(Fe,Mo)O_{3-x} (SFM) does not exceed 15 mol-%. SFM is in equilibrium with most of the compounds of the system SrO-Fe₂O₃-MoO₃. The oxygen content, the a axis parameter, and the resistivity of SFM increases with increasing Mo content. The oxygen analysis of SFM indicate mixed valent states of Fe (Fe³⁺/Fe²⁺) and or Mo (Mo⁶⁺/Mo⁵⁺). Magnetoresistance was not observed in SFM samples annealed in air. SFM annealed in Ar atmosphere with 5% H₂ show significantly higher Mo contents up to 50 mol-% and magnetoresistance was observed in those samples.
- 12:00 **LUNCH**

SYMPOSIUM L

Tuesday, June 18, 2002
Mardi 18 juin 2002

Afternoon
Après-midi

Session II

- L-II.1** 14:00 STRUCTURAL ASPECTS OF CHARGE ORDERING IN OXIDES: MANGANITES AND NICKELATES
J. Rodríguez-Carvajal(a), M. Daoud-Aladine(a), L. Pinsard-Gaudart(b), M.T. Fernández-Díaz(c), and A. Revcolevschi(b), (a)Laboratoire Léon Brillouin, CEA/Saclay, 91192 Gif sur Yvette Cedex, France, (b)Laboratoire de Chimie des Solides, Université Paris Sud, 91405 Orsay Cedex, France, (c)Institut Laue Langevin, 38042 Grenoble, France
 In all descriptions of electronic and magnetic properties of oxides the ionic image, attenuated with a dose of covalence, is largely used. This image is based in the following concepts: i) The breaking of the degeneracy of d levels by the crystal field, ii) the Hund rules for the intra-atomic exchange and iii) the Goodenough-Kanamori-Anderson for the magnetic interaction in insulators. These ideas allow solid state chemists and physicists to interpret qualitatively many of the electronic and magnetic properties of (mostly insulating) oxides. The ionic image is also largely used to interpret the physical properties of oxides in the boundary of a metal-insulator transition. However the phenomenon of charge localisation does not need to be at the atomic level, making the concept of ionisation state not appropriate. We shall present two family of compounds where the insulating ground state takes place through a charge ordering that cannot be interpreted in terms of integer valences. One family shows the so called charge disproportionation as observed in some Fe and Ni perovskites. There the high temperature phase is metallic (or semiconductor with a relatively high carrier mobility) and the low temperature phase is insulating, with a state that can be described as the condensation of a commensurate charge density wave, giving rise to a formal non integer valence at the transition metal ions sites. The other family is constituted by some of the nearly half-doped manganites, where formal Mn^{3+} and Mn^{4+} exist in similar proportions. We present the recent results, obtained from high resolution diffraction techniques (synchrotron radiation and neutron diffraction) in powders and single crystals, suggesting that the charge ordering is established by the formation of ferromagnetic coupled Mn-pairs with an electron confined in a kind of molecular orbital of the pair through the connecting oxygen atom.
- L-II.2** 14:40 INFLUENCE OF CATION VACANCIES ON STRUCTURAL AND MAGNETIC PROPERTIES OF $La_{1-x}MnO_{3+d}$ NANOPOWDERS
G. Dezanneau, H. Roussel, M. Audier, H. Vincent, Laboratoire des Matériaux et du Génie Physique, BP46, Domaine universitaire, 38402 Saint Martin d'Hères Cedex, France, A. Sin, Pirelli Cavi e Sistemi S.p.A., Viale Sarca 222, 20126 Milano, Italy, O. Isnard, 25 Avenue des Martyrs, BP 166, 38042 Grenoble cedex 9, France
 $La_{1-x}MnO_{3+d}$ ($x=0-0.3$) nanopowders were prepared by a new sol-gel method. From composition measurements and XRD, we can define two ranges of compositions. For $La/Mn < 0.9$, we should consider the demixtion of the powder into $La_{0.9}MnO_3$ and Mn_3O_4 phases. For $La/Mn > 0.9$, the high oxygen excess leads to consider vacancies on both La and Mn sites. Both hypotheses are supported by magnetic measurements, which show a constant Curie temperature of 295 K for $La/Mn < 0.9$, while for $La/Mn > 0.9$, the occurrence of vacancies on Mn sites progressively impedes the ferromagnetic interactions, leading to a general lowering of Curie temperatures. Combined X-ray/neutron Rietveld refinements have been used to quantify the amounts of vacancies on both La and Mn sites. Results obtained are in good agreement with composition measurements and show that the diminishing Curie temperature can be related to an increasing amount of vacancies on Mn site. In the extreme case of the $La_{0.93}Mn_{0.93}O_3$ compound, a cluster-glass behaviour is observed. Finally, neutron diffraction has been performed as a function of temperature in order to determine the nature of magnetic interactions for all compositions. For ferromagnetic compounds the magnetic moment lays in the [012] direction of the hexagonal R-3c cell, corresponding to direction [100] in the ideal cubic perovskite. For the cluster-glass compound, no magnetic contribution has been observed, which may indicate a very small size for ferromagnetic clusters.
- L-II.3** 15:00 HEXAGONAL RARE EARTH (R = EU-DY) MANGANITES: XRD AND HREM STUDY OF EPITAXIALLY STABILIZED FILMS
A.A. Bosak(a,b), I.E. Graboy(b), C. Dubourdieu(a), J.-P. SÈnateur(a), O.Yu. Gorbenco(b), A.R. Kaul(b), H.W. Zandbergen(c), V.L. Svechnikov(c), (a)Laboratoire des Matériaux et du Génie Physique, INPG, BP 46, 38402 St. Martin d'Hères, France (b)Department of Chemistry, Moscow State University, 119899 Moscow, Russia, (c) National Centre for HREM, Laboratory of Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, Netherlands
 Epitaxial thin films of $R MnO_3$ (R = Sm, Eu, Gd, Dy) were prepared using liquid injection MOCVD. The formation of high-temperature hexagonal modification of $Dy MnO_3$ and non-existing as bulk hexagonal $Eu MnO_3$ and $Gd MnO_3$ was observed on $ZrO_2(Y_2O_3)$ (111) substrates at 900°C due to epitaxial stabilization. XRD patterns of 100-nm-thick films $Dy MnO_3$, $Gd MnO_3$ and $Eu MnO_3$ deposited on $ZrO_2(Y_2O_3)$ (111) are essentially different from those on perovskite substrates or $ZrO_2(Y_2O_3)$ (001), observed reflections are typical for hexagonal $Lu MnO_3$ -type structure. The hexagonal phases appear as c-oriented with strict epitaxial relations. All films are stretched in plane, as follows from XRD data, but the unit cell volume remains close to that extrapolated from data for heavier rare earths. The hexagonal phase grew in the vicinity of interface and the perovskite component formed in the upper part of the film. The details of films structure were studied by HRTEM and electron diffraction. High epitaxial quality of films and the absence of extra simple oxides (R_2O_3 , Mn_3O_4) are proven. Domain structure and stacking faults are evidenced. Following our estimations, the energy gap between hexagonal and perovskite phases does not exceed 10 kJ/mole, and the latter is stabilized by the free energy gained from diminishing the surface energy term due to coherent interface formation.
- 15:20 **BREAK**

SYMPOSIUM L

Session III

- L-III.1** 15:40 **PEROVSKITE MANGANITES AND LAYERED COBALTITES POTENTIAL MATERIALS FOR THERMOELECTRIC APPLICATIONS.**
A. Maignan, S. Hebert, Li Pi, D. Pelloquin, C. Martin, Laboratoire CRISMAT, ISMRA/CNRS, UMR 6508, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex 4, France
 Thermoelectric (TE) generators are non polluting devices to convert heat energy to electrical energy by using waste heat of engines or factories. TE conventional materials are not suitable for high T applications but metal-transition oxides are very promising candidates. On the one hand, the n-type part of these devices could be played by electron-doped perovskite manganites such as $\text{Ln}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x \sim 0.9$ (Ln = lanthanide). On the other hand, the role of p 'leg' of these TE generators could be played by 'misfit' layered cobaltites. At room temperature, these manganites and cobaltites with low resistivities (ρ), exhibit large thermopower (S) and low thermal conductivity (κ). We show that the best figures of merit, $Z = S^2/\rho\kappa$, are obtained for $\text{CaMn}_{1-y}\text{M}_y\text{O}_3$ ($y = 0.04-0.06$ and $M = \text{Ru}^{5+}/\text{Mo}^{6+}$) and Pb-based misfit cobaltites. For the manganites, substitution at the B-site of the perovskite of a M cation with a higher oxidation state than tetravalent allows to create a small concentration of electron carriers without increasing the thermal conductivity as much as in the series of $\text{Ln}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \sim 0.90$). Among the misfit cobaltites based on Bi, Tl or Pb, the best TE properties have been found in the $[\text{Pb}_{0.4}\text{Co}_{0.6}\text{Ca}_2\text{O}_3]_{\text{RS}}[\text{CoO}_2]_{1.6}$ compound where RS stands for the three Rock-Salt type layers intergrown with one $[\text{CoO}_2]$ layer made of edge-shared CoO_6 octahedra and where 1.6 qualifies the incommensurable-nature of the structure. High temperatures measurements confirm the good TE properties up to 800 K.
- L-III.2** 16:20 **PEROVSKITE MANGANITES: POTENTIAL MATERIALS FOR MAGNETIC COOLING AT OR NEAR ROOM TEMPERATURE**
Yunhui Xu, P. Das, M. R. Koblischka, U. Hartmann, Institute of Experimental Physics, University of Saarbrücken, 66041 Saarbrücken, Germany, and M. Meier, Institute of Technical Physics, University of Saarbrücken, 66041 Saarbrücken, Germany
 Perovskite manganites are known as the functional materials of colossal magnetoresistance and used as magnetic sensors. We report on the synthesis and the crystal-structural characterization of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$, and $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ polycrystalline bulk materials. Detailed measurements of the magnetization as function of temperature and magnetic field for these manganite bulk samples were carried out. Significant entropy changes near the Curie temperatures are obtained from the magnetization data. The specific heat changes of these samples near their phase transition temperatures are derived from magnetic measurements. Our results and the relevant data from various references are summarized. Furthermore the magnetocaloric effects and potential applications in magnetic cooling of these materials are evaluated.
- L-III.3** 16:40 **CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF $\text{Nd}_{1-x}\delta_x\text{MnO}_3$ PEROVSKITE $x < 0.15$**
N. Ihzaz(a), S. Zemni(a), J. Dhahri(a), H. Vincent(b), M. Oumezzine(a), (a)Laboratoire de Physico-Chimie des Matériaux, Faculté des Sciences de Monastir, 5019 Monastir, Tunisie, (b)Laboratoire des Matériaux et de Génie Physique, ENSPG, BP 46, 38402 Saint Martin d'Hères cedex, France
 A comparative study on magnetic properties has been performed for A-site substituted perovskites $\text{Nd}_{1-x}\delta_x\text{MnO}_3$ ($0 < x < 0.15$), where δ is a vacancy. The samples were prepared by standard ceramic technology. The phase composition and lattice parameters were controlled by X-ray diffraction. All the compounds crystallize in a pure single phase perovskite-type with orthorhombic space group Pnma. The magnetization measurements suggest the coexistence of ferromagnetic and antiferromagnetic interactions. At low temperature the spontaneous magnetization evolution can be well understood by the forming of a canted ferrimagnetic arrangement on Mn and Nd sites. Neutron diffraction study confirming this interpretation is in progress.

SYMPOSIUM L

Wednesday, June 19, 2002
 Mercredi 18 juin 2002

Afternoon
 Après-midi

Session IV

- L-IV.1** 14:00 **GROWTH OF MgB₂ THIN FILM BY PULSED LASER DEPOSITION**
M. Ionescu, J. McKinnon, A. V. Pan, D. Q. Shi, A. Li and S. X. Dou, Institute for Superconducting & Electronic Materials, University of Wollongong, NSW 2522, Australia
 The recent discovery of metallic-like superconductivity in bulk MgB₂ material [1] opened a new class of possible applications in current transport, magnetic field devices and electronic devices. Fabrication of thin films is essential in order to explore the device applications, and in spite of a few reports [2,3,4], this still remains a challenge. The main reasons for this are the high vapour pressure of Mg even at low temperatures, and the high susceptibility of Mg to oxidation. A number of c-axis oriented MgB₂ films were grown on Al₂O₃ (1102) and MgO (100) substrates under different growth conditions, using a stoichiometric target. The morphology of the films was characterised by AFM and SEM. Also, the phase and the orientation relative to the substrate were investigated by X-ray diffraction, and superconducting properties by SQUID magnetometer.
 [1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani and J. Akimitsu, Nature 41, 63, (2001)
 [2] C. B. Eom, M. K. Lee, J. H. Choi, L. Belenky, X. Song, L. D. Cooley, M. T. Naus, S. Patnaik, J. Jiang, M. Rikel, A. Polyanskii, A. Gurevich, X. Y. Cai, S. D. Bu, S. E. Babcock, E. E. Hellstrom, D. C. Larbalestier, N. Rogado, K. A. Regan, M. A. Hayward, T. He. J. S. Slusky, K. Inumaru, M. K. Haas and R. J. Cava, Nature, 411, 558, (2001)
 [3] W. N. Kang, H.-J. Kim, E.-M. Choi, C. U. Jung, S.-I. Lee, Science, 292 no.5521, 1521, (2001)
 [4] X. H. Zeng, A. Sukiasyan, X. X. Xi, Y. F. Hu, R. Wertz, Q. Li, W. Tian, H. P. Sun, X. Q. Pan, J. Lettieri, D. G. Schlom, C. O. Brubaker, Z.-K. Liu, Q. Li, Appl. Phys. Lett. 79, 12, 1840, (2001)
- L-IV.2** 14:40 **KINETIC STUDIES FOR THE FORMATION AND SUPERCONDUCTING PROPERTIES OF Tl-1223 FILMS PREPARED BY SPRAY PYROLYSIS**
S. Phok(a), D. De-Barros(b), C. Peroz(c), P. Tixador(c), F. Weiss(b), Ph. Galez(a) and J.L. Jorda(a), (a)LAIMAN-Université de Savoie, B.P. 806, 74016 Annecy Cedex, France, (b)LMGP, INPG, 38402 St. Martin d'Hères Cedex, France, (c)CNRS/CRTBT-LEG, B.P. 166, 38042 Grenoble Cedex 09, France
 Tl-1223 superconducting thick films with J_c, measured by a screening method, as high as 1 MA/cm², have been prepared in a two step process: the precursor “Ba/ sub 2/Ca/ sub 2/Cu/ sub 3/O/ sub x/ ” was first sprayed on an AlLaO/ sub 3/ substrate at high temperature and further ex- situ thallinated, following a procedure already applied for bulk sample.
 The kinetic for the formation of the superconducting phase has been studied in order to control the grain growth and to precise the conditions for optimum superconducting properties. The effects of doping elements on crystallization and microstructure are also analyzed.
- L-IV.3** 15:00 **A STUDY OF GRAIN ORIENTATION OF ALKALI DOPED POLYCRYSTALLINE YBCO CERAMICS USING AN EBSD TECHNIQUE**
A. Koblishka-Veneva, F. Mücklich, Institute of Functional Materials, University of the Saarland, P.O. Box 151150, 66041 Saarbrücken, Germany and M.R. Koblishka, Institute of Experimental Physics, University of the Saarland, P.O.Box 151150, 66041 Saarbrücken, Germany
 Electron backscatter diffraction (EBSD) provides a method for measuring a large number of individual grain orientations and relating them directly to the microstructural features.
 We have established a sample polishing procedure to obtain intense Kikuchi patterns without an additional carbon coating of YBCO ceramic superconductors. We have successfully obtained Kikuchi patterns on polycrystalline, bulk high-T_c superconductors (Rb₂CO₃-, K₂CO₃-, KClO₃-doped and undoped YBa₂Cu₃O_x).
 We present Kikuchi patterns, pole figures and orientation maps of the samples. It is shown that the samples with Rb₂CO₃ and K₂CO₃ additives do not exhibit a very pronounced texture (i.e. preferred orientation). On the polycrystalline KClO₃-doped YBCO samples we find two major grain orientations (0 0 1) and (1 0 0) normal to the sample surface, while the pure sample does not exhibit any orientation maxima. This observation is ascribed to the effect of a liquid phase due to the KClO₃-additive during the preparation process.
- 15:20 **BREAK**

Session V

- L-V.1** 15:40 **RECENT ADVANCES IN OVERPRESSURE PROCESSING 2223 BSCCO WIRE**
E.E. Hellstrom(a), Y. Yuan(a), J. Jiang(a), X.Y. Cail(a), D.C. Larbalestier(a) and R.K. Williams(b), (a)Applied Superconductivity Center, University of Wisconsin-Madison, Madison WI 53706, USA, Oak Ridge National Laboratory, Oak Ridge TN 37831, USA
 At present several manufacturers worldwide produce long lengths of 2223 BSCCO wire that have been used to build demonstrator motors, generators, faculty current limiters, and transmission cables. It is thought that the critical current density of 2223 wires can increase significantly because only a fraction of the 2223 oxide core carries super current due to poor connectivity between the grains. Overpressure (OP) processing can remove the pores and may heal cracks, which should improve the overall current density. In addition, OP processing may be a single step processes to make 2223 wires. We will compare the microstructure of the 2223 core in wire processed at 1 bar total pressure and in at ~150 bar in the OP system. The 2223 core densifies during overpressure processing at pressures ranging from ~125 to 180 bar (180 bar is the highest pressure used in the OP system). The lower pressure limit at which OP processing densifies the 2223 core will be reported. Critical current densities will be reported on OP processed multifilament and monocoil wires.

SYMPOSIUM L

- L-V.2** 16:20 **THE ND₁₂₃SS SOLID SOLUTION**
Philippe Galez, Christiane Bertrand and Joel Le Roy, LAIMAN-ESIA, Université de Savoie, BP 806, 74016 Annecy, France
The Nd(Ba_{1-x}Nd_x)₂Cu₃O_{7+d} solid solution, Nd₁₂₃ss, has been investigated by neutron powder diffraction combined with Rietveld analysis. It is confirmed that the crystal structure of its Nd-rich limit, Nd(Ba_{0.55}Nd_{0.45})₂Cu₃O_{7.33}, is satisfactorily described in space group Bmmm (a = 7.7679(3) Å, b = 3.8538(2) Å, c = 22.959(1) Å) with a four-fold superstructure with respect to the orthorhombic cell of YBCO, due to ordering between Ba and Nd atoms in the bridging layer. However, differences with previous works [1] are encountered. They concern exclusively the distribution of O atoms in the $\frac{1}{2}$ chain layer. Bond strength calculations following the method given by Brown [2] show that charge transfer from the $\frac{1}{2}$ chains to the planes is not sufficient to induce superconductivity and agree well with a model by Kramer et al [3]. Our results also give strong indications that ordering also occurs for lower Nd contents.
[1] V.V. Petrykin, P. Berastegui, M. Kakihana, Chem. Mater. 11 (1999) 3445
[2] I.D. Brown, J. Solid State Chem. 90 (1991) 155
[3] M.J. Kramer, S.I. Yoo, R.W. MacCallum, W.B. Yelon, H. Xie, P. Allenspach, Physica C 219 (1994) 145
- L-V.3** 16:40 **STUDY OF THE BaO-CuO-O SYSTEM**
T.K. Jondo, Université du Bénin, BP 418, Lomé, Togo; S. Phok, P. Galez and J.L. Jorda, LAIMAN-Université de Savoie, BP 806, 74016 Annecy Cedex, France
The BaO-CuO-O system has been investigated by differential thermal analysis coupled to a thermogravimetry, and high temperature x-ray diffraction in oxygen flowing conditions. The starting materials, barium peroxide and copper oxide have been selected in order to avoid carbonate impurities and to favour the formation of the over-oxidized Ba₂/CuO_{3+x} and Ba₂/Cu₃O_{5+y} phases. The results may be summarized in the following:
- We did not find structural changes for Ba₂/CuO_{3+y} up to the decomposition temperature T=1288 K.
- BaCuO₂ is the only phase belonging to the BaO-CuO isoplethic line and was found to be congruent melting at 1311 K.
- Oxygen is removed from Ba₂/Cu₃O_{5+y} at 1083 K. The low oxygen content Ba₂/Cu₃O_{5+z} is then decomposed, forming BaCuO₂ and CuO at 1166 K.
The formation and phase relationship are described and compared with thermodynamic calculations from literature.

SYMPOSIUM L

Thursday, June 20, 2002
 Jeudi 20 juin 2002

Morning
 Matin

Session VI

- | | | |
|---------------|-------|--|
| L-VI.1 | 9:00 | <p>'A' CATION CONTROL OF PEROVSKITE PROPERTIES
 J. Paul Attfield, Dept. of Chemistry and IRC in Superconductivity, University of Cambridge, UK
 The materials properties of many ABO₃ perovskites result primarily from the B cations, but are tuned by the cation(s) at the A sites. Notable examples are ferroelectric titanates, magnetoresistive manganites, and layered A₂BO₄ type superconducting cuprates. The A cation control of these properties can be described through a simple ionic approach by considering the sizes and charges of the A cations. The size control is approximated well by the mean A cation radius, equivalent to the traditional perovskite tolerance factor, and the size variance which describes the mismatch in ionic radii. Studies in recent years have shown that the latter term is extremely significant; ferroelectric, ferromagnetic, superconducting and structural transition temperatures all vary linearly with the size variance. A variance vs. size plot defines the 'chemical window' which enables property variations to be displayed usefully. The control of phase separation phenomena in manganite perovskites and 1/8 doped La₂CuO₄ type materials has also been investigated.</p> |
| L-VI.2 | 9:40 | <p>STRUCTURE-PROPERTY RELATIONSHIPS OF UNDOPED AND DOPED HEXAGONAL BaTiO₃
 Derek C Sinclair, Department of Engineering Materials, Sir Robert Hadfield Building, University of Sheffield, Mappin Street, Sheffield S11 9QT, United Kingdom
 Ferroelectric BaTiO₃-based ceramics find applications in capacitors, thermistors and piezo-electric devices, and form the cornerstone of the electroceramics market. Although the electrical properties of tetragonal BaTiO₃ and doped t-BaTiO₃ have been widely studied, their defect chemistry is complex and poorly understood. In addition, very little is known about the high temperature, hexagonal (6H) polymorph, h-BaTiO₃ which exists only at temperatures > 1460 °C for undoped samples prepared in air. In this paper we present structure-property relationships for undoped and doped h-BaTiO₃ ceramics from experimental studies conducted in our laboratories. Oxygen-deficient (undoped) materials were prepared by reduction of stoichiometric t-BaTiO₃ in a vacuum furnace at temperatures above 1300 °C and under an oxygen partial pressure of 0.1 mbar. The 6-H structure is retained throughout where partial reduction of Ti^{IV} to Ti^{III} is accompanied by the formation of oxygen vacancies in the h-BaO₃ layers which separate pairs of occupied face-sharing octahedra, Ti₂O₆ and h-BaTi^{IV}_{1-x}Ti^{III}_xO_{3-x/2} (0 < x < 0.30). There is no evidence of oxygen vacancies associated with corner sharing TiO₆ octahedra. The Ti-Ti separation within face sharing dimers increases from 2.690(4) Å for x = 0 to 2.7469(30) Å for x = 0.30. BaTiO_{2.85} (x=0.30) is a band-gap semiconductor at 300K with a resistivity of 1 ohm.cm and an activation energy of 0.16 eV. A switch in conduction mechanism to variable range hopping of electrons between Ti^{III} and Ti^{IV} ions occurs on cooling below 240K.
 The solid solution limits and crystal chemistry of a wide range of doped h-BaTiO₃ (Mg, Zn, Al, Ga, Cr, Mn, Fe, Co, Ni, Co) prepared by the mixed oxide route and heated in air will be discussed. In contrast to undoped materials, most doped materials are dielectric at room temperature with permittivities in the range 40 –100. Several of the doped materials resonate at microwave frequencies which may lead to applications of h-BaTiO₃-based materials as microwave filters.</p> |
| | 10:20 | BREAK |
| L-VI.3 | 10:40 | <p>BASIC STRUCTURAL PRINCIPLES OF MINERALS: SOME EXAMPLES FOR THE RELATION BETWEEN STRUCTURE AND PROPERTIES
 Ekkehart Tillmanns, Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, Althanstr. 14, 1090 Wien, Austria
 Many oxide or sulfide mineral structures are based on more or less distorted close-packed arrangements of anions with cations occupying octahedral or tetrahedral voids. In close-packed oxygen atom layers oxygen can also in part be exchanged by cations of comparable size like barium. Examples are perovskite and the perovskite-related barium titanate compounds in the binary system BaTiO₃ - TiO₂, most of which have pseudo-hexagonal cell constants close to the ideal hexagonal values.
 Among rock-forming minerals the most important ones are the silicates with SiO₄ tetrahedra as basic units which can be connected to each other via common corners in 0 to 3 dimensions as isolated tetrahedra, groups of isolated tetrahedra or rings, infinite chains, sheets or 3-dimensional frameworks.
 Many silicate minerals have important technical applications which can be directly related to their crystal structures. The sheet silicates (micas like biotite, KMg₃ (OH)₂ Si₃AlO₁₀, or muscovite, K Al₂ (OH)₂ Si₃ Al O₁₀ and clay minerals like kaolinite, Al₄(OH)₈ Si₄ O₁₀) and the microporous framework silicates (zeolites, general formula: M_x/μ Al_x Si_{1-x} O₂ · nH₂O with cations M_{μ+} and x = 0.5) are chosen as examples.</p> |
| L-VI.4 | 11:20 | <p>MÖSSBAUER-SPECTROSCOPY OF FERROMAGNETIC MATERIALS
 G. Amthauer, University of Salzburg, Austria</p> |
| | 12:00 | LUNCH |

SYMPOSIUM L

Thursday, June 20, 2002
Jeudi 20 juin 2002

Afternoon
Après-Midi

Session VII

- | | | |
|----------------|-------------|---|
| L-VII.1 | 14:00 | <p>BA-BETA-ALUMINA PHOSPHORS: CRYSTAL CHEMISTRY AND STABILITY
Matthias Goebbels, Melanie Dauscher, Lehrstuhl fuer Mineralogie, University Erlangen, Germany Thomas Juestel, Philips Research Laboratories, Aachen, Germany</p> <p>The blue luminescent composition BaMgAl₁₀O₁₇:Eu²⁺ (abbreviation BAM:Eu) is widely applied in fluorescent lamps and plasma display panels. In general, its luminescence efficiency increases with increasing Eu²⁺ concentration, since the absorption of incident UV light goes up. However, the difference of the ionic radii between Ba²⁺ and Eu²⁺ should restrict the solid solution range to an extent that the ideal Eu-end member is not reached. As a consequence of the limited solubility, in those case where a high Eu concentration is doped into the lattice, the formation of different coexisting phases will be inevitably. These phases will influence the luminescent properties of the phosphor leading to a lower efficiency and stability.</p> <p>In this study, the phase relations of the quaternary system BaO-EuO-Al₂O₃-MgO have been investigated, with a focus on the compound BaMgAl₁₀O₁₇:Eu²⁺. The solid solution series has been determined as:</p> <p>BAM Ba_{1-x}Eu_xMgAl₁₀O₁₇ 0 < x < 0.47.</p> <p>In the Al-rich part of the quaternary system different phase polyeder have been found concerning the phases alumina, spinel, EuAl₁₁O₁₈, EuAlO₃ and BaAl₂O₄. The phase relations will be elucidated and discussed in detail.</p> |
| L-VII.2 | 14:40 | <p>PHASE FORMATION AND PHASE TRANSITION OF La_{1-x}A_xCoO₃ (A = Ca, Sr) APPLIED FOR BIFUNCTIONAL AIR ELECTRODES
Anke Weidenkaff, Stefan Ebbinghaus, Solid State Chemistry, University of Augsburg, 86159 Augsburg, Germany, Thomas Lippert, Macarena J. Montenegro, Dept. General Energy Research, Paul Scherrer Institute, 5232 Villigen, Switzerland, Christian Soltmann, Roland Wessiken, Swiss Federal Institute of Technology, 8093 Zurich, Switzerland</p> <p>The electrocatalytic activity and stability of oxygen electrode catalysts that will operate in anodic and cathodic modes will be a decisive factor in the technical realization of electrically rechargeable air based batteries and in solid oxide fuel cell technologies. Suitable candidates are calcium and strontium substituted rare earth cobaltates with perovskite structure. In order to study the influence of the A cation substitution on the structure and the properties of the perovskites, cobaltate nano particles were synthesized by decomposition of amorphous citrate- and tartrate complexes.</p> <p>The metal oxide phase formation process from the amorphous precursors was investigated with high temperature X-ray diffraction (HT-XRD), extended X-ray absorption fine structure (EXAFS), thermal analysis, and high resolution transmission electron microscopy (HRTEM) methods for the perovskite-type compounds La_{1-x}(Ca, Sr)_xCoO₃ (x = 0, 0.2, 0.4 and 0.5). The HT-XRD patterns of the substituted cobaltates at different temperatures indicate significant structural changes. Transmission electron micrographs show superstructures which may be explained by oxygen-deficient domains with brownmillerite structure.</p> <p>With the developed synthesis methods, phase, particle size and surface texture of the metal oxide particles can be designed to get both a maximum surface area and a stable structure.</p> |
| L-VII.3 | 15:00 | <p>SYNTHESIS OF THE NOVEL OXIDE Ag₂Cu₂O₄ BY ELECTROCHEMICAL OXIDATION OF Ag₂Cu₂O₃ AT ROOM TEMPERATURE. A REVERSIBLE STRUCTURAL REARRANGEMENT AND REDOX CONVERSION
D. Munoz, J. Oro, P. Gomez-Romero, J. Fraxedas, N. Casan-Pastor, Instituto de Ciencia de Materials de Barcelona, CSIC, Campus UAB, 08193 Bellaterra, Barcelona, Spain</p> <p>Electrochemical oxidation of the recently reported first mixed copper silver oxide Ag₂Cu₂O₃, at room temperature, yields to a copper silver mixed oxide, formulated as Ag₂Cu₂O₄, with one more stoichiometric oxygen, that can revert in alkaline media to the original precursor Ag₂Cu₂O₃. The new oxide can also be prepared by ozonization of the precursor Ag₂Cu₂O₃ at room temperature. This phase constitutes the second existing mixed silver copper oxide. Its structure has, however, changed with metal rearrangement, involving recrystallization at room temperature in alkaline media. Oxidation states, physical properties and structural aspects will be discussed.</p> |
| | 15:20 | BREAK |
| | 15:40-18:00 | POSTER SESSION |

SYMPOSIUM L

- L/P.01** LIFETIME OF UV-DETECTORS BASED ON CdTe MONOCRYSTALS: SURFACE STRUCTURE AGING
G. Khlyap, P. Sydorhuk, State Pedagogical University, 24 Franko str., Drogobych, 82100, Ukraine
The abstract reports first data of surface structure aging of the UV-sensitive metal-semiconductor structures based on CdTe monocrystals grown by Bridgeman technology after storage under the normal atmospheric conditions during 6 months. Sensitivity of the as-grown samples was determined after the UV-irradiation by means of electric-field measurements (the device scheme is available). The electric investigations performed immediately after the samples manufacture demonstrated the space-charge-limited current, in particular, mobility regime current and velocity saturation mode of the charge carriers transport through the space charge region localized at the near-contact subsurface area were observed. The same studies carried out after the storage exhibited considerable change of the current values and charge carriers transport character: only velocity saturation mode was registered. The numerical examinations of experimental results were shown the sufficient effect of the absorption of environmental oxygen on the electric properties of examined structures: the absorption process produces additional barriers appeared on the defects of the sample surface due to formation of the monolayer native oxide and comoving fluctuations of the charge carriers concentration in the generated substructure surface defect – native oxide. Some technological recommendations concerning the device recovering are proposed.
- L/P.02** EQUILIBRIUM SELF-ORGANIZATION – EVOLUTION WAY TO EQUILIBRIUM STATE
Anatolii Ya. Gubenko, Moscow Institute of steel and alloys, Festivalnaya 17,138, Moscow 125195 Russia
It was established that transition of matter from non-or equilibrium state to new equilibrium state actually occurred not at a point, but in range of variable parameter of state (RPS), whose extension may reach a few or even tens percent. Within the RPS the electrochemical, thermodynamically properties and interatomic interaction oscillate to given alternating peaks (dips). Along the ascending and descending branches of each peak (dip) the properties and interatomic interaction vary in opposite direction. Oscillation is accompanied by a thermal effect. In some case, the endothermic effect changes to an exothermic. Such a transition from one state to another may be considered as equilibrium self-organization (ESO) of matter, i.e. a evolution process to equilibrium state. ESO is realized through sustained interaction large-scale fluctuation of various physical quantities. The fluctuation nature of the process ESO is confirmed by oscillating changes X-ray and light scattering whose intensity is proportional to the amplitude of fluctuation. Each value of parameter of state corresponding set of large-scale fluctuations which produce in the matter an oscillating sequence of microstate differing interatomic interaction and in the whole set of properties. Therefore the liquidus and solidus in any binary and multi component phase diagrams contain nonmonotonic sections which correspond to RPS on the composition-property diagrams, in particular, into fields solid (liquid) solutions. ESO take place at phase transformation.
- L/P.03** CHEMICAL DIFFUSION IN UNDOPED ZnS AND IN UNDOPED CdSe
K. Lott, T. Nirk, O. Volobujeva, Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia
Chemical diffusion is the process by which gradients in the chemical potentials of the components of a crystal are removed. Measurement of the conductivity as a function of time after change of temperature (T) and component vapour pressure (p_{Zn} or p_{Cd}) is appropriate to study chemical diffusion. Chemical diffusion as a function of T and p_{Zn} or p_{Cd} has been studied in ZnS and in CdSe single crystals at high temperature. The coefficient of chemical diffusion was found to be almost independent of component vapour pressure for undoped CdSe, at high Cd vapour pressure region, the diffusion activation energy being equal to 0.41 eV. For ZnS the data corresponding to the diffusion in increased/decreased p_{Zn} produce different D values. It implies that the diffusion coefficients of dominant point defects representing excess or deficit of Zn in ZnS are different. Chemical diffusion in ZnS is more than one order of magnitude slower than in CdSe at the same conditions. Chemical diffusion in ZnS and in CdSe is more than three orders of magnitude faster than self-diffusion in these crystals at the same conditions. It was shown that the doubly ionized interstitial component atoms (zinc or cadmium atoms) were the dominating diffusible defects in ZnS and in CdSe in chemical diffusion process at high component vapour pressure.
- L/P.04** EFFECT OF HIGH TEMPERATURE - PRESSURE ON SOI STRUCTURES
A. Misiuk, J. Ratajczak, Institute of Electron Technology, Al. Lotnikow 46, 02-668 Warsaw, Poland; I.V. Antonova, Institute of Semiconductor Physics, RAS, Lavrentieva 13, 630090 Novosibirsk, Russia; J. Bak-Misiuk, Institute of Physics PAS, Al. Lotnikow 46, 02-668 Warsaw, Poland; B. Surma, Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warsaw, Poland and J. Jun, High Pressure Research Centre, PAS, Sokolowska 29/37, 01-142 Warsaw, Poland
Effect of annealing (HT, up to 1570 K) under enhanced argon pressure (HP, up to 1.23 GPa) on silicon – on – insulator (0.4 μm thick SiO_2 layer embedded in single crystalline Si) SOI structure was investigated by TEM, X-ray, FTIR and related methods.
SOI was prepared by bonding the oxidised Cz-Si wafer with the hydrogen – implanted one and cleavage of the last by the Smart Cut method.
Numerous defects at the SiO_2 / Si boundary are created at 1400 K under HP 0.6 GPa in the case of treatment for 5 h. The HT – HP treatment results in a shift of asymmetric stretching vibration mode associated with Si-O bonds towards lower frequencies.
The effects are related to HT – HP induced changes of misfit at the SiO_2 / Si boundary. That misfit exceeds the critical value for creation of defects and so results in irreversible structural and compositional changes.
This work was supported in part by the Polish Committee for Scientific Research (grant no. 8T11B 07219, at 2000 - 2002).
- L/P.05** CRYSTAL CHEMISTRY AND GROWTH OF SINGLE CRYSTALS – A COMPARISON BETWEEN QUARTZ AND GaPO_4
K. Jacobs and P. Hofmann, Institute of Crystal Growth, Max-Born-Str. 2, 12489 Berlin, Germany
The so called Grimm-Sommerfeld phases are derived from the group IV-A elements of the Periodic Table by substituting them alternately with atoms of two elements from groups left and right equidistant to the fourth main group. The crystal structure as well as the chemical and physical properties of these phases are usually closely related to their group IV-A parents. This is not limited to the group IV elements and their binary analogues, but it is also true for more complex compounds, such as the dioxides. Thus, AlPO_4 and GaPO_4 are closely related to SiO_2 in its different modifications. Some major physical and chemical properties of these compounds will be compared to those of SiO_2 . From a technical point of view the piezoelectric material GaPO_4 is most interesting. The presence of Ga-O and P-O bonds instead of the Si-O bonds only and their deviating ionicity and bond strength give it some advantage in comparison to quartz. Most attractive are the lack of several structural phases found in SiO_2 , and the thermal stability of some properties. Despite of the similarity between GaPO_4 and SiO_2 , the negative temperature coefficient of the solubility of GaPO_4 requires significant modifications of the hydrothermal technology, how it is commonly applied for the growth of artificial quartz single crystals.

SYMPOSIUM L

L/P.06 CRYSTAL GROWTH OF STOICHIOMETRIC LiNbO_3 : PHASE EQUILIBRIA IN THE TERNARY SYSTEM $\text{Li}_2\text{O}-\text{K}_2\text{O}-\text{Nb}_2\text{O}_5$

M. Ferriol, Laboratoire de Chimie et Applications, E.A. n° 3471, Université de Metz, rue Victor Demange, 57500 Saint-Avold, France, L. Poppl, Eötvös University, Budapest, Hungary, K. Polgár, A. Péter, Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Budapest, Hungary, M. Cochez, Laboratoire de Chimie et Applications, E.A. n 3471, Université de Metz, rue Victor Demange, 57500 Saint-Avold, France

One of the effective methods of growing stoichiometric LiNbO_3 single crystals is the high temperature top-seeded solution growth from $\text{K}_2\text{O}-\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ fluxes. The composition of the obtained crystal largely depends on the choice of the starting mixture.

To optimize both crystal quality and growth conditions, the knowledge of the phase relationships in the ternary system $\text{K}_2\text{O}-\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ are required.

The purpose of this communication is to present the results obtained on the solid-liquid equilibria studied by D.S.C. (Differential Scanning Calorimetry) and RX powder diffraction in the neighborhood of LiNbO_3 . Three isopleths of the system were investigated allowing to describe the liquidus surface near LiNbO_3 and to follow the evolution of the liquid and solid phases during the crystallization of a given starting mixture.

This work was supported by the Hungarian Scientific fund OTKA No. T034176 and the by European Union under Grant No. ICA1-CT-2000-700-29

L/P.07 ON THE INTERRELATION BETWEEN MICROSCOPIC AND MACROSCOPIC PROPERTIES OF MATERIALS

Anatolii Ya. Gubenko, Moscow Institute of Steel and Alloys, Festival'naya 17–138, 125195 Moscow, Russia

In any dependence of microscopic and macroscopic properties, there exist discrete intervals of the independent variables (concentration, temperature, and time) in which the interatomic interactions and, consequently all properties of a substance vary in an oscillating manner. Such a behavior is due to the fact that these properties are formed by large-scale fluctuations. Thus, in high-purity Si, Ge, as well as in Si and Ge doped with Au or Ag at the temperatures of the maximum solubility (T_{max}) of these components, the derivatives of their concentrations, electrical conductivities, densities, and other properties with respect to the above-mentioned independent variables change their signs. In pure Si and Ge at temperatures slightly above T_{max} , the dependences of the densities and vapor pressures over these elements reproduce the course of the retrograde solidus. At $T < T_{\text{max}}$, the Au and Ag ions are negative; at $T > T_{\text{max}}$ they become positive. At $T \ll T_{\text{max}}$, in discrete intervals in which phase transformations occur, the macroscopic and microscopic properties, including the spectrum of electron levels, vary in a similar manner. In ternary systems such as Si (Ge) doped with two impurities, e.g., Au and Sb, simultaneously, there is observed a correlated variation of macroscopic properties and the energy of ionization of defect complexes formed in them, their concentrations, spectra of electron levels, and the cross section for electron capture. Similar nonmonotonic and correlated changes in macroscopic and microscopic properties were revealed in GaAs and other compounds.

The interatomic interactions suffer substantial changes in the case of ultrathin layers as compared to bulk samples. In ultrathin layers, compounds can form that are absent in bulk substances. For the same reason, ultrathin layers exhibit different catalytic effects as compared to bulk samples. The above correlated changes in the microscopic and macroscopic properties, as well as changes in the types of reactions and reaction products in solid solutions took place only if the interatomic interactions changed. An analysis showed that the regular changes in the energies of ionization in Si and other semiconductors observed by many researchers occurred only in those cases where changes in the interatomic interactions occurred in these materials. Therefore, the interpretation of changes in the electrical properties, structure of defect complexes, and other properties will be incorrect without a proper allowance for changes in the interatomic interactions.

L/P.08 NATURE OF NONMONOTONIC CONCENTRATION, TEMPERATURE, AND TIME DEPENDENCES OF PROPERTIES, Anatolii Ya. Gubenko, Moscow Institute of Steel and Alloys, Festival'naya 17–138, 125195 Moscow, Russia

It has been established that the dependences of various properties of materials in discrete intervals of temperature, concentration, and time variations change in a correlated manner. For a given material, these dependences only slightly differ, and, in extremal points of oscillations, they are close to one another. Such dependences appear due to the fact that instabilities arise in materials caused by an increase in the free energy as compared to that of a regular solution. At certain magnitudes of the instability, large-scale fluctuations (LSFs) arise in materials to produce new states in them. With the help of LSFs, the material evolves to a new equilibrium state, i.e., phase transformations occur or other similar transitions. Phase transformations may occur even if the concentration of one of the components of the material is as low as $10^{-2}-10^{-6}$ at. % in the solid phase. The phase transformations are observed in the region of existence of solid solutions irrespective of the concentrations of the components. The oscillations of properties in a discrete interval reflect the character of the evolution and the rate of changes of LSFs. Along neighboring branches of oscillations in the discrete intervals of the above-mentioned independent variables, the changes of the entire set of properties, including the entropy, occur in the opposite directions. These changes are accompanied by alternating thermal effects.

The microscopic properties such as the interatomic interactions, motion and charge of the particles of the system, spectrum of electron levels, etc., also change in the opposite directions along the oscillation branches. Despite the probabilistic nature of LSFs, the states that are formed in discrete intervals are equilibrium. All the changes in the discrete intervals are controlled by probabilistic laws, and those outside these intervals are controlled by deterministic laws. Usually, several discrete intervals exist in materials and, consequently, a periodic alternation of probabilistic and deterministic laws occurs. In some extremal points of oscillations, the maximum values of entropy exceed its value in the equilibrium state to which the evolution is directed. All the above changes also occur when the independent variable is time. Therefore, the derivative of entropy with respect to time changes its sign, and the time produces states with unique properties. Such an evolution of a transition from one state into another takes place in any substances, including systems with chemical compounds. In this case, the evolution is directed from compositions with an excess of one of the components of the compound to compositions with an excess of the other component.

SYMPOSIUM L

- L/P.09** DECOMPENSATION OF INTERATOMIC FORCES IS THE SOURCE OF INTRINSIC STRESS AND INHERENT BRITTLENESS OF COMPLEX CERAMICS
V.V. Pokropivny, Institute for Problems of Materials Science of UNAS, Kiev, Ukraine
To present time it is not clear, how interatomic forces between heterogeneous atoms in ceramics relates to each other and how to estimate the level of intrinsic stress in dependence of both a crystalline structure of compound and an electronic structure of its component atoms. In a state equation an equilibrium position $r_0 = (3V_0/4)^{1/3}$ is the same for all interactions, namely, metal (Me) - nonmetal (X), Me-Me and X-X. In the lattice mixed potentials only nearest neighbours on distance r_1 is accounted as a rule, so $r_0 = r_1$.
In this work the mutual consistent set of interatomic potentials for TiB_2 compound was designed with account of two coordination spheres. At first the pure potentials Ti-Ti, B-B and their contribution were calculated in the state equation. Then by subtracting them from an atomization energy $E_{at}(V)$, a contribution from mixed potential Ti-B and its parameters were calculated. At that $r_1 < r_0 < r_2$.
Analysis of obtained potentials show that the nearest boron atoms are repulsed and cause lattice to burst, and vice-versa, the atoms of Ti are attracted and cause lattice to compress, while the atoms Ti-B are in equilibrium. Such a behaviour consists with conventional ideas about electron charge is transferred to acceptor boron ions B⁻.
Important conclusion is followed, namely, a stability in lattice TiB_2 stems from an equilibration of ions B⁻ repulsion with ions Ti⁺ attraction. But its failure in defects and deformed regions. For example, near metallic vacancy the uncompensated bursted stress is originated from ions B⁻.
Generalizing one can deduce the fundamental principle, namely: in heteroatomic compounds an latent internal stress is evident to exist, so an inherent brittleness of ceramics is caused by discompensation of interatomic forces near defects and at deformation rather than by directivity of covalent bonds. Hence an ideal stoichiometry and purity is a condition for the embrittlement to reduce. In non-stoichiometric functional gradient compounds the latent brittleness is inevitable, though it may be negligible. The proposed method make it possible to estimate.
- L/P.10** STOICHIOMETRIC CHARACTERIZATION OF AMINE INTERCALATED LEAD IODIDE
C.C. Coleman, W. Tikkanen, H. Goldwhite, T. Berhe, B. Magness and M. Gallegos, California State University, Los Angeles, USA
The stoichiometry and some optical spectral changes of semiconducting layer structured lead iodide intercalated with methylamine and ethylamine are reported. Vapor diffused purified lead iodide was used to make powder, thick film and thin film samples. Degassed host samples were exposed to guest gas pressures ranging from 1 to 20 Torr. Mass changes were determined by quartz spring and crystal oscillator methods. The intercalation of methylamine and ethylamine into lead iodide at low pressures results in a similar uptake of these two amines of somewhat greater than 1:1 guest to lead iodide host ratio. Intercalation saturation occurs in 3 hours. Deintercalation obtained by pumping takes 15 days suggesting the intercalated state is fairly stable. Optical data were obtained using thin film host samples. Both guests produce a 0.46 eV increase of the optical band edge energy upon intercalation. Deintercalation gravimetric data indicate there may be a second stage intercalation at lower guest pressures.
This work was supported by NSF DMR 9901165.
- L/P.11** MAGNETIC AND MAGNETOTRANSPORT PROPERTIES OF THE $La_{Ni_x}Co_{1-x}O_3$ SOLID SOLUTION ($x=0.2$ AND 0.6)
J. Androulakis, N. Katsarakis, Z.V. Viskadourakis and J. Giapintzakis, Institute of Electronic Structure and Laser, Foundation for Research & Technology-Hellas, PO Box 152, Vasilika Vouton, 711 10 Heraklion, Crete, Greece
A comparative study of the magnetic and magnetotransport properties between a semiconducting ($x = 0.2$) and a metallic ($x = 0.6$) member of the $LaNi_xCo_{1-x}O_3$ solid solution is presented. All powder samples were prepared by a citrate-gel method using high purity nitrates as starting materials. Structural characterization carried out by x-ray powder diffraction, EDX, and iodometry revealed that all samples were single-phase, with the correct cation and oxygen stoichiometry.
The overall magnetic behavior is strikingly similar for both compounds indicating that the magnetic interactions involved on both sides of the chemically induced metal-to-insulator transition are probably of the same origin. Our dc and ac susceptibility data are not consistent neither with the presence of a conventional spin-glass phase nor with the formation of superparamagnetic clusters at low temperatures and rather point to the occurrence of magnetic clusters with enhanced intracluster ferromagnetic correlations, which are randomly distributed in the paramagnetic matrix of $LaNi_xCo_{1-x}O_3$.
Regarding the magnetotransport properties, $LaNi_{0.6}Co_{0.4}O_3$ is a strongly correlated metal and exhibits small but negative magnetoresistance whereas $LaNi_{0.2}Co_{0.8}O_3$ shows semiconducting behavior and giant magnetoresistance at low temperatures. Plausible explanations concerning the origin of the magnetoresistance in both members of the $LaNi_xCo_{1-x}O_3$ solid solution will be discussed.
- L/P.12** CERAMOGRAPHIC ANALYSIS OF CERAMO-METAL BONDING INTERFACES
G. Lascar, University of Metz, IUT Metz, Dept G.M.P., Ile du Saulcy, 57045 Metz, France
Two protocols are used for the methodology of ceramo – metal assembly. The technique of transitional liquid state bonding (reactive brazing in a vacuum furnace) and the solid state bonding method (thermoccompression). Different reactions develop depending on nature of the materials and the method of bonding. The analysis of interfacial reactions presents difficulties because of the limited depth of reaction.
I propose to present the experimental results obtained by different analytical techniques (SIMS, X-ray diffraction with grazing incidence with angles varying between 0.2° and 0.5°)
- L/P.13** EPITAXIAL RELATIONSHIPS BETWEEN ZnO THIN FILMS AND CUBIC SYMMETRY SUBSTRATES
A. Gutiérrez-Llorente, R. Pérez-Casero, O. Pons-Y-Moll, J. Perrière, GPS, Univ. Paris VII, Tour 23, 2 Place Jussieu, 75251 Paris, France and W. Seiler, L3M, ENSAM, 151 Bd de l'Hôpital, 75013 Paris, France
Some compounds, such as AlN of GaN, usually showing a hexagonal crystalline structure when grown as bulk material, can also exhibit a less common cubic structure when deposited as thin films on appropriate cubic substrates. We investigate here the possibility that ZnO could have a similar behaviour, i.e. that a cubic ZnO phase could appear instead of the hexagonal classical one on cubic substrates.
Thus, ZnO thin films have been grown by pulsed laser deposition on various substrates: (001) SrTiO₃, (001) YSZ, (001) MgO and (012) Al₂O₃. Our results prove that, unlike AlN or GaN, PLD grown ZnO on these substrates remains hexagonal and shows a high (001) texturation and well defined film-substrate epitaxial relationships. Texture and film-substrate surface quality. Indeed, ZnO films grown on substrates with similar composition but varying surface morphologies can exhibit quite different textures and in-plane orientations.
The aim of this work is to get an insight on the main rules governing the epitaxial growth of ZnO films on crystalline bulk materials with cubic symmetry. The observed epitaxial relationships will be discussed on the basis of domain matching epitaxy and energetic arguments, assuming that the dominant interaction between the film and the substrate is electrostatic in nature because of the ionic character of the studied oxides.

SYMPOSIUM L

- L/P.14** YTRITIUM OXIDE, Y₂O₃, THIN FILMS: CHEMISTRY-STOICHIOMETRY-STRESS AND MICROSTRUCTURE
R.J. Gaboriaud and F. Paumier, Laboratoire de Métallurgie Physique, Université de Poitiers, UMR 6630 CNRS-SP2MI, BP 30179, 86962 Chasseneuil-Futuroscope cedex, France
Yttrium sesquioxide, Y₂O₃ has recently attracted much attention because of the large variety of its technical applications either in the opto-electronic, wave guide, metal-oxide-semiconductor devices or as a protective coating of materials in particularly severe environments. Recent works are devoted to the Y₂O₃ thin film deposition on Si or other model substrates because of its high dielectric constant (12-18) its high band gap (5.1 eV) and the low lattice mismatch between the Si and Y₂O₃ cubic lattice parameters. This work is focused on thin films of Y₂O₃ deposited either by laser ablation or by ion beam sputtering thin films are investigated by RBS, HRTEM, X-ray stress and electrical C-V measurements. The results are discussed as a function of both the deposition parameters (T, P(O₂), substrates) and the different post annealing treatments. In situ kinetic study of the thin film microstructure versus the annealing dwelling times and temperatures is carried out by X-ray diffraction experiments. This analysis is interpreted in terms of crystal chemistry and the stoichiometry-microstructure relationship.
- L/P.15** SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF COPPER HYDROXYSULFATES
S. Vilminot, M. Richard-Plouet, G. André*, D. Swierczynski, F. Bourée-Vigneron* and M. Guillot, IPCMS-GMI, UMR 7504, 23 rue du Loess, 67037 Strasbourg Cedex, France and *Laboratoire Léon Brillouin, CEA-Saclay, 91191 Gif-sur-Yvette Cedex, France
Cu₃(OH)₄SO₄ and Cu₄(OH)₆SO₄ have been obtained by hydrothermal synthesis at 170°C from copper sulfate and soda in aqueous suspension. No other phase has been evidenced in the CuSO₄-Cu(OH)₂ system under these conditions. Both compounds have been characterised by thermal analysis and IR spectroscopy. They are isostructural with the corresponding antlerite and brochantite minerals. Their nuclear structures have been refined from single crystal X-ray data and/or powder neutron data. Antlerite is built up by triple chains of edge-sharing octahedra around copper ions, these chains being connected by sulfate groups. For brochantite, two kinds of copper chains are linked together to form sheets. The sulfate tetrahedra bond these undulating sheets directly to one another. Magnetic properties reveal for antlerite the presence of ferromagnetic interactions as revealed by the small increase of the χ product from R.T. down to around 20 K, followed by a 3D ordering at 5 K, as confirmed from Cp measurements. The magnetic structure has been solved from neutron powder data collected at 1.4 K and evidences a statistical disorder of the magnetic moments of the central chain copper ions. Brochantite reveals an antiferromagnetic behaviour with 3D order at 6 K.
- L/P.24** LOW-TEMPERATURE STRUCTURES AND THERMAL EXPANSION OF THE LaGaO₃, NdGaO₃ AND La_{0.63}Nd_{0.37}GaO₃
A. Senyshyn, L. Vasylichko, D. Savvitskii, A. Matkovskii, "Lviv Politechnic" National University, 12 Bandera St., 79013, Lviv, Ukraine, M. Knapp, Darmstadt University of Technology, Institute for Materials Science, Petersenstrasse 23, 64287 Darmstadt, Germany, M. Berkowski, Institute of Physics Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
The perovskite-like gallate LaGaO₃ and NdGaO₃ have been studied intensively in the last years because of their attractive physical and chemical properties. Due to the low mismatch between lattice parameters and thermal expansion coefficients they are used as substrate materials for HTSC, CMR and GaN film deposition. The synchrotron powder diffraction experiments on the LaGaO₃, NdGaO₃ and La_{0.63}Nd_{0.37}GaO₃ crystals were carried out at HASYLAB/DESY. The full patterns for these compounds were collected at 10 K and refined in space group Pbnm using Rietveld method. It was estimated, that lattice parameters and cell volume increase nonlinearly with the temperature increasing in the temperature range 10 – 300 K. The obtained values of the cell volume for Nd_{0.37}La_{0.63}GaO₃ crystal agree well with ones, estimated from the Vegard’s rule, whereas strong deviations for the lattice constants are observed (negative for a- and b-parameters and positive for the c-constant). These deviations practically do not depend on the temperature, therefore it is possible to estimate the low-temperature behavior of the lattice constants for other La_{1-x}Nd_xGaO₃ compositions.
Acknowledgement. This work was supported by WtZ (UKR-012-97), Ukrainian Ministry of Science (Project No. 2М/1856-97) and Polish Committee for Scientific Research (Grant N 7 T08A 00520). A. Senyshyn acknowledge of the DAAD support (Leonhard – Euler program).
- L/P.25** INTEREST OF RAPID THERMAL ANNEALING (RTA) PROCEDURE FOR DENSIFICATION OF SOL-GEL INDIUM TIN OXIDE (ITO) THIN FILMS
K. Daoudi, B. Canut, J. A. Roger, C.S. Sandu, M. G. Blanchin, V.S. Teodorescu, DPM - UMR CNRS 5586, Université Claude Bernard - Lyon 1, 43 Bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France, M. Oueslati, Laboratoire de Physique de la Matière Condensée, Equipe de Spectroscopie Raman, Physique, Faculté des Sciences de Tunis, 1060 Le Belvédère, Tunis, Tunisie, B. Bessaïs, Laboratoire des Applications Solaires, Groupe de Photovoltaïque et des Matériaux Semiconducteurs, Institut National de Recherche Scientifique et Technique, BP 95, Hammam-Lif, Tunisie
Since highly conductive and transparent to visible light, Indium Tin Oxide (ITO) is an indispensable material for transparent electrodes in optoelectronic technologies. ITO thin films have been fabricated by numerous methods, but it is only in the last past years that the Sol-Gel route has been investigated.
In order to obtain a Sol-Gel ITO film, after dipping or spinning, the wafers are dried, then annealed in a conventional furnace at 500°C for one hour. These operations must be repeated several times (up to 5) to obtain a sufficient thickness for practical applications. Therefore the preparation of one multilayered sample with classical thermal annealing (CTA) holds out many hours. In this study, we present our firsts results on Rapid Thermal Annealing (RTA) of Sol-Gel ITO thin films compared with the classical procedure. At the same temperature of 500°C and with a 6 mn RTA treatment, the film exhibits electrical resistivity values close to the CTA ones. The optical and electrical properties of such Sol-Gel films are comparable with the best results reported so far.
The crystalline structure of the ITO films was visualized by high resolution transmission electron microscopy, and electron diffraction pattern compared with that of pure In₂O₃. The average grain size, measured from TEM micrographs, ranges from 5 to 20 nm. The process of film densification has been followed by Rutherford Backscattering Spectrometry coupled with cross-section observation.

SYMPOSIUM L

- L/P.26** CRYSTALLIZATION BEHAVIOR AND BRIDGMAN GROWTH OF $91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}9\text{PbTiO}_3$ FERROELECTRIC CRYSTALS
Jiayue Xu, Shiji Fan, Jian Tong, Renying Sun, Shanghai Institute of Ceramics, Chinese Academy of Sciences, China
Relaxor ferroelectric single crystal $91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}9\text{PbTiO}_3$ (PZNT91/9) has attracted much attention for its excellent properties of longitudinal coupling coefficients $k_{33} > 90\%$, effective piezoelectric coefficient $d_{33} > 2000$ pC/N and dielectric constants ~ 4000 with dielectric loss less than 1%. However, crystallization behavior is complicated due to its multi-components and it is different to grow practical size crystal. We have investigated the crystallization behaviour of $91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}9\text{PbTiO}_3$ (PZNT91/9) in different composition fluxes. It was found that B_2O_3 and PbF_2 fluxes are harmful to the crystallization of perovskite phase PZNT. $\text{BaTiO}_3\text{-PbO}$ flux is helpful to the crystallization of the perovskite but crystal yield reduced. Some composition of PbO flux is suitable to the growth of relaxor-ferroelectric PZNT91/9 crystal. Using 50mol% PbO as flux, (30mm (25mm PZNT91/9) single crystal was grown by the modified Bridgman method. The crystal has perovskite structure with with an amber color. The defects, such as domains and inclusions, were investigated and the properties were measured.
- L/P.27** MORPHOLOGY OF NANOSCALED LaMO_3 -PARTICLES AND THEIR CITRATE PRECURSORS
A. Weidenkaff, E. Krupicka and A. Reller, Department of Solid State Chemistry, University of Augsburg, Universitätsstr. 1, 86159 Augsburg, Germany
The ionic conductive properties of LaMO_3 -type perovskites have proven these systems to be promising candidates in the development of novel electrode materials for solid oxide fuel cells (SOFC). A fairly large amount of work has been performed in finding synthetic routes which lead to powdery products showing uniform particle geometry as well as high specific surface area.
In this work we present a systematic study of the morphology of the above mentioned LaMO_3 -perovskites containing additional transition metals as well as their citrate precursors by using electron microscopy, XRD and BET measurements.
The powder samples were obtained by thermal decomposition of the corresponding citrate precursors at the lowest possible temperature, which was determined by thermogravimetric analysis and XRD. This procedure offers a versatile synthesis route for tailoring functional materials based on mixed transition metal oxides. The specific surface area as well as the particle morphology determined by SEM of both the citrate precursors and the decomposition products are compared with respect to their uniformity as well as maximum surface area. The effect of the solvent used for the precursor synthesis, on the nanoparticle morphology will also be taken into evaluation.
- L/P.28** CRYSTAL FIELD SPLITTING OF HIGHLY EXCITED ELECTRONIC STATES OF THE $4f_{n-1} 5d$ ELECTRONIC CONFIGURATION OF TRIVALENT RARE EARTH IONS IN WIDE BAND GAP CRYSTALS
A.C. Cefalas, Z. Kollia, E. Sarantopoulou, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, Athens, Greece
Crystal field splitting of highly excited electronic states of the $4f_{n-1}5d$ electronic configuration of trivalent rare earth ions in different ionic host matrixes (YF_3 , LaF_3 , KY_3F_{10} and LiLuF_4) have been investigated by laser induced fluorescence at 157nm, and vacuum ultraviolet absorption spectroscopy. The energy position and the spacing of the levels of the $4f_{n-1}5d$ electronic configuration depend on the host matrix. Strong vacuum ultraviolet emission bands were observed, following crystal excitation at 157nm with the molecular fluorine laser. The emission bands were assigned to the interconfigurational $4f_{n-1} 5d - 4f_n$ dipole allowed transitions in RE ions, and they were assigned to the transitions between the edge of the lowest Stark component of the $4f_{n-1} 5d$ electronic configuration, and the levels of the $4f_n$ electronic configuration [1]. The experimental results can be explained by applying the crystal field model and taking into consideration that lanthanide contraction of the $4f_{n-1} 5d$ electronic configuration of the rare earth ions is taking place as well as for the $4f_n$ electronic configuration. References
[1] VUV Laser Spectroscopy of Trivalent Rare Earth Ions in Wide Band-Gap Fluoride Crystals, E. Sarantopoulou and A. C. Cefalas. In "Ultraviolet spectroscopy and UV lasers" edited by Marcel and Dekker, New York 2002.
- L/P.29** STRUCTURAL DETERMINATION OF PHYSICAL PROPERTIES IN CUPRATES
G.J. Babonas(a), R. Szymczak(b), M. Baran(b), A. Reza (a), V. Maltsev(c), J. Sabataityte(a), S. Dyeyev(b), (a)Semiconductor Physics Institute, Vilnius 2600, Lithuania, (b)Institute of Physics, PAN, Warsaw 02-668, Poland, (c)Moscow State University, Moscow 19899, Russia
Recently, the crystal structure of synthetic and natural Cu-O compounds was analyzed in the unified classification scheme. Structural units of cuprates as salts of hypothetical copper acid were distinguished and assumed to be responsible for characteristic physical properties of these Cu-O compounds.
In this work the optical and magnetic properties were studied in a series of synthetic and natural cuprates. The fine structure in the optical spectra of $(\text{M}_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$, CuGeO_3 , linarite $\text{PbCu}(\text{OH})_2(\text{SO}_4)$ and malachite $\text{Cu}_2(\text{OH})_2\text{CO}_3$ was correlated with the electronic excitations in particular structural units typical of cuprates. The energy of charge transfer transitions $p(\text{O})\text{-}d(\text{Cu})$ in the region 2-5 eV were dependent on the type of the Cu-O network. The fine structure of the near IR absorption band at 1-2 eV was shown to correspond to the regularities of local crystal field.
The temperature dependence of magnetic susceptibility was investigated on a series of Cu oxysalt minerals and compared with that for synthetic cuprates. The dimerization of magnetic moments was considered as a property of cuprates which was strongly dependent on the type of Cu-containing structural units. The observed relationship between the crystal structure and physical properties is promising in searches of new magnetic materials.
- L/P.30** HOMOGENEITY REGION OF $(\text{La,Sr})(\text{Ga,Mg})\text{O}_3$
P. Majewski, M. Rodzimek, F. Aldinger Max-Planck-Institut für Metallforschung, Heisenbergstr. 5, 70569 Stuttgart, Germany
 Sr and Mg substituted LaGaO_3 has been found to exhibit significant oxygen ion conductivity. Due to this property the compound is of technological interest for application as solid electrolyte of solid oxide fuel cells. The solid solubility of Sr and Mg is temperature dependent and decreases with decreasing temperatures that results in a significant decrease of the extension of the homogeneity region of $(\text{La,Sr})(\text{Ga,Mg})\text{O}_3$. In addition, the compound exhibits structural transformation from cubic to rhombohedral, and rhombohedral to orthorhombic with decreasing Sr and Mg content.

SYMPOSIUM L

- L/P.31** CORRELATION OF MAGNETIC AND THERMODYNAMIC PHASE DIAGRAMS OF THE SYSTEMS LaMnO_3 - SrMnO_3 AND LaMnO_3 - CaMnO_3
Peter Majewski, Fritz Aldinger Max-Planck-Institut für Metallforschung, Stuttgart, Germany
Phase equilibria within the pseudo binary systems LaMnO_3 (LM) - SrMnO_3 (SM) and LM - CaMnO_3 (CM) have been examined with special regard to the extension of the Sr and Ca solubility of LM at different temperatures, respectively. Our results indicate that the Sr and Ca solubility is temperature dependent, respectively. This behavior causes a miscibility gap between LM and SM as well as CM at lower temperatures that correlates with observed two magnetic phase region in the magnetic phase diagram, that is often attributed to magnetic phase separation. The phase transformation of LM from orthorhombic to rhombohedral with increasing Sr content has not been observed at high temperatures indicating that the orthorhombic modification of Sr doped LM represents the stable high temperature modification. The observed phase boundary between the orthorhombic and the rhombohedral (La,Sr/Ca) MnO_3 phase appears to correlate with the observed phase boundary between ferromagnetic insulator and ferromagnetic metal in the (La,Sr/Ca) MnO_3 system.
- L/P.32** INFLUENCE OF ION IRRADIATION ON PHASE TRANSFORMATION BEHAVIOR OF QUENCHED Ti-48Al-2Nb ALLOY DURING AGING
V.D. Melikhov, S.E. Romankov, T.V. Volkova, Institute of Physics & Technology, 480082, Almaty, Kazakstan
Influence of ion irradiation on phase transformation behavior of quenched Ti-48Al-2Nb alloy during aging at 650 and 8000C has been studied by X-ray diffraction. The Ti-48Al-2Nb alloy was prepared by electric arc melting in vacuum not worse than 10-3 Pa. The samples (8x8x1 mm) were annealed at 11500C for 160 h. Then ones were quenched in oil from 13000C after holding for 30 min before quenching. The quenched samples were irradiated by 60 keV Ti^+ ions up to dose 1017 ions/cm². The current density of ion beam was 10 mA/cm². The pulse repetition frequency was 25 Hz. The pulse length was 250 ns. The temperature during irradiation was 1500C. Then the quenched samples and quenched irradiated ones were aged in vacuum of 10-6 Pa at 650 and 8000C.
It was revealed that the preliminary irradiation of quenched samples greatly affects dynamics of phase transformations during aging. It was established that the speed of the phase transformations in preliminary irradiated and not irradiated samples is various. Structural changes occurring during ion irradiation of the quenched samples slow down processes of structural reformation and stabilize structure of quenched alloy at the initial stages of aging at 650 and 8000C.
- L/P.33** USE OF HETEROJUNCTIONS FOR ANALYSIS OF PROPERTIES OF SnS_2 -xSex CRYSTALS
Z.D. Kovalyuk, V.N. Katerinchuk, Chernivtsi Department of the Frantsevich Institute of Materials Science Problems, National Academy of Sciences of Ukraine, Chernivtsi, Ukraine
 SnS_2 -xSex-x (0<x<1) semiconductor compounds belong to the family of layered crystals. The perfect plates of such crystals were grown by the chemical transport method. The analysis of the properties of obtained crystals was performed on the base of detail measurement and comparison of characteristics of SnS_2 -xSex-InSe and SnS_2 -xSex-GaSe heterojunctions. The heterojunctions were prepared by the optical contact method of the semiconductors at room temperature. The band diagrams, mechanism of current transport through the barrier, and the region of spectral photosensitivity of the heterojunctions in dependence on the composition x were investigated. The observed regularities are described within the framework of the ideal p-n junction theory imaginations and evidence a high quality of grown SnS_2 -xSex crystals.
- L/P.34** LARGE-SCALE COMPUTER MODELING OF Li IMPURITIES IN KTaO_3 AND $\text{K}_{1-x}\text{Li}_x\text{Ta}_{1-y}\text{Nb}_y\text{O}_3$ PEROVSKITE SOLID SOLUTIONS
R.I. Eglitis, V.A. Trepakov, S.E. Kapphan and G. Borstel, University of Osnabrueck, Fachbereich Physik, 49069 Osnabrueck, Germany
The magnitudes of off-center Li displacements and the relaxation energies related to reorientation of Li are calculated in KTaO_3 using the semi-empirical Hartree-Fock-based method of Intermediate Neglect of Differential Overlap (INDO). The spatial extent of a lattice relaxation around Li impurities and contributions from different neighbours to the relaxation energy are discussed. Results are compared with available experimental information.
We have applied the INDO method for the study of interaction between Li impurities in KTaO_3 . The Li-Li interaction energy as a function of the Li-Li distance and orientation are calculated, including the lattice relaxation around Li-Li impurities. According to our calculations, the Li-Li interaction energies are smaller and less long-ranged than it was estimated from earlier shell model calculations.
Lastly, we performed theoretical modeling of KTaO_3 perovskites with a small amount of Li and simultaneously diluted by Nb ($\text{K}_{1-x}\text{Li}_x\text{Ta}_{1-y}\text{Nb}_y\text{O}_3$, KLTN). We compare our theoretical results with recent experimental results for the complex dielectric permittivity and Raman spectroscopy studies.
- L/P.35** SURFACE ENRICHMENT BY TIN FOR THE SACRIFICIAL ANODE Al-Sn ALLOY
Yu.Ya. Andreev, A.V. Goncharov, V.V. Musatov, Student of MISA, Moscow, Russia
It was studied a microdistribution of tin within the surface layer of Al-0.2 at. % Sn alloy after an anode working in water solution Na_2SO_4 at room temperature. By SIMS method it was found a dramatic enrichment by tin immediately (10-30 Å) on the surface alloy (in hundred-fold excess) and a diffusion distribution of tin in depth about 100-400 nm. Tin enrichment initiates depassivation of Al in water even without an anode working. This phenomenon was considered as the subject of solid-state chemistry. Using the condition of thermodynamic equilibrium of the surface layer with the bulk of a solid solution Al-Sn it was calculated the degree of tin enrichment that was equal to 136, which correlated with experimental data. The value of diffusivity $D(\text{Al})$ was calculated from depth of diffusion zone $D(\text{Al})=6 \cdot 10^{-14}$ cm²/s.

SYMPOSIUM L

- L/P.36** SYNTHESIS OF NANOSIZE b-SIALON POWDERS WITH CONTROLLED SIZE OF PARTICLES
N.V. Dolgushev, A.V. Zabolotsky, S.A. Suvorov, St.Petersburg Institute of Technology, Dept. of High-Temperature Materials, Moskovskii Pr. 26, St.Petersburg 198013, Russia
The definition of critical sizes region (CSR) of particles is given and the expressions for estimation of CSR margins are obtained. For example, CSR of some refractory substances particles are $D^*(MgO)=[1.26,11.78]$, $D^*(Al_2O_3)=[1.54,30.47]$, $D^*(SiO_2)=[1.49,116.93]$, $D^*(b-SIALON)=[1.55,42.35]$.
The stability criteria of particles with critical sizes are obtained and used for prediction of chemical transformations in systems of ultra dispersed particles. The similarity of a kinetic regime of the reactions between critical size particles to a kinetic regime of gas phase reactions is shown.
Synthesis of ultra dispersed b-SIALON powders with controlled size of particles in region of 50-150 nm and narrow distribution of particles is designed and carried out. The method of synthesis is based on the reaction of carbothermal nitration of kaolinite. As a result of gas-transport interaction the particles of carbon is transformed into particles of b-SIALON so, that size and shape of b-SIALON particles are determined by the size and shape of carbon particles used as precursor. An upper margin of b-SIALON CSR well matched with a theoretical estimation - 42 nm.
Formation ultra dispersed b-SIALON particles is finished for 5 minutes of synthesis of process. Obtained active to a sintering b-SIALON powder is used for manufacturing dense SIALON-based materials with bending strength 120 MPa at 1200C and high stability to oxidation up to 1500C.
- L/P.37** ORIENTATION IMAGING MICROSCOPY APPLIED TO BaTiO₃ CERAMICS
A. Koblichka-Veneva and F. Muecklich, University of the Saarland, Institute of Functional Materials, PO Box 151150, 66041 Saarbruecken, Germany
Sintered BaTiO₃ ceramics were investigated using orientation imaging microscopy (OIM), which is a method for measuring a large number of individual grain orientations and relating them directly to the microstructural features by means of evaluating electron backscatter Kikuchi patterns in scanning electron microscopy. Measurements of crystallographic orientations along with microscopic observations are the basis of quantitative investigations of the microstructure of crystalline materials.
By means of orientation imaging microscopy, we investigated the grain orientation distributions of various BaTiO₃ ceramic samples prepared using different preparation routes. We present details of the required surface preparation steps in order to enable an automated orientation mapping. The samples are characterized by pole figures and inverse pole figures, and grain orientation maps. Finally, the grain orientation distribution functions are obtained from the measured data. It is shown that the samples do not exhibit any preferred grain orientations.
- L/P.38** SPECTRAL AND THEORETICAL INVESTIGATION OF THE ELECTRONIC STRUCTURE OF THE ISOMORPHICALLY SUBSTITUTED CALCIUM COMPOUNDS
A.P. Shpak, V.L. Karbovskii, L.P. Kluyenko, A.G. Vakhney, A.I. Senkevich, Institute of Metal Physics, NAS of Ukraine, 36 Vernadsky blvd., 03680 Kiev, Ukraine and E.I. Getman, Donetsk State Univ, Donetsk, Ukraine
The electronic and local topological structure of calcium compounds $Ca_{10}(PO_4)_6-x(VO_4)_x(OH)_2$ ($x=0, 1, 3, 5, 6$) have been investigated by XPS, EXAFS, IR spectroscopy and quantum mechanical calculations with LMTO approximation. The aim of this work was to clear up changes in electronic structure initiated by isostructural substitutions and changes of near topological order. The electronic structure of studied compounds is described. It is shown that isovalence substitutions result in considerable shift of 1s oxygen electron binding energy (up to 1.1 eV) so as shifts of 2p electrons binding energies of calcium, phosphorus and vanadium.
Main changes in electron structure are attributed to decrease of oxygen tetrahedra symmetry.
- L/P.39** NUCLEATION AND CRYSTALLIZATION OF CaCO₃ IN APPLIED MAGNETIC FIELDS
S. Kobe(a), G. Dragic(a), M. Komej(a), E. Sarantopoulou(b), A. C. Cefalas(b), (a)Jozef Stefan Institute, Jamova 39, Ljubljana, Slovenia, (b)National Hellenic Research Foundation, TPCI 48 Vassileos Constantinou Avenue, Athens Greece
Various chemicals are usually used to prevent the accumulation of calcium carbonate scale on surfaces exposed to tap water, however, this increases the chemical pollution of the environment. CaCO₃ crystallizes in three different crystal forms: calcite, aragonite and vaterite. Calcite is usually associated with a hard scale whereas aragonite and vaterite are softer types of scale that are easily removed. It has been established that the nucleation and crystallization of calcium carbonate in tap water can be influenced by a magnetic field.
In the present study the nucleation and crystallization of the CaCO₃ from the model water with a defined chemical composition were studied using HREM and magnetic measurements. In a specially constructed cell where various parameters could be controlled the nano-sized particles were collected on a carbon grid and examined under the electron microscope (HREM and STEM using a high-angle annular dark-field detector). EDXS and EELS were used to characterize the particles. It was found that the magnetic field strongly influenced the ratio of calcite to aragonite and vaterite phases.
In addition the magnetic susceptibilities of crystals obtained by controlled drying of the model water were measured to monitor the difference between aragonite and calcite crystal forms of CaCO₃.
A theoretical explanation of the influence of the magnetic field on the preferential nucleation and further crystallization of aragonite instead of calcite is proposed.
- L/P.40** INFLUENCE OF THERMAL TREATMENT ON THE STRUCTURE OF Ti-Al FILMS
B.N. Mukashev, S.E. Romankov, T.V. Volkova, M.T. Tokenov, Institute of Physics & Technology, 480082 Almaty, Kazakhstan Republic
The modes of heat-resistant Ti-Al coatings plating were developed, when the alloy of the desired content was deposited on the backing by magnetron sputtering. Polycrystal materials with structure parameters similar to those of the plated alloy and other ones having different type of the structure lattice parameter sufficiently greater than that for the deposited alloy were used.
The produced Ti-Al films, which consisted of the mixture of two phases α -TiAl+Ti₃Al and had insular phase distribution, were annealed by step for 650 up to 8500C.
It was revealed that recrystallisation process during annealing sufficiently depended on the backing structure. The films on the backings with similar structure insular phase distribution became smooth with distinct texture already on the initial annealing stages (30 min at 6500C). For the films plated on the other backings the formation of intermediate phases was observed at the beginning of the annealing. At higher temperatures texture of the films became more distinct for both cases and their adhesion increased.

SYMPOSIUM L

- L/P.41** ORIENTATION IMAGING MICROSCOPY ANALYSIS OF BULK, MELT-TEXTURED YBCO SUPERCONDUCTORS
A. Koblishcka-Veneva, M.R. Koblishcka, Institute of Functional Materials, University of the Saarland, P. O. Box 151150, 66041 Saarbrücken, Germany, and K. Ogasawara, M. Murakami, SRL-ISTEC, Div. 3, 1-16-25 Shibaura, Minato-ku, Tokyo 105-0023, Japan
Bulk, melt-textured YBa₂Cu₃O_x (Y-123) superconductors are an important material for various applications including electric motors, fault current limiters and trapped field magnets. For these applications, it is essential to grow samples with large diameters up to several centimeters in diameter. To increase the flux pinning capabilities, an amount of Y₂BaCuO₅ (Y-211) is added prior to the melt-texturing. Therefore, the knowledge about the growth mechanism of Y-123 is very important.
In this contribution, we apply orientation imaging microscopy (OIM) to such melt-textured YBCO samples, which requires to perform an automated two-phase analysis. We obtain the orientations of the individual crystallites and the misorientation distributions for both Y-123 and Y-211. From the obtained data, we calculate the orientation distribution functions.
- L/P.42** LITHIUM-GADOLINIUM BORATE Li₆Gd(BO₃)₃ MODIFIED BY Na
R.P. Yavetskiy, A.V. Tolmachev, M.F. Dubovik, T.I. Korshikova, Institute for Single Crystals, National Academy of Sciences of Ukraine, Kharkov, Ukraine
The results of investigation of Li_{6-x}Na_xGd(BO₃)₃ solid state synthesis peculiarities are presented. The single crystals Li_{6-x}Na_xGd(BO₃)₃ up to 1 cm³ have been grown by Czochralski technique in platinum crucibles under air atmosphere. The differential-thermal analysis data show, that at the Na concentration growth the melting temperature and supercool of melt are decreasing. The absorption and photoluminescence spectra of pure and modified single crystals are investigated. The possibility of modification of Li₆Gd(BO₃)₃ single crystals by another alkali elements is discussed.
- L/P.43** HIGHLY PHOTOCONDUCTING SILLENITE SINGLE CRYSTALS
J. Zmija(a), M.T. Borowiec(b), L. Kovacs(c), A. Majchrowski(a), H. Szymczak(b) and T. Zayarnyuk(b), (a)Institute of Applied Physics, Military University of Technology, 00-908 Warsaw, Poland, (b)Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland, (c)Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, 1121 Budapest, Hungary
Single crystals of Bi₁₂TiO₂₀, Bi₄₀Ga₂O₆₃ and Bi₂₅FeO₄₀ (titanium, gallium, and iron sillenite) were grown with use of Top Seeded Solution Growth (TSSG) method. Mixed sillenites described by the formula Bi₁₂Ti_{1-x}M_xO₂₀ (M= V, Pb, Ga, x=0.2), some of them doped additionally with Cu were obtained, too. By proper selection of growth conditions uniform single crystals with totally flat (110) interfaces were grown from excess of Bi₂O₃. Real structure, photochromism and electron phototransport of simple and mixed sillenite single crystals have been studied by means of several experimental methods, namely: optical absorption of electron states, thermal bleaching, photoconductivity under permanent, chopped and pulse illumination, optical absorption of phonon states, and normal-incidence reflectance in UV. Photoconductivity and photochromic effect were investigated. Some thermally stimulated processes related to photochromic properties were observed. Correlations between photochromism and photo-conductivity were found. This work was partly supported by Polish State Committee on Science (KBN) (project No. 7T08 032 20).
- L/P.44** TURNING THE SHALLOW TRAP OF BaTiO₃ INACTIVE BY REDUCTION
Chi-Yi Huang, J.Y. Chang, Institute of Optical Sciences, National Central University, Jungli, Taiwan
Numerous applications have been described for the photorefractive effect. Due to its large electro-optic coefficients and self-pumped phase-conjugation, BaTiO₃ is a promising photorefractive material. The ideal BaTiO₃ is electron conductive, can be described by the one-center model and has a small dark conductivity. However, in general, the as-grown BaTiO₃ single crystals do not show a one-center behavior. In this report, we made a series of reduced BaTiO₃ single crystals. Their light-induced absorption spectra, dark conductivity, two-beam coupling gain and response time were measured. The results show that the shallow traps were turned inactive in the crystals reduced at the atmosphere between 1E-8 atm and 1E-12 atm oxygen partial pressures. Therefore, the photorefractive properties of such a crystal can be described by the one-center model.
- L/P.45** STRUCTURAL CHARACTERIZATION OF SOL-GEL LANTHANUM COBALTITE THIN FILMS
E. Bontempi(a), L. Armelao(b), D. Barreca(b), L. Bertolo(b), G. Bottaro(b), E. Tondello(b) and L.E. Depero(a), (a)INSTM and Laboratorio di Strutturistica Chimica, Dipartimento di Ingegneria meccanica, Università di Brescia, Via Branze, 38, 25123 Brescia, Italy, (b)INSTM and CNR, Dipartimento Chimica Inorganica Metallorganica e Analitica, Università di Padova, Via Marzolo 1, 35131 Padova, Italy
Mixed oxide based-materials belonging to the perovskite family (ABO₃) are interesting either for fundamental or technological reasons.
They are attractive for catalysis, oxygen sensing devices, solid oxide fuel cells and magnetic media [1].
To this regard, nanocrystalline systems are expected to show enhanced properties with respect to conventional ones [2].
Among the LaMO₃ (M = Co, Mn, Cu, ...) perovskite-type mixed oxides, lanthanum cobaltite is particularly promising for the above mentioned applications, thanks to the II and III oxidation states of Co [2].
In our previous work, some of the authors report the preparation of LaCoO₃ nanoparticles [3].
In this paper, we discuss the synthesis and characterization of LaCoO₃ thin films obtained by the sol-gel route.
In particular, to our knowledge, only few papers are present in literature concerning the sol-gel preparation of such materials.
The structure of the samples was investigated by Glancing Incidence X-Ray Diffraction (GIXRD) and X-Ray Microdiffraction, whereas the chemical composition and the electrical structure was studied by X-Ray Photoelectron Spectroscopy (XPS).
[1] Kendall KR, Navas C, Thomas JK, zur Loye HC. Chem. Mater. 1996; 8: 642.
[2] Peña MA, Fierro JLG. Chem. Rev. 2001; 101: 1981.
[3] L. Armelao, G. Bandoli, D. Barreca, M. Bettinelli, G. Bottaro, A. Caneschi, submitted.

SYMPOSIUM L

- L/P.46** **MAGNETIC PROPERTIES OF Ga-DOPED LANTHANUM MANGANITE WITH CONTROLLED OXYGEN STOICHIOMETRY**
B. Vertruven, LCIS, Chemistry Institute B6, Sart Tilman, 4000 Liège, Belgium, S. Hébert, A. Maignan, C. Martin and B. Raveau, CRISMAT, 6 Bd du Maréchal Juin, 14050 Caen, France
A few years ago, the discovery of colossal magnetoresistive properties in $\text{La}_{1-x}\text{AxMnO}_3$ compounds renewed the interest for the lanthanum manganite family. It turns out that the double exchange between Mn^{3+} and Mn^{4+} species plays a key role in the physical properties of these materials. However, the physics of stoichiometric LaMnO_3 is also very attractive, with Jahn-Teller distortions and super-exchange interactions between Mn^{3+} ions.
The complete $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ solid solution was prepared in evacuated containers in order to control the oxygen stoichiometry. LaMnO_3 is indeed well-known for its ability to take up excess oxygen when synthesized in too oxidative conditions. The synthesis of stoichiometric Ga-doped lanthanum manganite enables us to study a system where only superexchange interactions are present and where the Mn^{3+} ions are diluted by non magnetic Ga^{3+} (d10). The structural characterization was performed by X-ray diffraction, HREM and electron diffraction. Magnetic measurements were also carried out : temperature and field dependences of the magnetic moment, temperature and frequency dependences of the AC susceptibility.
- L/P.47** **EFFECT OF HEAT TREATMENT AT ENHANCED PRESSURE ON ELECTRICAL AND STRUCTURAL PROPERTIES OF ELECTRON IRRADIATED SILICON**
W. Jung, I.V. Antonova, A. Misiuk, C.A. Londos, M. Prujnszczyk, Institute of Electron Technology, Al. Lotnikow 32/46, 02-668 Warsaw, Poland, Institute of Semiconductor Physics, RAS, Lavrientieva 13, Novosibirsk, Russia The University of Athens, Physics Department, Panepistimiopolis Zografos, 157 84 Greece
Effect of annealing at 300-650°C under enhanced pressure (up to 1.2 GPa) in argon ambient on defect-interstitial oxygen interaction in oxygen-containing Czochralski grown silicon (Cz-Si) subjected to electron irradiation (doses up to 10^{17} cm^{-2} , 2.5 MeV) was investigated by IR absorption and electrical C-V methods. The density of vacancy-related defects VO, VO₂ and carrier concentration profiles were determined after subjecting the samples to annealing in the temperature range of 350 - 650°C under enhanced argon pressure up to 1.2 GPa. The stress - induced increase in electron concentration was detected in the Cz-Si electron irradiated samples after 1.2 GPa pressure treatment at 450°C and 650°C for 10 hours. The effect of n-type layer formation in the initial p-type samples, dependent on electron dose was also observed. The increase in electron dose causes the decrease in electron concentration. Observed effects can be partly explained as the result of irradiation and pressure-stimulated interaction of oxygen interstitials with irradiation-induced defects (generation of thermal donors and thermal acceptors).
- L/P.48** **THE EVOLUTION OF DISLOCATION STRUCTURE OF NaCl TYPE SINGLE CRYSTALS DEFORMED AT THE SMALL CROSS SECTION/HEIGHT RATIO**
Andrey Boyarintsev, Alexandr Gektin, Valeriy Shlyakhturov, Institute for Single Crystal, Kharkov, Ukraine
The NaCl type crystal plastic yield cannot be realized by dislocations sliding along the easy-slide planes at samples with a/c ratio (where a - crystal height, c-typical cross section size) less than 1. The slip plane block in the central area does not allow to sustain the uniform plastic flow.
The real modelling of the mass transfer process in a crystal by crystalline material shift imaging during the deformation process using markers and structure investigations allowed to determine stress fields and crystal dislocation structure non-uniformity. Four crystal regions characterized by different dislocation structures and interdislocation interaction mechanism have been singled out. The evolution of the crystal structure was investigated and the structure state diagram depending on preliminary rate of deformation was made for each crystal region.
Interdislocation interaction mechanisms providing plastic deformation process at the stage of formation and development of sliding under conditions when it is formally prohibited, have been considered.
- L/P.49** **EFFECT OF SUBSTRATE SURFACE ION BOMBARDMENT ETCHING ON REACTION BETWEEN CHROMIUM THIN FILMS AND STEEL SUBSTRATES**
R. Gheriani(a), R. Halimi(b), R. Bensaha(b), (a)Laboratoire Physique des Matériaux, Université de Ouargla, Algérie, (b)Unité de Recherche Physique des Matériaux et Applications, Université de Constantine, Algérie
In this work we study the interaction between chromium thin films and steel substrates 100C6 type treatment contain about 1% of carbon atoms. Chromium films are deposited at 200°C by magnetron sputtering. Two series of samples are prepared, the first is distinguished of the second by ion bombardment etching before chromium deposition. The samples are subjected to high vacuum annealing at a temperature between 450 and 700°C, two chromium carbides are formed (Cr₇C₃ and Cr₂₃C₆) and grow until total consumption of chromium film. The microhardness increase with the increase of annealing duration, attain a maximum then decrease progressively. The increase of Hv is caused by carbon diffusion, carbides formation; however the decrease of Hv is caused by iron diffusion. The microhardness of first series is twice as big then second series, this important difference is caused by the effect of substrate surface ion bombardment etching. The formation and growth mechanism of this carbides are discussed and based on thermodynamics consideration
- L/P.50** **NEW BORATE CRYSTALS CONTAINING NEODYMIUM AND YTTERBIUM**
A. Majchrowski(a), E. Michalski(a), Z. Mierczyk(b), K. Wozniak(c) and L. Dobrzycki(c), (a)Institute of Applied Physics, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland, (b)Institute of Optoelectronics, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland, (c)Chemistry Department, Warsaw University, 1 Pasteura Str., 02-093 Warsaw, Poland
Borate single crystals have been widely investigated due to their potential applications in nonlinear optics (NLO) - second and higher harmonics generation (down to UV) of laser radiation, and in self-frequency doubling (SFD) lasers. The paper describes our efforts to grow newly discovered BiB₃O₆ (BIBO) NLO single crystals containing rare earth elements to use them as active media in SFD lasers. We found that both Nd and Yb ions do not substitute bismuth ions sufficiently to obtain lasing materials, but on the other hand new phases crystallising simultaneously with BIBO:RE were discovered. These new phases contain high concentration of rare earth ions. The paper gives some optical properties and structural data on these materials.

SYMPOSIUM L

- L/P.51** NON DESTRUCTIVE DETERMINATION OF RARE EARTH ION CONCENTRATION IN LASER CRYSTALS USING THE VIBRATING SAMPLE MAGNETISATION METHOD
S. Kobe, B. Podmiljak, P.J. McGuinness, E. Sarantopoulou, Z. Kollia, A. Vourdas and A. C. Cefalas, Ljubljana, Slovenia
The importance of investigating the properties of wide band dielectric monocrystals doped with trivalent RE ions is based on the development of new UV and VUV coherent or incoherent light sources [1-3]. The efficient operation of such elements is based on the homogeneous distribution of the trivalent RE ion dopant over the volume of the crystal host. In order to investigate the concentration of the trivalent RE ions in wide band gap fluoride dielectric crystals in a non-destructive way, we have used the vibrating sample magnetometer (VSM) for the first time to our knowledge to determine the concentration of RE ions in different crystal hosts such as KY₃F₁₀, LiYF₄ etc by measuring their magnetic moment. The method is based on forcing oscillations of optical samples in a magnetic field to produce an alternating electro-magnetic field within a set of suitably placed pick-up or sensing coils. This induced EM field is directly proportional to the magnetic moment of the sample. Samples of different shapes were placed in the measuring zone of the VSM, and the moment vs field was measured between -10 kOe and +10 kOe. With this experimental method concentration of the RE ions could be determined within 0.1% accuracy in a non-destructive way.
[1] R. W. Waynant, P. H. Klein Appl. Phys. Lett. 46 (1985) 14.
[2] J. Thogersen, J. D. Gill, H. K. Haugen, Opt. Comm. 132 (1996), 83.
[3] E. Sarantopoulou, Z. Kollia and A. C. Cefalas. Microelect. Eng. 57, 93, 2001.
- L/P.52** MICROSTRUCTURE AND TRANSPORT PROPERTIES OF HETERO-EPITAXIAL NDNiO₃ FILMS WITH METAL-INSULATOR TRANSITION
P. Laffez(a), O. Lebedev(b), G. Banerjee(c), R. Desfeux(d), (a)Laboratoire de Physique de l'Etat Condensé - UMR CNRS 6087, Université du Maine, Avenue O. Messiaen, 72085 Le Mans cedex, France, (b)EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium, (c)Exp. Cond. Matter Phys. Division, Saha Institute of Nuclear Phy./AF Bidhan nagar, Calcutta 700064, India, (d)Laboratoire de Physico-Chimie des Interfaces et Applications, Université d'Artois, Rue Jean Souvraz, BP18, 62307 Lens Cedex, France
Neodymium nickelate thin films have been elaborated onto NdGaO₃ substrates by RF magnetron sputtering and post-annealing treatment under oxygen pressure. Transport properties are found to strongly depend on thickness. Thick films show transport properties close from bulk ceramics while very thin films exhibit a transition from metal to insulator in a wide temperature range with high resistivity. Structure and surface morphology of the films have been investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM) respectively. Thin film (20nm) are heteroepitaxial grown while thicker film (50nm) shows a granular structure. Relationship between microstructure and transport properties is discussed.
- L/P.53** RELATIONSHIP BETWEEN STRAIN AND METAL-INSULATOR TRANSITION IN NDNiO₃ THIN FILMS
P. Laffez(a), P. Goudeau(b), M. Zaghrioui(c), F. Capon(a) E. Elkaim(d), D. Thiaudière(d), (a)Laboratoire de Physique de l'Etat Condensé - UMR CNRS 6087, Université du Maine, Avenue O. Messiaen, 72085 Le Mans cedex, France, (b)Laboratoire de Métallurgie Physique - UMR CNRS 6630, Université de Poitiers, Avenue Marie et Pierre Curie, B.P. 30179, 86962 Futuroscope Chasseneuil cedex, France, (c)Laboratoire d'Electrodynamique des Matériaux Avancés - FRE CNRS 2077, Université FranAois Rabelais, Parc de Grandmont, 37200 Tours cedex, France, (d)Laboratoire pour l'Utilisation du Rayonnement Electromagnétique - UMR 130 CNRS, Université Paris Sud, Bât. 209D, B.P. 34, 91898 Orsay cedex, France
The RNiO₃ perovskites (R=rare earth) are well-known for their metal to insulator transition, which temperature can be modulated by changing the nature of the rare earth. It makes this family of oxide very attractive for several applications such as thermocromic coating. In this work we have studied NdNiO₃ thin films, on two different substrates (NdGaO₃, Si), with different thickness and orientation. The temperature of the metal to insulator transition vary in the range 150K-200K.
Residual stress in films were analyzed using the sin²y method. Each film exhibits in plane tensile stress which magnitude depends on the synthesis conditions. A possible relationship between the metal-insulator transition temperature and residual stress is discussed
- L/P.54** X-RAY MICRO ANALYSIS OF OPTICAL MATERIALS FOR 157nm PHOTOLITHOGRAPHY
E. Sarantopoulou(a), G. Drazic(b), S. Kobe(b), Z. Kollia(a), P. Argitis(c) A. C. Cefalas(a), (a)National Hellenic Research Foundation, TPCI 48 Vassileos Constantinou Avenue, Athens Greece, (b)Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia, (c)Institute of Microelectronics, NCSR "Demokritos", Aghia Paraskevi, Atiki 15310, Greece
Next generation microelectronic circuits will have minimum dimensions below 100 nm. It is envisioned that 157nm laser lithography will be the next step of optical lithography [1]. At 157nm vacuum ultraviolet (VUV) illumination of the mask target lithographic features with dimensions less than 0.10µm on the photoresist could be achieved. However, there are problems related with the design of the optical projection system. This is mainly because most of the materials in one hand have high absorption coefficient and their optical properties degrade constantly with time under VUV irradiation. Taking into consideration the imaging requirements for this type of application, the refractive index variation over the illuminated volume of the optical material should be better than 10⁻⁶, and hence optical elements should be prepared from ultra high purity materials. Crystals have been examined by using high-resolution field emission gun transmission electron microscopy and scanning transmission electron microscopy (FEG-TEM/STEM). The Jeol 2010 F microscope equipped by the energy dispersive X-ray spectroscopy (EDXS) has been proved to be an efficient quality control technique for identifying defects and various impurities in crystal samples.
[1] A. C. Cefalas, E. Sarantopoulou, P. Argitis and E. Gogolides, Appl. Phys. A. 69 (1999) 929.
- L/P.55** GROWTH AND PROPERTIES OF PURE AND LANTHANUM-SUBSTITUTED Sr₂FeMoO₆ SINGLE CRYSTALS
P. Decorse, P. Berthet, J. Berthon, P. Reutler, R. Suryanarayanan, A. Revcolevschi, LPCES-UMR8648, Bât.414, E. Foy, A.M. Haghiri-Gosnet, IEF-UMR 8622, B, t.220, Université Paris Sud, 91405 Orsay, France
Double perovskites of the Sr₂FeMoO₆ (SFMO) family are the subject of a large investigation effort since they exhibit extrinsic magnetoresistance in low magnetic fields and have high Curie temperatures. The growth of single crystals of these materials makes it possible to study their intrinsic magnetic and transport properties and, therefore, to reach a better understanding of the extrinsic properties of the polycrystalline samples.
Pure and lanthanum-substituted SFMO single crystals were grown by the floating zone method in an image furnace. The quality of the crystal depends on several parameters such as the preparation conditions of the feeding rod, the growth atmosphere and the growth speed. The last parameter has a direct influence on the Fe/Mo ordering in the double perovskite and on the Curie temperature of the as-grown crystal, but it appears impossible to reduce it enough without inducing the precipitation of a parasitic phase. This limitation comes from the difficulty to perform the growth under a convenient oxygen partial pressure. However, the Curie temperature of the samples may be increased by a thermal treatment of the as-grown crystal. Lanthanum-substituted samples exhibit higher Curie temperature than pure SFMO but their saturation magnetization decreases with their lanthanum content.

SYMPOSIUM L

- L/P.56** **STUDIES OF LAYERED Ti₃SiC₂ BY HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY**
Hans Starnberg and Sven Stoltz, Dept of Physics, Göteborg University and Chalmers University of Technology, 412 96 Göteborg, Sweden, and Michel Barsoum, Dept of Materials Engineering, Drexel University, Philadelphia PA 19104, USA
During the past five years a new class of layered ternary carbides and nitrides with extraordinary physical properties has attracted much attention [1]. These compounds can be considered as thermodynamically stable nanolaminates, and are electrically and thermally conductive, readily machinable, tolerant to thermal shock, plastic at high temperatures, and exceptionally damage tolerant. They are also elastically rigid, lightweight, and maintain their strength to high temperatures. They are distinguished from other layered materials by the metallic nature of their bonding and by unusual deformation mechanisms. A prominent member of this new class of ceramics is Ti₃SiC₂, which is also creep, fatigue and oxidation resistant. Recently it was found that both the thermopower and Hall coefficients of Ti₃SiC₂ are vanishingly small over a wide temperature range [2]. We have studied fractured surfaces of coarse-grained Ti₃SiC₂ by means of photoelectron spectroscopy at the MAX-II synchrotron radiation facility in Lund, Sweden. High-resolution C 1s, Si 2p, Ti 2p, Ti 3s and Ti 3p core-level spectra are reported and interpreted in terms of crystallographic and electronic structure. Valence band spectra are found to be in reasonable agreement with band calculations.
[1] M W Barsoum, Prog. Solid St. Chem. 28 (2000) 201.
[2] H-I Yoo, M W Barsoum & T El-Raghy, Nature 407 (2000) 581.
- L/P.57** **ROOM TEMPERATURE RESISTIVITY AND INFRARED PROPERTIES OF Nd_{0.7}Eu_{0.3}NiO₃ THIN FILM FOR THERMOCHROMIC APPLICATION**
F. Capon, P. Laffez, J-F. Bardeau, P. Simon, P. Lacorre, Université du Maine, Laboratoire de Physique de l'Etat Condensé, Avenue O. Messiaen, 72085 Le Mans cedex, France
Eu_{0.3}Nd_{0.7}NiO₃ thin films were deposited on Si (100) by RF-sputtering and subsequent annealing. This film exhibit insulator to metal (MI) transition around room temperature. Electrical properties are associated with an optical shift in the infra red range. Measurements in the wavelength range from 2 microns to 25 microns spectra reveal contrast in reflectivity (30%) and transmission (55%). Effect of thickness is study in order to determine the optimal infrared properties.
- L/P.58** **COMPARISON OF SCINTILLATION PROPERTIES OF YAlO₃ ACTIVATED WITH Ce AND Pr IONS**
Z. Galazka(a), A.J. Wojtowicz(b), M. Wisniewska(b), W. Drozdowski(b), P. Szupryczynski(b), Lukasiewicz(a), (a)Institute of Electronic Materials Technology, 133 Wolczynska Street, 01-919 Warsaw, Poland, (b)Institute of Physics N. Copernicus University, Grudziadzka 5, 87-100 Torun, Poland; T.
In this communication we report on scintillation and spectroscopic properties of YAlO₃ (YAP) crystals activated with Ce and Pr ions. We present results of various measurements, such as scintillation pulse and emission time profiles, light yield, and excitation and luminescence spectra obtained at various temperatures. Light yield of YAP was found to be dependent on level of activation and best results, i.e. 12100 ph/MeV and 4600 ph/MeV, were achieved for nominal Ce and Pr concentration of 0.1 at. %, respectively. Decay time constants were found to be 18.8 ns and 8.3 ns for Ce and Pr activator, respectively, which are probably very close to the corresponding radiative lifetimes. The obtained spectroscopic results confirm the recombination model of scintillation light production [1, 2].
[1] A. J. Wojtowicz, J. Glodo, A. Lempicki, and C. Brecher, "Recombination and Scintillation Processes in YAlO₃:Ce", J. Phys.: Condens. Matter, 10 (1998) 8401-15;
[2] A. J. Wojtowicz, J. Glodo, W. Drozdowski, K. R. Przegietka, "Electron Traps and Scintillation Mechanism in YAlO₃:Ce and LuAlO₃:Ce Scintillators", J. Lumin. 79 (1998) 275-291.
This work was supported by the Polish Committee of Scientific Research, KBN (grants 8T11B02917 and 2P03B04914).
- L/P.59** **Sr₆V₂O₁₁ AS POSSIBLE RESISTIVE BARRIER FOR HIGH TEMPERATURE SUPERCONDUCTORS CABLES PROCESSING**
Alain Zaragoza, Sovanary Phok, Christine Opagiste, Jean-Louis Jorda, LAIMAN - ESIA, Université de Savoie, France
In the innovative resistive barrier concept for the processing of high temperature superconducting cables, several mixed oxides have been claimed as promising materials. Amongst them, earth zirconates have been tested and recent development concerns Sr/sub 6/V/sub 2/O/sub 11/.
In addition to a high stability, the conditions for use of these barriers include good deformation properties and chemical homogeneity. Sol-gel methods of preparation using acrylamide as polymerisant agents may fulfill these requirements in particular because they produce after calcination, systems with a very fine granulometry.
Here we present the compared formation and preparation of submicrometric BaZrO/sub 3/, SrZrO/sub 3/ and Sr/sub 6/V/sub 2/O/sub 11/ obtained by sol-gel technique and analysed by means of differential temperature analysis and high temperature X-ray diffraction.
- L/P.60** **STOICHIOMETRIC CHARACTERIZATION OF AMINE INTERCALATED LEAD IODIDE**
C.C. Coleman, W. Tikkanen, H. Goldwhite, T. Berhe, B. Magness, M. Gallegos, California State University, Los Angeles, USA
The stoichiometry and some optical spectral changes of semiconducting layer structured lead iodide intercalated with methylamine and ethylamine are reported. Vapor diffused purified lead iodide was used to make powder, thick film and thin film samples. Degassed host samples were exposed to guest gas pressures ranging from 1 to 20 Torr. Mass changes were determined by quartz spring and crystal oscillator methods. The intercalation of methylamine and ethylamine into lead iodide at low pressures results in a similar uptake of these two amines of somewhat greater than 1:1 guest to lead iodide host ratio. Intercalation saturation occurs in 3 hours. Deintercalation obtained by pumping takes 15 days suggesting the intercalated state is fairly stable. Optical data were obtained using thin film host samples. Both guests produce a 0.46 eV increase of the optical band edge energy upon intercalation. Deintercalation gravimetric data indicate there may be a second stage intercalation at lower guest pressures.
This work was supported by NSF DMR 9901165.

SYMPOSIUM L

- L/P.61** CHARACTERIZATION OF TRANSPARENT AND CONDUCTIVE ZnO:Ga THIN-FILMS PRODUCED BY RF SPUTTERING AT ROOM TEMPERATURE
V. Assunção, E. Fortunato, A. Marques, R. Martins Department of Materials Science/CENIMAT, Faculty of Sciences and Technology, New University of Lisbon and CEMOP-UNINOVA, 2829-516 Caparica, Portugal
In this study we present for the first time (as far as acknowledged by the presenting authors) the lowest value for the electrical resistivity of Ga doped zinc oxide (ZGO) deposited at room temperature by RF magnetron sputtering. In order to improve the performances of these transparent conductive oxides, we have varied the deposition pressure from 2.1E-2 to 1.5E-3 mbar, keeping constant all the other deposition parameters. In order to correlate the deposition conditions with the properties presented by the films a set of characterization techniques have been used. The films have been characterized through electrical (four point probe and Hall effect), optical (UV-VIS), structural (X-ray diffraction spectroscopy) and morphological (Scanning Electron Microscopy and Atomic Force Microscopy) techniques. The preliminary results show that, as the deposition pressure decreases, the electrical resistivity, Hall mobility and carrier concentration are improved to values of: 4.3E-4 ohm.cm, 14.2 cm²/Vs and 1.0E21 cm⁻³, respectively. For all the films studied the optical transmission was higher than 85% in the visible range. However, for the near IR region we start to observe a decrease in the optical transmission due to the increase associated with the carrier concentration. The structural properties reveal that the films present a high degree of crystallinity associated to a hexagonal structure, and present a strong preferred orientation with the c axis perpendicular to the substrate.
- L/P.62** EFFECT OF THE SUBSTITUTION OF Na+ IN PLACE OF Ca2+ IN THE PEROVSKITE Pr_{0.7}Ca_{0.3}MnO₃
K. Cherif(a), S. Zemni(a), J. Dhahri(a), M. Oumezzine(a) and H. Vincent(b), (a)Laboratoire Physico-Chimie Structurale, Département de Physique, Faculté des Sciences de Monastir, 5019 Monastir, Tunisie, (b)Laboratoire des Matériaux et de Génie Physique, ENSPG, BP 46, 38402 Saint Martin d'Hères cedex, France
We have investigated the structural, magnetic and transport properties of polycrystalline Pr_{0.7}Ca_{0.3-x}NaxMnO₃. Single phase samples are obtained in the range 0 < x < 0.2 using neutral NaCl fluxes at a relatively low temperature of 900°C. Powder X-Ray diffraction patterns are indexed in the orthorhombic perovskite structure with Pnma space group. The lattice parameters and cell volume increase with average ionic radius <rA>. Magnetisation and resistivity measurements versus temperature show that all our samples exhibit a semiconducting paramagnetic-metallic ferromagnetic transition when the temperature decreases. The Curie temperature T_c increase with the Mn⁴⁺ content.
- L/P.63** HOLMIUM-POTASSIUM DOUBLE TUNGSTATE SINGLE CRYSTAL GROWTH
A. Majchrowski(a), J. Zmija(a), M.T. Borowiec(b), H. Szymczak(b), and T. Zayarnyuk(b), (a)Institute of Applied Physics, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland, (b)Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
Holmium-potassium double tungstate KHo(WO₄)₂, as other rare earth double tungstates, shows the high temperature irreversible structural phase transition. Owing to this, KHo(WO₄)₂ single crystals were grown with use of the Top Seeded Solution Growth (TSSG) technique, which allows to lower the temperature of crystallisation below the temperature of phase transition. Seeds for TSSG method were obtained with use of the spontaneous crystallisation [1]. As a result transparent, brownish crystals confined with flat planes were obtained. The dimensions of homogeneous, high quality crystals reached about 20x15x15mm.
Holmium-potassium double tungstate has at room temperature the monoclinic α-KY(WO₄)₂ structure (C₂h6-C₂/c symmetry). This monoclinic chain-layered structure is a reason of strong anisotropy of many physical properties of this crystal. In particular, holmium-potassium double tungstate belongs to the class of biaxial crystals and is pleochroic (trichroic). This work was supported by Polish State Committee on Science (KBN) (project No. 2 P03B 141 18).
[1] A.Majchrowski, M.T.Borowiec, E.Michalski, J.Zmija, V.P.Dyakonov, H.Szymczak, T.Zayarnyuk, M.Baranski, Cryst. Res. & Tech., 36(3), (2001), 283.
- L/P.64** STRUCTURAL AND MECHANICAL CHARACTERIZATION OF THIN FILMS OF TANTALUM CARBIDES
Y. Hadjar, Institut de Tronc Commun Sciences Exactes et Technologie, Université de Batna, Algérie, R. Halimi, Laboratoire Couches Minces et Interfaces, Université Mentouri, 25000 Contantine, Algérie and F. Tancret, Laboratoire Génie des Matériaux, Ecole Polytechnique de l'Université de Nantes, La Chantrerie, rue Christian Pauc, BP 50609, 44306 Nantes Cedex3, France
In the present work we are intending to elaborate and to study thin film coating of tantalum carbides on steel substrates of XC100 type (according to AFNOR norms). The procedure used in order to prepare the samples consist on depositing, by electron gun evaporation, a thin film (4 mm thickness) of tantalum on steel substrates containing 1%wt.of carbon; then, annealing the system (substrate/coating) in vacuum at a temperature at which the carbon of the substrate may diffuse into the Ta metallic film. This fact leads to the formation of tantalum carbides. The structural analysis is carried out by using X-ray diffraction, electron microscopy and Auger electron spectroscopy. The mechanical characterization is performed by measuring the microhardness and adhesion. It is found that at annealing up to 800°C two carbides (Ta₂C and TaC) are formed. During the subsequent heat treatment from 900°C to 1100°C, the Ta₂C compound transforms completely into TaC phase. The mechanism of the carbides is discussed. Moreover, the microhardness and adhesion of the films increase significantly with increasing of annealing temperature.
- L/P.65** MICROSTRUCTURE AND PROPERTY CHANGES CAUSED BY DIFFUSION DURING HEAT TREATMENT OF TITANIUM COATING ON STEEL
Y. Benarioua, Département de Génie Mécanique, Université de M'sila, BP 166, 28000 M'sila, Algérie, and R. Halimi, Laboratoire Couches Minces et Interfaces, Université Mentouri, 25000 Contantine, Algérie
A study has been made on Ti coatings (* 4 *m thickness) deposited by direct current magnetron sputtering onto high carbon ball bearing (120 C4) steel substrates kept at 150°C. The samples were subjected to high vacuum annealing at a temperature between 500 and 1100°C for 1 hour. the structure and morphology were studied by X-ray diffraction, scanning electron microscopy and microprobe analysis. The adhesion and microhardness measurements were carried out using a scratch and vikers testers respectively. It was found that the reaction leads to the formation and growth of TiC compound at temperatures above 600°C. After annealing at 1100°C only the single TiC phase was observed. Moreover, a significant increase in microhardness and adhesion of the films with increasing of annealing temperature was also observed.

SYMPOSIUM L

- L/P.66** INFLUENCE OF MICROSTRUCTURE AND PHASE COMPOSITION ON CORROSION RATE OF FUNCTIONAL Zn-Ni COATINGS
E. Beltowska-Lehman, P. Ozga and Z. Swiatek, Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 30-059 Krakow, 25 Reymonta Str., Poland
The electrocrystallization processes of Zn-Ni films from weakly acid sulfate solutions with the addition of citrate and acetate complexing compounds have been compared. The deposition kinetics and the influence of electrolyte composition on the Zn-Ni alloy composition and on some physicochemical properties (corrosion resistance, texture, phase composition, morphology) were determined. It was found that the properties of coatings obtained under the same operating conditions in electrolytes with the same [Ni(II)]/[Zn(II)] concentration ratio and pH but containing different complexing agents were different. The composition of the deposits and their phase structure were found to depend on the complexing species present. Coatings deposited from acetate solutions are richer in Ni than those from citrate solutions. The corrosion resistance of a Zn-Ni alloy depends in practice on the percentage of Ni, but in sulfate-citrate electrolytes, layers containing less Ni were obtained with the same corrosion resistance as Ni-rich coatings deposited from acetate solution. The corrosion current decreases more rapidly with increasing Ni content. This effect is connected mainly with phase composition. In citrate solutions practically single-phase (hexagonal h) deposits were obtained which provide better protection with a lower corrosion rate in comparison with alloys consisting of three phases (hexagonal h, monoclinic d, orthorhombic g) deposited from acetate baths.
- L/P.67** CRYSTAL CHEMISTRY VERSUS GROWTH PROCESSES FOR EPITAXIAL GATE DIELECTRICS
J. Fompeyrine(a), J.W. Seo(a,b), H. Siegwart(a), C. Rossel(a) and J.-P. Locquet(a), (a) IBM Research, Zurich Laboratory, Ruschlikon, Switzerland, (b) Institut de Physique, Uni Neuchatel, Neuchatel, Switzerland
In the coming years, aggressive scaling in CMOS technology may trigger the transition from silicon dioxide to alternate gate dielectrics. If chemical and structural integration issues can be solved, epitaxial dielectrics will be a first step towards many novel device structures and functions. Looking at this perspective, we will first discuss various crystal chemistries, structures and properties, and then stress the importance of atomically controlled processes. These remarks will be illustrated using selected examples chosen in the open literature or in our own work. They will range from simple binary oxides like rare-earth oxides to more complex materials, including SrTiO₃ perovskite or La₂Zr₂O₇ pyrochlore. We will more in detail report on this latter example, and underline what atomic processes are involved, and how do they impact the overall dielectric properties. We will in particular discuss the growth conditions of Zr-based pyrochlores on various Si surfaces, and the impact of ex-situ annealing on the dielectric properties of MOS structures.
- L/P.68** STRUCTURAL FACTOR IN Ni-Cu-Mo FUNCTIONAL LAYERS PRODUCED BY ELECTROCRYSTALLIZATION
E. Beltowska-Lehman, Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 30-059 Krakow, 25 Reymonta Str., Poland
Ternary Ni-Cu-Mo films with various compositions, which are difficult or even impossible to obtain by conventional thermal methods (because of the lack of mutual solubility of Mo and Cu and the large difference in their melting points) can be electrodeposited at room temperature from aqueous electrolytes. These layers derived from Ni-based binary alloys show promising anticorrosion properties in many aggressive environments. Ni-Cu-Mo coatings of different composition were electrodeposited from citrate-ammonia baths in potentiostatic and galvanostatic regimes under controlled hydrodynamic conditions. The present work is aimed at structural characterisation of Ni-Cu-Mo electrodeposits (surface morphology, phase composition, preferred orientation, lattice imperfections, internal stresses), that among other things influence the coating's corrosion resistance. The surface morphology and preferred orientation of the deposits was strongly correlated with chemical composition. X-ray diffraction patterns of all Ni-Cu-Mo coatings (Cu-based and Ni-based) exhibit mainly the fcc phase structure of Ni-Cu solid solution with a lattice parameter intermediate between those of Cu and Ni, which decreases when the nickel content increases. These results should be helpful in determining the electrocrystallization conditions for Ni-Cu-Mo alloys that provide the best corrosion protection.
- L/P.69** DEFECT CHEMISTRY OF ADAMANTINE CHALCOGENIDE SEMICONDUCTORS AND ELECTRONIC PROPERTIES SELF-STABILIZATION
J.F. Guillemoles, Laboratoire d'Electrochimie et de Chimie Analytique, ENSCP (CNRS UMR 7575), 11 rue Pierre et Marie Curie, 75232 Paris Cedex 05, France
CIGS (Cu(In,Ga)Se₂) solar cells have demonstrated both very high performance and exceptional insensitivity to radiation damage or impurity. Facts related to stability of CIGS electronic properties will be briefly reviewed. Then potential underlying reasons for this exceptional behaviour will be exposed. The role of the interactions between point defects in the stabilisation will be stressed. Their connection to the phase diagram of the ternary will also be discussed. A mechanism by which association of point defects may lead to self-healing of potentially harmful deep centers is proposed. Last, a generalisation of the above mechanisms to others members of the chalcogenide adamantine family will be attempted in view of the present understanding of this effect.

SYMPOSIUM L

Friday, June 21, 2002
Vendredi 21 juin 2002

Morning
Matin

Session VIII

- L-VIII.1** 9:00 **ANION ORDERING IN FLUORINATED CUPRATES**
J. Hadermann, O.I. Lebedev, G. Van Tendeloo, EMAT, University of Antwerp (RUCA) Groenenborgerlaan 171 B-2020 Antwerpen, Belgium; and A.M. Abakumov, M.G. Rozova, A.M. Alekseeva, E.V. Antipov, Department of Chemistry, Moscow State University, Moscow 119899, Russia
A combination of the TEM and XRD techniques has been applied to characterise the structure of several cuprates fluorinated by XeF₂. The results of this investigation show that, besides such obvious result of fluorination as the tuning of a doping level, the complicated interplay of the reactions of anion insertion and anion exchange at the interaction of the material with XeF₂ opens new possibilities for the structure modification of the already well known superconductors and for the creation of new structures which could be considered as potential superconductors if the appropriate amount of holes will be introduced into the conductive band. The appearance of additional anions due to fluorine insertion or to anion exchange of 1O²⁻ for 2F⁻ result in structural transformations including changes in the coordination polyhedra, interatomic distances and space symmetry, up to a complete structural reorganization. In the case of anion deficient materials, the introduction of fluorine into the structure can eliminate the anion-vacancy ordering which often causes the absence or distortion of the (CuO₂)-planes, thus making the structure suitable for superconductivity.
- L-VIII.2** 9:40 **WHAT MAKES THE OXYGEN TRANSFER IN BISMUTH-BASED MATERIALS ?**
Rose-Noëlle Vannier, Laboratoire de Cristallographie et Physico-chimie du Solide, CNRS-UMR 8012, Ecole Nationale Supérieure de Chimie de Lille, B.P. 108, 59652 Villeneuve d'Ascq Cedex, France
Pure oxide ion conductors can be used as electrolyte in many applications: oxygen sensors, Solid Oxide Fuel Cells, Ceramic Oxygen Generators... In this field, bismuth-based oxides are displaying the best conductivity at moderate temperature 300-600°C. Depending on the dimensionality of their structures, these materials can be classified into three groups. The correlation between their structural characteristics and their electrical properties will be presented. Because of the sensitivity of bismuth towards reduction, these materials cannot be used in Solid Oxide Fuel Cells but their use as electrolyte in electrically driven oxygen generator is extensively studied. In such a classical device, electrode materials are added at the surface of the membrane to allow the oxygen transfer into the electrolyte. However for bismuth-based materials, under working conditions, an unusual behaviour was observed. High oxygen transfers were obtained with membrane simply made of a dense ceramic sandwiched between two gold grids as current collectors. The exceptional properties of the BIMEVOXes materials were characterised combining in-situ X-ray diffraction and ¹⁸O/¹⁶O isotopic exchange and the oxygen transfer explained.
- 10:20 **BREAK**
- L-VIII.3** 10:40 **IMPORTANT PARAMETERS IN THE DENSIFICATION OF BULK ZrW₂O₈**
C. De Meyer(a), L. Vandepierre(b), I. Van Driessche(a), E. Bruneel(a), S. Hoste(a), (a)Dept. Inorganic and Physical Chemistry, University of Ghent, Krijgslaan 281, Bld. S3, 9000 Gent, Belgium, (b)Dept. Materials Science and Metallurgy, University of Cambridge, New Museum Site, Pembroke Street, Cambridge, UK
Since the discover of the large isotropic negative thermal expansion behaviour in zirconium tungstate, this compound has received a lot of interest. Due to these properties, the compound can find several applications. For example, its use in composites might be a key to compensate for the undesired positive expansion of other phases, resulting in materials with tailored overall thermal expansion. These and other applications require dense bulk ZrW₂O₈. Most of the current research concentrates on the theory behind this exceptional behaviour and on phase transformations occurring with increasing temperature of pressure. However, the influence of the synthesis conditions on the properties of the final material and the development of convenient synthetic routes and of the scalability of its manufacture to industrial level still needs closer examination. Because literature on the microstructure, density and sintering of ZrW₂O₈ is very limited, these were investigated in particular in this research. The influence of the sintering conditions (time, temperature, precursor and sintering crucible) on phase-purity, density and mass loss due to WO₃-evaporation and decomposition are investigated.
- L-VIII.4** 11:20 **SYNTHESIS AND CRYSTAL STRUCTURE OF NOVEL RUDDLESDEN-POPPER STRONTIUM NIOBIUM OXYNITRIDES**
G. Tobías, J. Oró-Soler, D. Beltrán-Porter and A. Fuertes, Institut de Ciència de Materials de Barcelona (C.S.I.C.), Campus U.A.B., 08193 Bellaterra, Spain
The family (SrO)(SrNbO_{2-x}N)_n constitutes the first example of strontium niobium Ruddlesden-Popper oxynitrides and provides layered structures to obtain mixed valence niobium compounds with a variety of oxidation states and transport properties[1]. We have prepared members with n=1 (Sr₂NbO_{2.8}N) and n=2 (Sr₃Nb₂O_{4.7}N₂) by solid state reaction of Nb₂O₅ and SrCO₃ at 900-1050 °C under ammonia flow. Samples were air sensitive and their handling was done in an inert atmosphere. A reduced sample from n=1 phase was prepared by treating Sr₂NbO_{2.8}N at 447°C in Ar/H₂ (95:5, V:V). The compounds were characterized by X-ray powder diffraction, electron diffraction and XEDS analysis. Chemical compositions were determined by plasma absorption analysis (for cation contents), elemental analysis (for C and N contents) and thermogravimetric analysis (TGA) performed in O₂ and Ar/H₂. The crystal structures have been solved by Rietveld refinement using X-ray powder diffraction data. The compounds crystallize in the I4/mmm space group and show a range of anionic stoichiometry that modulates, together with the N/O ratio, the formal oxidation state of niobium and therefore the resultant physical properties.
[1] G.Tobías, et. al., Inorg. Chem. 40, 6867 (2001).

SYMPOSIUM L

L-VIII.5

11:40

MAGNELI PHASES OF TITANIUM OXIDES (Ti_nO_{2n-1}) FOR TRIBOLOGICAL APPLICATIONS

C. Langlade, D. Treheux, STMS Department, IFoS laboratory, Ecole Centrale de Lyon, 69134 Ecully cedex, France

Thermally and oxidatively stable compounds having low shear strength and low wear rate remain of great interest for most tribological applications. Among others candidates, the various oxides of the Magneli series seem to have some real potential. Since the first theoretical paper from A. Magneli in the early fifties, numerous studies have investigated their crystal structure and some aspects of their properties. The objective of this paper is to clarify their crystal structures and specific defects and to review some of the valuable characterization methods as well as their tribological properties.