

Abstracts of Forthcoming Articles

Ionic Conductivity of Pure, Ca²⁺-, and Sr²⁺-Doped Single Crystals of LiCl. M. SHARON* AND R. R. PRADHANANGA, Department of Chemistry, Indian Institute of Technology, Bombay-400076, India. Single crystals of pure and doped LiCl were grown by the Bridgeman technique. The ionic conductivities of pure, Ca²⁺- and Sr²⁺-doped crystals of LiCl in the temperature range 250–580°C are reported. The enthalpy of formation of Schottky defects, enthalpy of migration of the Li⁺ vacancy, and enthalpy of association of (Sr²⁺ ion–Li⁺ vacancy) have been calculated by detailed isotherm calculation. The various conductivity parameters are: Enthalpy of formation of Schottky defects: 1.66 ± 0.03 eV; Enthalpy of migration of the Li vacancy: 0.59 ± 0.03 eV; Enthalpy of association between Sr²⁺–Li⁺ vacancy: 0.61 ± 0.02 eV.

Self-Compensation in Lanthanum-Doped Strontium Titanate. N. G. EROR* AND U. BALACHANDRAN. Oregon Graduate Center, Beaverton, Oregon 97006. Gravimetric measurements on pure and lanthanum-doped SrTiO₃ have shown that the reversible change of oxygen content between specified states of oxidation and reduction is proportional to the dopant concentration. These measurements indicate that the donor-dopants are electronically compensated by additional oxygen uptake in the oxidized state. The range of this reversible change in oxygen stoichiometry is up to more than an order of magnitude larger than the oxygen nonstoichiometry of the undoped SrTiO₃. A single phase region from La_{0.2}Sr_{0.8}Ti_{0.8}Ti_{0.2}O₃ to La_{0.2}Sr_{0.8}Ti⁴⁺O_{3.10} has been confirmed for lanthanum-doped SrTiO₃. The gravimetric measurements can be explained by a model involving a shear structure.

Preparation of TaS₃ under High Pressure. S. KIKKAWA,* M. KOIZUMI, S. YAMANAKA, Y. ONUKI, R. INADA, AND S. TANUMA, The Institute of Scientific and Industrial Research, Osaka University, Osaka, 565, Japan. Monoclinic TaS₃ is prepared without the coexistence of the orthorhombic TaS₃ and TaS₂ under high pressure in a cubic anvil device. Lattice parameters are $a = 9.552 \text{ \AA}$, $b = 3.345 \text{ \AA}$, $c = 14.925 \text{ \AA}$, and $\beta = 109.98^\circ$. The compound is a semiconductor with transitions at 200 and 250 K.

Etude des phases β et haute pression du phosphate tricalcique par la RPE de l'ion Cu²⁺. S. S. ROMDHANE, G. BACQUET,* ET G. BONEL, Laboratoire de Physique des Solides, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France. Copper (II)-doped powdered samples of β -Ca₃(PO₄)₂ and of its high-pressure phase, which is an isotype of Ba₃(VO₄)₂, were studied by ESR. In each case the RT spectrum is due to a unique type of defect exhibiting orthorhombic and respectively axial symmetry. The spin-Hamiltonian parameters were determined using the method proposed by Rollmann and Chan for polycrystalline specimens. With stressed samples the contribution of each of both copper isotopes was resolved. Our results show that isolated copper ions substitute preferentially for calcium in Ca(III) sites of β -calcium orthophosphate, these sites corresponding to the Ca(I') ones in the high-pressure phase.

Phase Relations of Ternary Compounds in the Ba–Fe–S System. T. P. PERNG, N. KIMIZUKA, AND H. STEINFINK,* Materials Science Laboratories, Department of Chemical Engineering, The University of Texas, Austin, Texas 78712. The phase relations of the ternary phases at 900 and 700°C were determined by heating mixtures in the regions BaS–FeS–FeS₂ and Fe–FeS–BaS and identifying the products by powder X-ray diffraction. The stable ternary phases at 900°C are BaFe₂S₃, Ba₂FeS₃, Ba₆Fe₈S₁₅, a solid solution BaFeS₂–Ba₇Fe₆S₁₄, Ba₂FeS₄, the infinitely adaptive series Ba₃Fe_{1+x}S₅, $\frac{1}{2} \leq x \leq \frac{2}{3}$, and Ba₉Fe₁₆S₃₂, which belongs to the infinitely adaptive series Ba_{1+x}Fe₂S₄. At 700°C the stable ternary phases are: BaFe₂S₃, Ba₂FeS₃, BaFeS₂–Ba₇Fe₆S₁₄ solid solution, Ba₆Fe₈S₁₅, Ba₂FeS₄, Ba₃Fe₄S₁₁, and two infinitely adaptive series Ba₃Fe_{1+x}S₅ and Ba_{1+x}Fe₂S₄. A stable ternary phase at 700 and 900°C with probable composition Ba₂Fe₄S₅ was found in the Fe–FeS–BaS section.

Magnetic Interactions in Ternary Cobalt Oxide with Cubic Perovskite Structure. H. TAGUCHI, M. SHIMADA,* AND M. KOIZUMI, The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka, 565, Japan. Magnetic properties were measured on the cubic perovskite systems

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SrCoO_{3-x} , $(\text{La}_{1-x}\text{Sr}_x)\text{CoO}_3$ ($0.5 \leq x \leq 1.0$) and $\text{Sr}(\text{Co}_{1-x}\text{Mn}_x)\text{O}_3$ ($0 \leq x \leq 1.0$). From the result, it is found that Sr^{2+} and La^{3+} ions strongly affect the spin state of the Co^{3+} ion and that the Mn^{4+} ion located at the octahedral site affects the spin state of Co^{4+} ion. The magnetic properties (T_c , T_θ , and σ) are explained by the magnetic interaction $\text{Co}^{3+}-\text{O}-\text{Co}^{3+}$, $\text{Co}^{3+}-\text{O}-\text{Co}^{4+}$, $\text{Co}^{4+}-\text{O}-\text{Co}^{4+}$, $\text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$, and $\text{Mn}^{4+}-\text{O}-\text{Co}^{4+}$ in these systems.

A New Monoclinic Phase in the $\text{Fe}_2\text{O}_3-\text{TiO}_2$ System. I. Structure Determination and Mössbauer Spectroscopy. M. DROFENIK,* L. GOLIC, D. HANZEL, V. KRASEVEC, A. PRODAN, M. BAKKER, AND D. KOLAR. Jozef Stefan Institute, E. Kardelj University, Jamova 39, 61000 Ljubljana, Yugoslavia. Single crystals with compositions within the $\text{Fe}_2\text{O}_3-\text{TiO}_2$ system were grown from a flux containing various amounts of the basic oxides. Apart from the known pseudo-brookite (Fe_2TiO_5) and rutile (TiO_2) structures, a new monoclinic polytype of Fe_2TiO_5 was found, which was isostructural with V_3O_5 . The structure was determined by X-ray analysis and Mössbauer spectroscopy contributed data on hyperfine parameters and the magnetic ordering temperature.

A New Monoclinic Phase in the $\text{Fe}_2\text{O}_3-\text{TiO}_2$ System. II. The Defect Structure. V. KRASEVEC,* A. PRODAN, M. BAKKER, M. DROFENIK, L. GOLIC, D. HANZEL, AND D. KOLAR, Jozef Stefan Institute, E. Kardelj University, Jamova 39, 61000 Ljubljana, Yugoslavia. Defects in monoclinic Fe_2TiO_5 were studied by electron microscopy and diffraction. The monoclinic structure found, which is isostructural with V_3O_5 , can be derived in a simple way from a hexagonal close packed structure and can be considered as a member of the family of crystallographic shear structures, derived from rutile. Two different slips corresponding to two hexagonal basal ones, were found to cause stacking faults, antiphase boundaries, and two different crystallographic shear planes.

La solution solide $\text{Cr}_{1-x}\text{Ir}_x\text{O}_2$. P. MAESTRO, G. DEMAZEAU, ET M. POUCHARD,* Laboratoire de Chimie du Solide, Université de Bordeaux I, 351, cours de la Libération, 33405 Talence Cedex, France. A new solid solution $\text{Cr}_{1-x}\text{Ir}_x\text{O}_2$ ($0 \leq x \leq 1$) has been prepared using oxidizing agents under pressure. The magnetic study shows the importance of the spin-orbit coupling and the weakening of the ferromagnetic interactions with increasing iridium content.

$\text{Ln}(\text{Fe}^{3+}, \text{M}^{2+})\text{O}_4$ Compounds with Layer Structure [$\text{Ln} = \text{Y}, \text{Er}, \text{Tm}, \text{Yb}, \text{and Lu}; \text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Cu}, \text{and Zn}$]. N. KIMIZUKA* AND E. TAKAYAMA, National Institute for Research in Inorganic Materials, 1-1, Namiki, Sakuramura, Niiharigun, Ibaraki-ken, Japan 305. A series of new compounds $\text{Ln}(\text{Fe}^{3+}, \text{M}^{2+})\text{O}_4$ [$\text{Ln} = \text{Y}, \text{Er}, \text{Tm}, \text{Yb}, \text{and Lu}; \text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Cu}, \text{and Zn}$] were successfully synthesized and their lattice constants were determined. These compounds have the same crystal structure as YbFe_2O_4 and Fe^{3+} and M^{2+} are both surrounded by five oxygen ions forming a trigonal bipyramid. The synthetic conditions are presented. They are strongly dependent upon the constituent cations of the compound.

Electrical and Thermoelectric Properties of Undoped MnO Single Crystals. M. PAI AND J. M. HONIG,* Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. The electrical resistivity and Seebeck coefficients of pure MnO single crystals have been measured above the Néel temperature. The material is p type in this temperature range. The results are interpreted on the basis of small-polaron hopping involving charge carriers in one or more sets of transport levels.

Crystal Chemistry of M_{12}P_7 Phases in Relation with the M_2P Phosphides. S. MAAREF, R. MADAR, P. CHAUDOUET, J. P. SENATEUR,* AND R. FRUCHART, E.R. 155, Section de Genie Physique ENSIEG, Domaine Universitaire, B.P. 46, 38402 St. Martin d'Herès, France. A structural model for the description of transition metal phosphides has been applied to the determination of the structural relation between M_{12}P_7 and M_2P hexagonal phases. The correctness of this approach has been tested by the prediction of the substitutional ordering in M_{12}P_7 phases.

Lattice Vibration Spectra. XXVI. Far-Infrared Spectra of the Ternary Skutterudites $\text{CoP}_{3-x}\text{As}_x$, $\text{CoAs}_{3-x}\text{Sb}_x$, and $\text{MGe}_{1.5}\text{Y}_{1.5}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}; \text{Y} = \text{S}, \text{Se}$). H. D. LUTZ* AND G. KLICHE. Laboratorium für Anorganische Chemie der Universität Siegen, Adolf-Reichwein-Strasse, D-5900 Siegen 21, West Germany. The infrared spectra of the skutterudite solid solutions $\text{CoP}_{3-x}\text{As}_x$ and $\text{CoAs}_{3-x}\text{Sb}_x$ and the ordered ternary skutterudites $\text{MGe}_{1.5}\text{Y}_{1.5}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}; \text{Y} = \text{S}, \text{Se}$) have been studied. In the system $\text{CoP}_{3-x}\text{As}_x$ a complete mixed crystal series has been obtained. In the system $\text{CoAs}_{3-x}\text{Sb}_x$ a miscibility gap has been found. The infrared spectra of the mixed crystals are influenced