

FA2-MS14-P06

Diffraction study of doped apatite-type $\text{La}_{9.33+x}(\text{Si}_{1-y}\text{Al}_y\text{O}_4)_6\text{O}_{2+\square}$ ($A=\text{Fe, Al, Mg}$). Přemysl Beran^a, Ezhil Jothinathan^b, Jozef Vleugels^b, Omer van der Biest^b.

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Apatite type lanthanum silicates, $\text{La}_{9.33+x}(\text{SiO}_4)_6\text{O}_{2+3x/2}$, are a new class of electrolyte material reported to have better oxygen ion conductivity in the intermediate temperature (600–800°C). There is limited information on cation doping and defect processes at the local structural level, particularly the role of dopants on the Si site and the effect of vacancies in the La-occupied channels. It is known that it is possible to tailor the conductivity of these electrolytes by substitution either on silicon or on lanthanum site. In spite of their well established conductivity, the exact mechanism of conduction is still unclear. Two kinds of diffusion pathways have been proposed in the literature – a direct linear path along the hexagonal axis and non-linear, sinusoidal-like path through interstitial oxygen ions [1–4]. In this work we present the diffraction study of silicon site substituted lanthanum silicates by iron, aluminium, magnesium and as well both iron and aluminium at RT and also working temperature (800°C). The powders were prepared by using a modified sol-gel method [5] with appropriate cationic ratio. Phase purity and basic structural investigation were made using the laboratory X-ray powder diffraction. This shows that all samples present $P6_3/m$ symmetry. To describe the influence of doping on the Si site on the conducting channel and on the distribution of the mobile oxygen ions – diffusion pathways – we made Rietveld analysis of the neutron diffraction data not only at RT, where low conductivity is present, but also at working temperature, where the oxygen ion conduction occurs. Results are discussed from the point of view of structural changes of conducting channels and compared with the two diffusion pathways models proposed for these kinds of materials.

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Keywords: lanthanum silicate, fuel cells, neutron powder diffraction

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Structure and optical properties of natural low dimensional semiconductors. Robert S. Black^a, David G. Billing^a. ^aMolecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, PO Wits 2050, Johannesburg, South Africa.

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Inorganic-organic hybrids have been of great interest from a crystal engineering point of view because of the ability to template metal halides into interesting structural motifs.

However, they have a much greater practical use. They can be used to template bulk materials into low dimensional semiconductors, by taking an inorganic semiconductor material, and intercalating organic amine cations to change the materials dimensionality, and in so doing, altering the optical properties of the material. The features most greatly affected by a change in dimensionality is, firstly, the band structure i.e., the tuning of the band gap, secondly, the electron mobility of the compound, and thirdly and most importantly, the ability confine the electron and hole orbit's (excitons), which drastically alters the materials recombination luminescence (Fig.1). A further advantage of inorganic organic hybrids is that they self assemble and are easily solution processed into thin films, this has positive implications regarding cost and the ease of processability for further technological applications such as LCD's displays [1]. Previously published results show the binding energy of the excitons increase as the dimensionality is decreased i.e. from 3D to 2D and from 2D to 1D. However there is a much larger increase in the binding energy from 2D to 1D systems as seen in Fig.1. Here we report the structure and optical properties of 1D hybrids with the general formula $(\text{RN}^+)\text{PbI}_3$, in which we further investigate the tunability of the band structure, the large binding energy associated with the excitonic behavior, and charge transfer effects between wires and spacers [3–5].

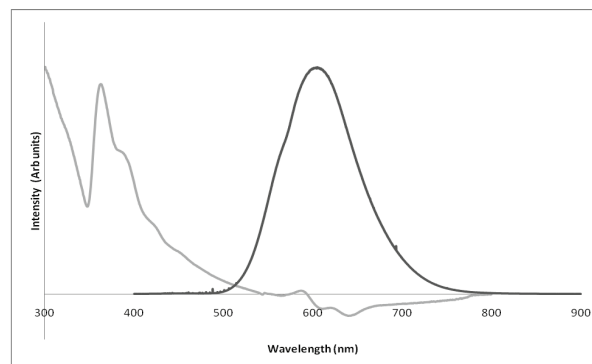


Fig.1. The binding energy effect as displayed in (piperidiumim)PbI₃ wires where we see the 1s exciton absorption peak at 365nm and the resultant 600nm photoluminescence emission both at 77K.

Keywords: Natural quantum wires, Inorganic-organic hybrids, Photoluminescence

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Crystalline compounds of the system glycine – ZnCl₂ – H₂O: crystal growth and optical properties. L. Bohaty^a, A.A. Kaminskii^b, P. Becker^a. ^aInstitute of Crystallography, University of Cologne, Germany. ^bInstitute of Crystallography, Russian Academy of Sciences, Moscow, Russia.

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In the system $\text{NH}_2\text{CH}_2\text{COOH}$ (= glycine) – ZnCl_2 – H_2O four structurally well characterised crystalline compounds are

known: $\text{Gly}_3\cdot\text{ZnCl}_2$ (space group $Pbn2_1$), $\text{Gly}_2\cdot\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ (space group $C2/c$), $\text{Gly}\cdot\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ (space group $P2_1/a$) and $\text{Gly}\cdot\text{ZnCl}_2$ (space group $P2_1$), (gly = abbreviation of glycine) [1-5]. In recent studies crystals of the polar compound $\text{Gly}_3\cdot\text{ZnCl}_2$ turned out to be attractive optical materials, that show both, phase-matchable second harmonic generation (SHG) and efficient frequency conversion by stimulated Raman scattering (SRS) with a rather large Raman shift of about 3000 cm^{-1} [2, 6]. Motivated by these results we focused our interest on the further glycine compounds listed above. In the present contribution we report on crystal growth of $\text{Gly}_2\cdot\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ and of $\text{Gly}\cdot\text{ZnCl}_2$, together with their basic linear optical properties. Large single crystals of $\text{Gly}_2\cdot\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ were grown from aqueous solution at 38°C by controlled slow evaporation of the solvent. Within three months crystals with dimensions up to $5 \times 4 \times 3\text{ cm}$ were obtained. Crystal growth of $\text{Gly}\cdot\text{ZnCl}_2$ was performed at 50°C and resulted in crystals of dimensions up to $2.5 \times 1 \times 0.7\text{ cm}$ after a growth period of six months. Refractive indices and their dispersion were determined by the prism method in the wavelength range of $0.365 - 1.083\ \mu\text{m}$. These results establish the essential prerequisites for further nonlinear optical investigations. In the centrosymmetric crystals of $\text{Gly}_2\cdot\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ SRS will be unaffected by $\chi^{(2)}$ -based nonlinear optical processes such as SHG and sum frequency generation (SFG), while the polar crystals of $\text{Gly}\cdot\text{ZnCl}_2$ are expected to allow the study of both, SHG and cascaded $\chi^{(2)} + \chi^{(3)}$ nonlinear processes.

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Keywords: glycine zinc chloride, crystal growth, optical properties

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Synthesis and structural properties of ZnO films grown by spray pyrolysis of zinc acetate solution.
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Crystalline ZnO films have a wide variety of applications in the manufacturing of devices such as gas sensors, flat panel displays, transparent electrode materials, solar cells, electroluminescent diodes, etc. The films used have a range of crystal structures and morphologies, and many different methods such as sputtering[1], vacuum evaporation[2] thermal oxidation of Zn films, atomic layer epitaxy and spray pyrolysis. This last technique can be distinguished from the others due to its simplicity, low cost and efficiency, and it provides a powerful tool for creating diverse film structures (from the point of view of grain habits and their associations)

with significant differences in morphology, by varying the of pyrolysis conditions.

The morphology and some principal details of the crystallographic grain structure of zinc oxide thin (50–300 nm) films obtained from acetate $\text{Zn}(\text{CH}_3\text{CO}_2)\cdot 2\text{H}_2\text{O}$ solution by spray pyrolysis deposition were studied using X-ray diffraction (XRD), extreme high-resolution scanning electron microscopy (XHR SEM) and Transmission Electron microscopy (TEM) methods. Direct correlation between the pyrolysis temperature and several fundamental nanoscale grain shapes and crystallographic features successively replacing each other with T_{pyr} was shown.

The X ray diffraction patterns of the films were recorded using a diffractometer with monochromatic Cu K radiation. XRD and TEM results show that these nanoparticles are composed of ZnO with hexagonal structure. The parameters of the hexagonal elementary cell are as follows: $a = 3.2539(1)\ \text{Å}$, $c = 5.2098(3)\ \text{Å}$, $c/a = 1.6011$, $V = 47.77\ \text{Å}^3$. The microstructure of the film was studied with the electron microscope. From these studies it was observed that the orientation of the grains was uniform and the crystallites were very small in size. The morphology qualitatively remained the same and variation in film thickness

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Keywords: nanoparticles, TEM, ZnO, thin film

FA2-MS14-P10

Effects on the physical properties of cation substitution in (La, Sr) CoO_3 perovskite system. A. Cheikhrouhou^{a,b}, M. Koubaa^a, N. Mahfoudh^a, W. Cheikhrouhou-Koubaa^a. ^aFaculté des Sciences de Sfax, B.P.1171, 3000, Sfax, Tunisie. ^bInstitut NEEL, B.P.166, 38042 Grenoble-France.

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Cobaltites with general formula $\text{Ln}_{1-x}\text{M}_x\text{CoO}_3$ (Ln is a rare earth element and M is a divalent alkali earth element) have received recently considerable interest due to their potential technological applications. Several studies have been reported on strontium doped LaCoO_3 compounds because of its complex phase diagram. At low Sr doping a spin glass (SG) and/or cluster glass (CG) behavior is observed at low temperature, whereas larger Sr doping leads to ferromagnetic ordering. In this work, we present the effects of both (La,Sr)-site and Co-site substitutions on the physical properties in the (La,Sr) CoO_3 powder system. Our samples have been elaborated using the solid state reaction method at high temperatures. The Rietveld refinements of the X-ray diffraction patterns recorded at room temperature show that our compounds are single phase and crystallize in the rhombohedral structure with $\overline{R3c}$ space group. The zero field cooled (ZFC) and field cooled (FC) magnetization curves at 50mT show thermomagnetic irreversibility. The magnetic phase at low temperature is found to be correlated to the $\text{Co}^{3+}/\text{Co}^{4+}$ ratio as well as the A-site average ionic radius. The magnetic entropy change, $|\Delta S_M|$, as a function of temperature and magnetic applied field has been determined from the isothermal magnetization measurements using the Maxwell relations.