

structure is obtained, at room temperature, and it is measured in a cyclic slow warming process [3]. The differences among successive phases consist in slight rotations around the S-O bond without space group changes (P2<sub>1</sub>nb). However, these results could be explained by the mixture of two different  $\alpha$  and  $\beta$  phases, which can coexist at room temperature, or ferroic domains [4].

In order to clarify this disagreement, we have studied single crystals with the  $\beta$ -LAS structure, confirmed by X-ray diffraction, at room temperature. Single crystals of LAS were obtained from aqueous solutions and they were slowly evaporated at room temperature. Thermal analysis DSC was carried out at different cyclic warming rates from 173 to 600K. The temperature dependency of the electrical impedance, at the same temperature range, in a cyclic process, and as a function of frequency (from 0.1 KHz to 1 MHz) was measured. Several anomalies in the curves from 350K to 380K (possible new phases), and peaks broadening, showing a pretransition, around 460K (corresponding to the ferroelectric-paraelectric transition) were observed in both techniques, when the warming rate was slow. Also, a detailed single crystal X-ray diffraction study is presented. Crystal structures at several temperatures between 200 to 550K were solved during a slow warming process. The different structures were compared and transition mechanisms were discussed according to the dielectric measures. Moreover, a second harmonic generation experiment was performed on the same crystals, in a cyclic process, with different warming rates and the same temperature range, in order to confirm the non-centrosymmetric space group found by X ray diffraction.

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#### MS25 P11

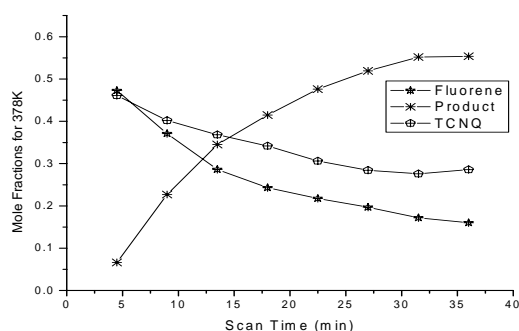
**Surface vs. bulk kinetics in a solid-state reaction by Raman/XRPD experiment** D. Viterbo,<sup>a</sup> S. Kumar,<sup>a</sup> A. Arrais,<sup>a</sup> F. Carniato,<sup>a</sup> G. Croce,<sup>a</sup> E. Boccaleri,<sup>a</sup> M. Milanese,<sup>a</sup> W. van Beek<sup>b</sup> <sup>a</sup>DiSTA, Università del Piemonte Orientale, Alessandria, Italy <sup>b</sup>SNBL, ESRF, Grenoble Cedex, France.

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**Keywords:** In-situ time-resolved powder diffraction, IR and Raman spectroscopy, Reaction kinetics.

Recently we obtained, by dissolution of the reactants in a polar solvent and subsequent crystallization, three co-crystalline complexes between fluorene, showing C<sub>2v</sub> symmetry, and three electron withdrawing D<sub>2h</sub> compounds [1]. In this paper, we report on the solid state synthesis of the fluorene/7,7,8,8-tetracyanoquinodimethane (TCNQ) molecular complex, obtained by heating the reactants in a sealed glass capillary. The kinetic features of the reaction have been monitored by a novel in situ simultaneous Raman/X-ray Powder Diffraction (Raman/XRPD) experiments, performed at the SNBL of the European Synchrotron Radiation Facility. The invaluable added value of the simultaneous RAMAN/XRPD multi-technique experiment is the perfect synchronization of the two probes with the reaction coordinate and the

elimination of possible bias caused by different sample holders and conditioning modes used in an “in situ but separate” approach. On one hand, Raman allowed the characterization of the reaction kinetic in the first steps of the reaction at the surface of TCNQ crystallites. On the other hand, the kinetic of the reaction in the bulk up to completion was characterized by XRPD. Rietveld refinement gave the trends of the molar fractions of reactants and product during the reaction (Figure 1). The activation energy resulted higher in the bulk than at the surface and the best kinetic model was the 2D contracting area model, thus suggesting that the reaction start on the larger crystal faces of the TCNQ platelet-like crystals and proceed toward the inner part of the crystals.



**Figure 1:** Evolution of the mole fraction, obtained by Rietveld refinement of reactants and product during the *in situ* simultaneous isothermal experiment at 378 K.

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#### MS25 P12

**Crystal structure and some physical properties of BaPb<sub>0.7-x</sub>M<sub>x</sub>Bi<sub>0.3</sub>O<sub>3-δ</sub> (M=In,Sb)** Antoni Winiarski<sup>a</sup>, Katarzyna Balin<sup>a</sup>, Weronika Moras<sup>a</sup>, Jan Heimann<sup>a</sup> and Ewa Teper<sup>b</sup>, <sup>a</sup>August Chełkowski Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland, <sup>b</sup>Faculty of Earth Sciences, University of Silesia, Sosnowiec, Poland. E-mail: [awini@us.edu.pl](mailto:awini@us.edu.pl)

**Keywords:** oxides, perovskites, Vegard's law

Ba(Pb,Bi,Sb)O<sub>3</sub> system was previously investigated by R. Nagarajan [1] and K. Bente *et al* [2], [3]. Polycrystalline BaPb<sub>0.7-x</sub>M<sub>x</sub>Bi<sub>0.3</sub>O<sub>3-δ</sub> (M = Sb, In) compounds were prepared by sintering of starting materials BaCO<sub>3</sub>, SrCO<sub>3</sub>, PbO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>5</sub> in air or in oxygen atmosphere. The samples were powdered in an agate mortar and examined with the use of Siemens D5000 X-ray Powder Diffractometer to determine crystal structure and the upper limit of lead atom replacement by Sb or In atoms. Electrical resistivity and X-ray photoelectron spectroscopic (XPS) measurements were performed to explain deviations from the Vegard's law. Philips XL30 ESEM-TMP environmental scanning electron microscope with EDS equipment (energy dispersive X-ray analysis) was used to determine chemical composition of grains and intergranular compounds. BaPb<sub>0.7-x</sub>Sb<sub>x</sub>Bi<sub>0.3</sub>O<sub>3-δ</sub> compounds crystallize in tetragonal structure (space group I4/mcm) whereas superconductor BaPb<sub>0.7-x</sub>Sb<sub>x</sub>Bi<sub>0.3</sub>O<sub>3</sub> crystallizes in monoclinic structure and the  $\beta$  angle

increases with higher concentration of antimony. The analysis of diffraction patterns of  $\text{BaPb}_{0.7-x}\text{Sb}_x\text{Bi}_{0.3}\text{O}_3$  points to increase in the tilt angle of  $(\text{Pb,Bi,Sb})\text{O}_6$  octahedrons with increased concentration of antimony. The  $a$  and  $c$  crystal lattice parameters and the volume of  $\text{BaPb}_{0.7-x}\text{Sb}_x\text{Bi}_{0.3}\text{O}_{3-\delta}$  unit cell linearly decrease with the increase in the  $x$  index up to  $x = 0.3$ . The measured  $a$  and  $c$  parameters do not depend on the  $x$  for  $x > 0.3$ . Electrical resistivity rapidly increases for  $x > 0.3$ . The binding energy of Pb4f and Bi4f levels in XPS spectra can be measured only for  $x < 0.3$ , because the photoelectric lines are broader and splitted above this value. Therefore we conclude that the upper limit of Pb replacement by Sb is equal to 0.3. Scanning electron microscopic observation and energy dispersive X-ray analysis (EDS) show second phase that crystallizes among  $\text{BaPb}_{0.7-x}\text{Sb}_x\text{Bi}_{0.3}\text{O}_{3-\delta}$  grains. This phase isolates the grains and causes that resistivity rapidly increase for the samples with  $x > 0.3$ . The  $\text{BaPb}_{0.7-x}\text{In}_x\text{Bi}_{0.3}\text{O}_{3-\delta}$  compounds crystallize in I4/mcm tetragonal structure. Measured  $a$  and  $c$  crystal lattice parameters as well as the volume of the unit cell decrease with the increase of indium content but non-linear decrease of the  $a$  and  $c$  parameters is observed. The measured lattice parameters are constant for  $x > 0.2$ . Electrical resistivity rapidly increases for the  $x$  parameter higher than 0.2 as well as the width of the Bi4f, Pb4f and Sb3d photoelectric lines. It points that the upper limit for Pb replacement by In in  $\text{BaPb}_{0.7-x}\text{In}_x\text{Bi}_{0.3}\text{O}_{3-\delta}$  is for  $x = 0.2$ . Applying different techniques we discuss relations among crystal structure, electronic structure and physical properties in the  $\text{BaPb}_{0.7-x}\text{M}_x\text{Bi}_{0.3}\text{O}_{3-\delta}$  ( $M = \text{Sb, In}$ ) system.

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#### MS25 P13

**The relation between symmetry and the FTIR spectra of the kaolinite and dickite, M. Zamama<sup>a</sup> and M. Berraho<sup>a</sup>, Department of Chemistry, University of Marrakech, Morocco.** E-mail: [zamama@ucam.ac.ma](mailto:zamama@ucam.ac.ma)

**Keywords:** Kaolin, symmetry, FTIR

The structural analysis of the clay minerals is more difficult than that of the almost perfect crystals. In the case of the phyllosilicates, the particle sizes which constitute the material are so small to be studied by the monocrystals method which gives precise structural information. In the other hand, the hydrogen atoms position is uncertain and conflicting results was published about the symmetry mode when we take into account the hydrogen atoms coordinates (1,2). The present study concerns the kaolinite and dickite which are polytypes and belong to the phyllosilicates family. The corresponding structural formulas of one half of the unit cell are, respectively,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  and  $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ . This material, is described as a stacking of the layers which consists of a tetrahedral and the octahedral sheets sharing a common plan of oxygen atoms and hydroxyl groups. The polar nature of the structure, with hydroxyls on the one surface of the layer and the oxygen atoms at the other surface, allows hydrogen bonds to form between the adjacent layers. The OH groups play an important role in the attraction between the layers. Little information are

known about the strengths and the nature of the hydrogen bonds in those particular structures. The infrared spectroscopy gives indications on the orientation of the OH groups and the corresponding absorption bands in the infrared spectrum depends strongly on the defects existing in the mineral. For this reason, the position of hydrogen atoms in the structure is important. In this study, our aim is to distinguish between the structure of dickite and kaolinite. In order to predict the infrared spectrum for the OH groups, we propose to specify the environment of the hydroxyls groups according to the symmetry. The experiments of the intercalation (3) demonstrate that OH groups frequencies are sensitive to the variation of the  $d_{001}$  distance. For this reason, we consider that the environment of the hydroxyl groups is determined essentially by the symmetry of the interfoliar space. We have constructed two fundamental entities: the tetrahedral sheet and the octahedral sheet. This analysis is made in 3 stages with decreasing symmetries: we consider the models of the perfect crystal, the crystal with a deformed layers and the symmetry of the real crystal. We have determined that the P3 symmetry of the interfoliar space symmetry is conserved in the perfect crystal and the crystal with a deformed layers. On basis of this symmetry, the FTIR spectra are discussed and compared to the spectrum of the real crystal.

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#### MS25 P14

**Anomalous X-ray Scattering and absorption spectroscopy Investigate the Morphology of FePt Monolayer Nanoparticle on Surface Modified Substrates, Tzu-Wen Huang,<sup>a</sup> Kuan-Li Yu,<sup>b</sup> Yen-Fa Liao<sup>a</sup> and Chih-Hao Lee<sup>a</sup>** <sup>a</sup>Department of Engineering and System Science, National Tsing-Hua University, Hsinchu, Taiwan, <sup>b</sup>National Synchrotron Radiation Research Center, Hsinchu, Taiwan.  
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**Keywords:** FePt nanoparticle, X-ray absorption spectroscopy, Anomalous Grazing Incident Small Angle X-ray Scattering

The structural stability of self-assembled FePt monolayer nanoparticles on functional substrate with the Au overlayer during the annealing were studied. To deposit a monolayer of particles under control, the functional substrates such as polyethylenimine (PEI) or [3-(2-aminoethylamino)propyl] trimethoxysilane (APTS) modified silicon wafers were used to capture the FePt nanoparticles coated with oleic acids. With the X-ray diffraction, anomalous X-ray absorption spectroscopy and the anomalous grazing incidence small angle x-ray scattering techniques, the FePt nanoparticles monolayer were found to be free from coalescence and convert into ordered alloy under the annealing process after 5-10 nm of Au overlayer deposited on the top of FePt nanoparticles. The result indicates that the particle size  $4.5 \pm 0.5$  nm is typically unchanged, but the distance between particles is reduced from  $7.5 \pm 1.5$  nm to  $5.5 \pm 1.1$  nm after annealing. The results suggest that the 5 nm Au coverlayer is an effective diffusing barrier layer to prevent the FePt