MS31 P01

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

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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 $LiBH_4$

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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

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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 antagonists that show close molecular similarity. The crystal structures of unknown pseudo-polymorphic forms of Naltrexone hydrochloride and Naloxone hydrochloride were determined from X-ray powder diffraction data, using the DASH and TOPAS programs [2-3]. With the availability of these newly determined crystal structures and applying hot-humidity stage X-ray powder diffraction in combination with other analytical techniques, a detailed insight into the mechanism of hydrate formation of these narcotic antagonists could be obtained.

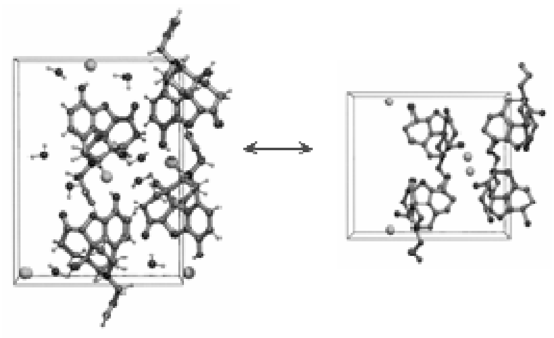

Figure 1. The crystal structure of the Naloxone hydrochloride di-hydrate (left) and anhydrate (right)

[1] Le Dain A.C.; Madsen B.W.; Skelton B.W.; White A.H., *Aust.J.Chem.,* 1992, 45, 635.
[2] David W.I.F.; Shankland K.; Van de Streek J.; Pidcock E.; Motherwell W.D.S.; Cole C.J., *J.Appl.Cryst.*, 2006, 39, 910.
[3] Bruker AXS, *TOPAS V2.1: General profile and structure analysis software for powder diffraction data. - User's Manual,* 2003, Bruker AXS, Karlsruhe, Germany.

MS31 P04

X-ray Powder Diffraction Methods in the Investigations of Fibrillar Trimolybdates.

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Keywords: powder diffractometry, Rietveld refinement powder pattern decomposition, inorganic structure determination

Due to morphology and a large surface, fibrilar trimolybdates are a very attractive family of compounds, as potential catalysts and ingredients of composite materials. Since fibrillar crystals are too small for single crystal study, their structures are investigated by X-ray powder diffraction techniques, only. Recently, such studies are carried out mainly by direct methods (using EXPO package [1]) or by global optimisation techniques (FOX programme [2]). In our lab we have synthesised more than a dozen of such compounds. First crystal structures of fibrillar trimolybdates were solved, from powder data [3], also in our laboratory. In this report we describe, synthesis and crystal structure determination of a few new trimolybdates. Most of the investigated trimolybdates are built of infinite polymeric $Mo_3O_{10}^{-2}$ anions and diammonium cations - $^+NH_3$-R-N^+H_3, where R represents aromatic or aliphatic radical. The studied compounds were synthesised by slow crystallisation from water solution containing MoO_3, relevant diamine and water. The obtained solids were thoroughly investigated by analytical, spectroscopic and X-ray methods. In our presentation we are going to describe in details:

- Used for years methods in structure solution of trimolybdates, (emphasising the pitfalls and problems one can come across in the crystallographic investigations).
- Some regularities observed in crystal structures of trimolybdates with organic and inorganic cations.
- Known and potential applications of molybdates.

[1] Altomare A, Burla M, Camalli M. Carrozzini B. Cascarano G, Giacovazzo C, Guagliardi,A. Moliterni,G.;Polidori G. Rizzi R.J., Appl. Cryst. **32** (1999) 339-340.
[2] V. Favre-Nicolin V, Cerny R, J. Appl. Cryst. 35 (2002) 734
[3] Łasocha W, Jansen J, Schenk H,. J. Solid State Chem., 109, 1-4 (1994)

MS31 P05

Study of Anatase to Rutile Phase Transition in Titanium Dioxide (TiO_2) thin films by sol–gel dip–coating method

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Keywords: TiO_2, sol–gel, anatase.

Titania films are one of the hotly investigated transition metal oxide thin films lately, due to the wide and versatile range of application possibilities these films offer. The domains of application touched by this material are optical filters, optical waveguides, chemical sensors, solar cells, thin film capacitors, electrochromic materials and more [1–3]. Titanium dioxide thin films have been prepared from tetrabutyl-orthotitanate solution and buthanol as a solvent by sol gel dip-coating technique [4–6]. The deposits are carried out on sapphire (mono–crystalline) substrates, annealed between 600 to 1400°C. Structural and optical properties of TiO_2 thin films prepared using a sol–gel process have been examined at different treatment temperatures and for different layer counts (number of dippings). The morphology, surface structure and composition of the films were investigated by X-ray Diffraction (XRD), Raman Spectroscopy, Scanning electron microscopy (SEM), Optical Microscopy, Infrared and Ultraviolet spectroscopy. The as-deposited TiO_2 thin films crystallize in anatase phase between 600 and 800°C, and into the anatase–rutile phase at 1000°C, and further into the rutile phase at 1200°C. It was found that the film consisted of titanium dioxide nanocrystals. The nanocrystals size of TiO_2 thin films is increased with increasing treatment temperature.

[1] Bennett J.M; Pelletier E; Albrand G; *Appl. Opt.* 1989, 28, 3303.
[2] Desu S.B; *Mater. Sci. Eng.* 1992, B 13, 299.
[3] Gratzel M; *Comment. Inorg. Chem.* 1991, 12, 93.
[4] Mechiakh R; Bensaha R; *M. J. Condensed Mater*. 2006, 7, 54.
[5] Mechiakh R; Bensaha R; *C. R. Physique.* 2006, 7, 464.
[6] Mechiakh R; Meriche F; Kremer R; Bensaha R; Boudine B; Boudrioua A; *JNOG, Chambéry, France.* 2005, 258