

PS10.07.08 DIELECTRIC CHARACTERISTICS OF PURE & MIXED RARE EARTH (La,Nd) HEPTAMOLYBDATE CRYSTALS GROWN BY GEL ENCAPSULATION TECHNIQUE. Sushma Bhat, S. K. Khosa, P. N. Kotru, R. P. Tandon*, Department of Physics, University of Jammu, Jammu-180004 (India)*, National Physical Laboratory, New Delhi, India

Single crystal growth of single rare earth heptamolybdates (where R=La,Nd) and mixed (La,Nd) is achieved using the system $R(NO_3)_3 - MoO_3 - NH_4OH - HNO_3 - Na_2SiO_3$ by gel encapsulation technique. The crystals are characterized using X-ray and electron diffraction, IR spectroscopy, SEM and optical microscopy. Dependence of dielectric constant, dielectric loss and conductivity of the samples subjected to different frequencies of the applied a-c fields at different temperatures is studied. The dielectric constant of the materials increase sharply, attains a peak value then decreases rapidly, as the temperature is raised. Dielectric loss and conductivity are strongly temperature and frequency dependent. The sharp rise of dielectric constant with temperature at 10^3 Hz for $T < T_0$ (T_0 being the transition temperature) is attributed to the contribution to a major contribution from space charge polarization. The functional relationship between the dielectric constant (ϵ) and conductivity (σ) and temperature T is theoretically linked to analytical expressions of the type $\epsilon = a_0 + a_1 T^2$ and $-\ln \sigma = a + b(T - T_0)^2$ for $T < T_0$. The indications of these materials being ferroelectric are suggested by the non-linearities and anomalous behaviour of dielectric constant near the transition temperature and further supplemented by the results of preliminary hysteresis experiments.

PS10.07.09 X-RAY DIFFRACTION STUDIES OF THE STRUCTURAL ORIGIN OF SOME OPTICAL EMISSION BANDS IN ION-DOPED NaCl CRYSTALS. A. E. Cordero-Borboa, Instituto de Física, UNAM. A.P. 20-364, D.A. Obregon Mexico D.F. 01000, Mexico.

X-ray diffraction studies were carried out together with luminescence measurements for NaCl:Sr²⁺:Eu²⁺, NaCl:Eu²⁺ and NaCl:Pb²⁺ single crystals under thermal annealing treatments at 200°C. The weak diffracted beams, coming out from the precipitation of secondary phases into the NaCl matrixes, were enhanced by using a simple pneumatic grinder designed and built to obtain small single-crystal spheres of optimum size for minimize the absorption effects. This device offers an advantage over previous grinder systems in that it allows the selection in advance of the final diameters of the crystal spheres by means of pneumatic expulsion through a standard brass gauze. It was found that the precipitation of a secondary SrCl₂ phase and a fluorite-type EuCl₂ phase into the NaCl matrixes are responsible for the presence of emission bands peaking at 407 and 410 nm in the optical fluorescence spectra of specimens annealed for long periods.

PS10.07.10 THE CRYSTAL STRUCTURE OF Cd₄GeSe₆, A II₄ IV VI₆ SEMICONDUCTING MATERIAL. J.M. Delgado*, J.A. Henao*, A.E. Mora** and M. Quintero**. *Departamento de Química and **Departamento de Física, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela

X-ray quality single crystal fragments of Cd₄GeSe₆ were isolated from polycrystalline samples prepared by direct fusion of the elements in sealed, evacuated quartz ampoules. The stoichiometric proportion Cd:Ge:Se::2:1:4 was used because it was originally intended to prepare Cd₂GeSe₄, a II₂ IV VI₄ semiconductor, instead of the II₄ IV VI₆ finally obtained. The chemical composition of this phase was established using a Kevex EDX equipped Hitachi S-1250 SEM. The structural study carried out using single crystal diffraction techniques showed that this material crystallizes in the monoclinic space group Cc, with $a=12.843(2)$, $b=7.411(1)$, $c=12.855(2)$ Å, $Z=4$. Its structure can be described as a superstructure based upon a MgCu₂-type of structure. The superstructure nature of this material was deduced from Buerger precession photographs and confirmed in the structural analysis using the intensity data collected with a four-circle single-crystal x-ray diffractometer.

A detailed discussion of the different structure types reported for the II₄ IV VI₆ family of semiconductors is presented. This work was supported by CONICIT, Programa de Nuevas Tecnologías, Grant NM-18. JAH thanks UIS, Bucaramanga, Colombia for a fellowship.

PS10.07.11 MOLECULAR METALS: STRUCTURE AND PROPERTIES. O.A. Dyachenko, V.V. Gritsenko, S.V. Konovalikhin, R.N. Lyubovskaya, E.B. Yagubskii, R.B. Lyubovskii, Institute of Chemical Physics, RAS, Chernogolovka MD 142432 Russia, and E.Canadell, ICMAB, Campus de la UAB, 08193 Bellaterra, Spain

The structure-conductivity relationships were derived from crystal-line diffraction experiments for the salts based on bis(ethylenedithio)tetrathiafulvalene (ET) and 5,6-dihydro-1,4-dithiin-2,3-dithiol (DDDT), which are potential electronic materials. As a subject for crystallochemical analysis were chosen the family of molecular conductors (ET)₈[Hg₄X₁₂(PhY)₂] (X=Y=Cl, metal down to 1.3 K; X=Cl, Y=Br, T_M=10 K; X=Br, Y=Cl, T_M=90 K; X=Y=Br, T_M=125 K), the first stable down to 1.3 K molecular metals, [Ni(DDDT)₂]₃(AuBr₂)₂ and [Pd(DDDT)₂]₃Ag_{1.54}Br_{3.50}, in the M(DDDT)₂ family of conducting complexes, as well as such relative compounds as molecular semiconductors (ET)₈[Hg₄Br₁₂(MeC₆H₄Cl)₂], (ET)₈[Hg₄Cl₁₂]₂C₆H₆, (ET)₄[Hg₂I₆] and investigated recently new organic metals (BEDO)₄Pt(CN)₄H₂O and (BEDO)₂Cl₂H₂O. In order to understand the structure-property problem in this case, we have performed a multistage crystallochemical analysis of the investigated salts by the scheme: Composition → Anion and anionic layer structure → Conducting layer structure (packing and overlapping types, shortened intermolecular contacts) → Conductivity. On the basis of this analysis it has been established, that: i) the packing type of a conducting layer determines the conductivity type (superconductor, metal, semiconductor), and ii) there is an inverse dependence between the temperatures of metal-insulator transitions (T_M) and the densities of conducting layers. Tight-binding band structure calculations have been carried out for comparison of the electronic structures of relative molecular metals.

PS10.07.12 COMPARATIVE INVESTIGATIONS OF Nb AND Ta DOPED KTiOPO₄ MATERIALS BY HIGH-RESOLUTION X-RAY DIFFRACTION. C.J. Eaton, P.A. Thomas, Department of Physics, University of Warwick, Coventry, CV4 7AL, UK. K. B. Hutton, R.C.C. Ward, University of Oxford, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, UK

Doping of the KTiOPO₄ (KTP) family of materials with ions such as Ta and Nb yields promising non-linear optical materials with increased birefringence but modified physical properties, such as mechanical strength. In this work, 10% niobium doped KTP, and 1% tantalum doped KTP have been studied using high-resolution x-ray diffraction to investigate the crystal quality compared with that of pure KTP. Topographs and reciprocal-space maps are shown and indicate that there is a degree of mosaicity within the material, with both similar and differing d-spacings in the mosaic blocks. These microstructural features are discussed in relationship to the crystal growth and quality of doped KTP and the suppression of growth along the [100] direction in particular.

In addition, second-harmonic generation studies have been made to image the mosaic blocks, and energy-dispersive x-ray analysis has been performed to determine if dopant levels are homogeneous throughout the sample.

PS10.07.18 THE POPULATION AND STRUCTURAL CHANGES OF THE METASTABLE STATE II IN SODIUMNITRO-PRUSSIDE ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$) AT 60 K. J. Schefer(*), T. Woike(**), S. Hauss hl(**), T. Fernandez(***) and G. McIntyre (***) (*) Laboratory for Neutron Scattering ETHZ+PSI, Paul Scherrer Institute, CH 5232 Villigen PSI, Switzerland (** Institute for Kristallographie,) University at K In, D 50764 K In, Germany (** Institute Laue Langevin ILL, Rue des *) Martyres, F-38042 Grenoble Cedex, France

Long-living metastable states are of fundamental interest for information storage and for the investigation of the correlation between electron density, chemical bond and structural behavior. This is of special interest as such systems can be used for holographic data storage yielding storage densities of up to 10 GByte/cm³.

We present population dynamic and structural properties of the metastable electronic excited state MS_{II} in nitroprusside $[\text{Fe}(\text{CN})_5\text{NO}]_2$. The population of MS_{II} was performed in a two step process: Firstly by irradiation with light of $\lambda = 476.5\text{nm}$ in order to excite MS_{I} by about 50% and secondly by irradiation with light of $\lambda = 1064\text{nm}$ to transfer 30% of the anions from MS_{I} to MS_{II} . The population is determined by Mössbauer spectroscopy in dependence on light exposure. Structure analysis of a single crystal with 30% of the anions in MS_{II} and 70% in the ground state has been done using neutron single crystal diffraction.

PS10.07.19 CALCULATION OF THE LINEAR AND NON-LINEAR OPTICAL SUSCEPTIBILITIES IN KTP AND MXO_4 CRYSTALS ($\text{M}=\text{Ga}, \text{Al}; \text{X}=\text{P}, \text{As}$) Ch. Schetelich and P.A. Thomas Physics Department, University of Warwick, UK.

Bond polarisability calculations were carried out using Levine's model of the linear and nonlinear susceptibilities, which is based on the Phillips - Van Vechten dielectric theory. Bond properties, such as homopolar and heteropolar energy gaps, the ionicities and susceptibilities have been computed for the different bonds in KTP (KTiOPO_4) and MXO_4 crystals ($\text{M}=\text{Ga}, \text{Al}; \text{X}=\text{P}, \text{As}$). We found a satisfactory agreement between the theoretical and experimental values of the averaged macroscopic linear susceptibilities. The simple extension to the anisotropic linear case using a sum over the products of the direction cosines and the isotropic bond polarisability has been proved as inappropriate. A different approach using anisotropic bond polarisabilities suggested by Levine is under investigation. A comparison of the values of the nonlinear optical susceptibility obtained by both calculations and experiments is given for KTP.

PS10.07.20 AGGREGATION OF DIVALENT IMPURITIES IN CODOPED NaCl AND KCl SINGLE CRYSTALS. Jacques Soullard, Instituto de Fisica, UNAM, 01000 Mexico D.F., Mexico

The formation energy of small clusters in NaCl and KCl single crystals codoped with Mn^{2+} and Pb^{2+} impurities has been calculated by means of a static simulation of ionic crystals. The results are used to study quantitatively the structure of the equilibrium state of crystals as a function of temperature.

At high temperature, in both systems, the equilibrium state is characterized by isolated defects: doubly charged substitutional impurities, cation vacancies and dipoles. The manganese dipoles are found in the n.n. and n.n.n. configurations, the ratio of their concentration being dependent on the host matrix. For the lead dipoles the n.n. configuration is dominant in both systems.

In the system NaCl : Mn,Pb dimers and trimers form when the temperature is less than 450K. The nucleation planes of dimers are {110} and {111}, at 300K the trimer concentration is much greater than the dimer concentration and about 50% of trimers have a mixed character. In the system KCl : Mn,Pb, the formation of dimers and trimers becomes significant for temperature less than 500K. The nucleation planes of dimers

are {110} and {100}, at 300K the equilibrium state is characterized by a high concentration of dimers, only 10% of dimers are of mixed type.

These results agree qualitatively well with the experimental results. The host matrix where the concentration of closed Mn-Pb pairs is the highest (NaCl) is the most efficient to transfer energy from Pb to Mn; as a consequence, it presents the most intense fluorescence. The differences between the aggregation processes of the two systems can be understood considering the relative solubility of impurities and the binding energy per dipole of clusters.

PS10.07.21 ANTIMONY - DOPED TIN OXIDE THIN FILMS (SnO_x) MADE BY EVAPORATION METHOD. Vo Vong, Laboratory of Electron Microscopy, Vietnam National Center for Natural Science & Technology, Nghiado - Tuliem-Hanoi - Vietnam

Tin and Antimony, which have mass-rate 10:1; pure 99,99%, were evaporated simultaneously at the two differential sources in high vacuum of 10^{-5} Torr. The substrate temperature is changed as following 100°C, 120°C, 150°C and 200°C.

Thin films $\text{Sn}(\text{In})\text{O}_x$ were annealed in air and in oxygen for 120 min. at the temperatures 150, 180, 210, 230, 250, 300, 350, 400 and 450°C. Changes of the films in process of the heat treatment were studied by transmission electron microscopy, scanning electron microscopy, electron and X-ray diffraction and measurements of transmittances as the function of wavelength.

High-quality $\text{Sn}(\text{In})\text{O}_x$ thin films are found to be strongly dependent on parameters such as the antimony content, a deposition temperature, a temperature of the annealing

Under optimum conditions we received thin films with a electrical resistivity of $15\ \Omega\text{cm}$. Thickness of the films above 0,3 - 0,5 μm , $\lambda = 0,4 - 0,7\ \mu\text{m}$ transmittance is reachable 92%.

Based on our experimental results the changes of mechanical, chemical and physical properties of films can be explained by the changes of the x-value.

PS10.07.22 Ba_2ErCl_7 : A NEW TERNARY RARE EARTH CHLORIDE WITH BARIUM. M. S. Wickleder, Ph. Egger and J. Hulliger, Institute for Inorganic Analytical and Physical Chemistry, University of Berne, Freiestr. 3, 3012 Berne, Switzerland

Our search for new erbium based upconversion materials has lead to the new compound Ba_2ErCl_7 with isolated sevenfold coordinate Er^{3+} ions within a network of edge and corner sharing $[\text{BaCl}_9]$ polyhedra. The $[\text{ErCl}_7]$ polyhedron can be described as a monocapped trigonal prism which, due to the site symmetry C_1 of the Er^{3+} ions in the space group $P2_1/c$, is slightly distorted (for the crystallographic data see table 1). The structure contains two crystallographically different Ba^{2+} ions (Ba1 and Ba2). Each of them is ninefold coordinated by Cl- ions and the $[\text{BaCl}_9]$ polyhedra are linked to form chains running along the c-axis (Ba1) and the a-axis (Ba2), respectively. The chains are connected to form a three dimensional network that contains the Er^{3+} ions.

Tab.1 Crystallographic Data for Ba_2ErCl_7

Crystal System	monoclinic	Atomic Coordinates			
		x/a	y/b	z/c	
Space group	$P2_1/c$	Er	0.2170	0.6269	0.2180
Lattice Parameters	a = 679.4 pm b = 1552.5 pm c = 1049.6 pm $\beta = 90.54^\circ$	Ba1	0.7365	0.7798	0.4508
		Ba2	0.2644	0.5610	0.6765
		Cl1	0.9991	0.6044	0.4294
		Cl2	0.4892	0.7573	0.1980
		Cl3	0.0007	0.7725	0.2053
		Cl4	0.4875	0.6049	0.4145
		Cl5	0.2932	0.4595	0.2133
Z	4	Cl6	0.8693	0.5705	0.1236
		Cl7	0.2896	0.6399	0.9710