MS31 P01

Impedance spectroscopy characterization and powder diffraction of $BaTi_{1-X}SN_XO_3$

M.A. El Idrissi Raghni, B. Lmouden, A.Outzourhit,, M.L. Hafid, F.Bensamka, A. Thalal Laboratoire des Sciences des Matériaux., Faculté des Sciences Semlalia, université Cadi Ayyad, Marrakech, Morocco..

Keywords: ceramics, structure, dielectric

The Barium Titanate ceramics are interesting to study because of their simple structures and of the modulation of their properties by insertion of a dope. In fact, the substitution of the ion Ti^{4+} by Sn^{4+} modifies appreciably the dielectric and structural properties of $BaTiO_3$.
.The present conducted research works concern the characterization of these ferroelectric materials by X-ray diffraction, SEM microscopy, UV-visible spectroscopy, and impedance spectroscopy.
The analysis of the samples by scanning electron microscopy shows that the obtained powders are cubic size grains perfectly homogeneous (about 0.2□). The cell parameters and size of the grains have been determined from X-rays spectrum. The evolution of theses parameters related to the synthesis conditions and the thermal processing will be discussed.
Impedance spectroscopy measurements have been performed on these ceramics and the results were analyzed using the empiric Cole-Cole model. A procedure to evaluate the electric properties of the grain boundary and bulk grain has been developed based on electric polarization model of double layer dielectrics.

MS31 P02

Looking at hydrogen atoms with X-rays: comprehensive synchrotron diffraction study of $LiBH_4$

Yaroslav Filinchuk, Dmitry Chernyshov, *Swiss-Norwegian Beam Lines at ESRF, Grenoble, France.*
E-mail: Yaroslav.Filinchuk@esrf.fr

Keywords: synchrotron powder diffraction, hydrogen storage, analysis of disordered structures

Being considered as one of the most promising candidates for hydrogen storage, $LiBH_4$ has become the subject of intensive theoretical and experimental investigations. Two $LiBH_4$ polymorphs are known at ambient pressure, with a transition at ~380 K. Substantial theoretical and experimental efforts have been made to characterize their crystal structure. Certain discrepancies remained, however:

- in the low-temperature (LT) phase, all theoretical studies showed nearly ideal tetrahedral geometry of the BH_4 unit, while experiments described it as considerably distorted;
- the high-temperature (HT) phase, reported from synchrotron powder diffraction data to be hexagonal [1], was found unstable by theory; a monoclinic structure has been suggested from *ab initio* calculations [2].

In order to resolve these discrepancies, synchrotron diffraction on single crystals. It shows that in the LT polymorph the BH_4 group has a geometry of a regular tetrahedron. The space group $P6_3mc$ has been determined unambiguously for the HT phase. Anisotropic displacement ellipsoids, refined also for hydrogen atoms, reveal a libration-like smearing of the BH_4 group, which is well approximated by a TLS model.The revealed disorder suggests that the unaccounted entropy is the reason why *ab initio* calculations have failed to evaluate correctly the stability of the $P6_3mc$ structure.
A more accessible technique, synchrotron powder diffraction, was evaluated for its ability to provide accurate information on the positions of hydrogen atoms. Refinement of the LT structure from the integrated 2D diffraction images (MAR345 detector) resulted in a non-distorted BH_4 geometry. We conclude that the previous powder diffraction studies done with 1D detectors suffer from a poor powder average. The HT phase remains hexagonal from the polymorphic transition at 381K up to decomposition at ~560K. Refinement of the TLS tensor showed that the libration-like disorder of the BH_4 group is nearly isotropic, in agreement with the single crystal experiment.
In the presentation, B-H distances will be compared with those obtained from DFT calculations and from neutron powder diffraction study of triply isotopically substituted $^7Li^{11}BD_4$ [3]. Libration corrections and displacement of the electron cloud relative to an average nuclear position of an H-atom will be discussed. Positions of H-atoms and structural changes in $LiBH_4$ were tracked by synchrotron powder diffraction from 80 to 400K with ~1K step. These results and results of combined Raman spectroscopy / powder diffraction study using a fast-readout CCD detector will also be presented.
Contrary to general belief that only neutron diffraction is capable to locate hydrogen, we show that for light hydrides the contribution of H-atoms to X-ray diffraction intensities is sufficient not only to accurately localize hydrogen atoms, but also to see and quantify the disorder of the BH_4 unit.

[1] Soulié J.-P., Renaudin G., Černý R., Yvon K., *J. Alloys Compd*., 2002, 346, 200.
[2] Łodziana Z., Vegge T., *Phys. Rev. Lett*., 2004, 93, 145501.
[3] Hartman M.R. et al. *J. Solid State Chem*., 2007, in press.

MS31 P03

Studies on the Hydrate Formation of Two Narcotic Antagonists by (Real-Time) Powder Diffraction

Carmen Guguta, René de Gelder, *Molecular Materials, Institute for Molecules and Materials, Radboud University Nijmegen, The Netherlands.*
E-mail: c.guguta@science.ru.nl

Keywords: crystal and powder X-ray diffraction structure analysis, hot-humidity powder diffraction, hydrate formation

Many drugs on the market are available in crystalline form due to reasons of stability and ease of handling during the various stages of drug development. Phase transitions such as polymorph interconversion, desolvation, formation of hydrates and conversion of crystalline to amorphous forms may occur during various pharmaceutical processes. These may alter properties like the dissolution rate and transport characteristics of a drug. Hence it is desirable to choose the most suitable and stable form of a drug in the initial stages of its development.
Crystallographic studies are essential for the determination of the pseudo-polymorphic behavior of compounds and for the understanding of pseudo-polymorphism on a molecular scale. We have been engaged in a study that focused on hydrate formation of Naloxone hydrochloride and Naltrexone hydrochloride [1], two potent narcotic