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 (P2₁nb). However, these results could be explained by the mixture of two different α and β phases, which can coexist at room temperature, or ferroic domains [4].

In order to clarify this disagreement, we have studied single crystals with the β-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,[a] S. Kumar,[a] A. Arrais,[a] F. Carniato,[a] G. Croce,[a] E. Boccaleri,[a] M. Milanesio,[a] W. van Beek[b] [a]*DiSTA, Università del Piemonte Orientale, Alessandria, Italy* [b]*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_{2v} symmetry, and three electron withdrawing D_{2h} 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.
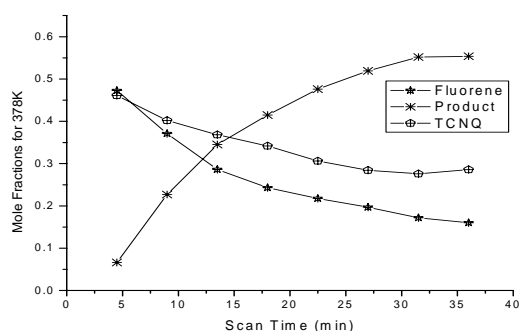

Figure 1: Evolution of the mole fraction, obtained by Rietvel refinement of reactants and product during the *in situ* simultaneous isothermal experiment at 378 K.

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MS25 P12

Crystal structure and some physical properties of $BaPb_{0.7-x}M_xBi_{0.3}O_{3-\delta}$ (M=In,Sb) Antoni Winiarski[a], Katarzyna Balin[a], Weronika Moras[a], Jan Heimann[a] and Ewa Teper[b], [a]*August Chełkowski Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland,* [b]*Faculty of Earth Sciences, University of Silesia, Sosnowiec, Poland.* E-mail: awini@us.edu.pl

Keywords: oxides, perovskites, Vegard's law

$Ba(Pb,Bi,Sb)O_3$ system was previously investigated by R. Nagarajan [1] and K. Bente *et al* [2], [3]. Polycrystalline $BaPb_{0.7-x}M_xBi_{0.3}O_{3-\delta}$ (M = Sb, In) compounds were prepared by sintering of starting materials $BaCO_3$, $SrCO_3$, PbO_2, Bi_2O_3, In_2O_3 and Sb_2O_5 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. $BaPb_{0.7-x}Sb_xBi_{0.3}O_{3-\delta}$ compounds crystallize in tetragonal structure (space group I4/mcm) whereas superconductor $BaPb_{0.7-x}Sb_xBi_{0.3}O_3$ crystallizes in monoclinic structure and the β angle