MS25 P08

Contribution of microchemical surface analysis of Archaeological artefacts

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Keywords : Archaeological, Lead, Copper, XRF, SEM, EDS, patina.

Many analytical methods have been used to identify the chemical composition of archaeological artefacts [1-4].

Museum CIRTA of the town of Constantine has a collection of more than 35000 coins and statuettes going back to Numide, Roman, Republican, Vandal and Byzantine times and is struck in the name of the cities, of the kingdoms and the empires.

Surface analysis of these coins gives informations about the chemical composition and leads to recommendations for restoration and presevation.

This work is a contribution of microchemical surface study of three coins with the effigy of the *Numide King Massinissa* (between 3rd and 2nd century before Jesus Christ).

Scanning electron microscopy coupled with energy dispersive spectrometry (SEM + EDS) and energy dispersive fluorescence spectrometry (XRF) were used. The bulk of three coins is massif homogeneous metallic. Two coins are manufactured with lead (99.896% and 61.56%) and were probably conserved differently. The third one is from copper (92.28%).

The optic microscopy (OMP) and SEM pictures of coins show heterogeneous surface with typical lead alteration products white patina of plumbonacrite, cerussite and hydrocerussite and red patina of cupric oxide on the cupric artefact.

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MS25 P09

Effects of Er^{3+} and Yb^{3+} doping on phase transitions of $LiNH_4SO_4$.

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Keywords: $LiNH_4SO_4$, phase transition, rare earth.

We are interested in the study of crystalline structure, dielectric and optical properties of different matrices, especially ferroic tungstates and molybdates because they have possible applications as laser crystals when they are doped by active ions [1]. It is known that the molybdates and tungstates often have very close structural relation with sulfates. Moreover, there are phase transitions in sulfates which remind of the transitions in molybdates and tungstates (or vice versa). It would be interesting to compare these phenomena in both compound classes [2].

This work is concerned with the structural, dielectric, and optical study of the sequence of phase transition in $LiNH_4SO_4$ (LAS), doped by Er^{3+} and Yb^{3+} at different concentrations. Single crystals were obtained from slow evaporation of aqueous solutions. ICP and optical emission experiments have confirmed the presence of the rare earths in the prepared samples. We have solved the structure, at room temperature, of several single crystals by X-ray diffraction of different concentrations and dopes, and we have observed some changes with respect to the expected polar orthorhombic space group ($P2_1nb$). For example, a monoclinic centrosymmetric space group ($P2_1/c$) is observed in a single crystal doped by Yb^{3+} at 1% mol.

In order to detect changes in the sequence of phase transition, specially for crystals with different structures at room temperature, we have carried out different experiments in the same temperature range in a cyclic process. From thermal analysis DSC, dielectric spectroscopy and SHG, we have observed the influence of the rare earth with respect to the pure compound [3]: 1) the ferroelectric-paraelectric transition temperature (460K) increases and 2) the ferroelastic-ferroelectric transition (285K) vanishes. Also, we have characterized the crystal phases at different temperatures in the temperature range 200 to 550K, for several single crystals with different structures, at room temperature, by X-ray diffraction and luminescence experiments.

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MS25 P10

New experimental results to clarify the sequence of phases of $LiNH_4SO_4$.

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Keywords: $LiNH_4SO_4$, phase transition, ferroic.

$LiNH_4SO_4$ (LAS) has been the object of many experimental researches, because it exhibit a sequence of phase transitions in the temperature range 10 to 615 K and a variety of structural phase, some of them still controversial [1,2]. The most recent discussion is focused on a new sequence of phases reported when the β-LAS 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 ($P2_1nb$). 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.

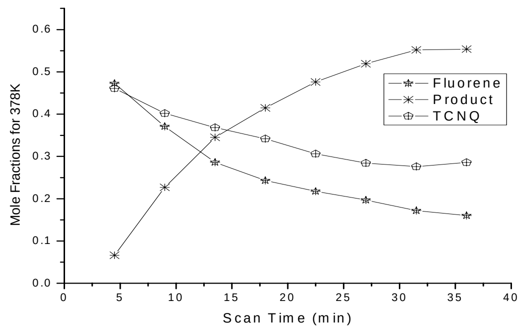

Figure 1: Evolution of the mole fraction, obtained by Rietvel refinement of reactants and product during the *in situ* simultaneous isothermal experiment at 378 K.

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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