

by resonant ultrasound spectroscopy [1,2]. The different chemical compositions of the investigated crystals allow for a systematic study of the influence of the Li, Na and Fe content on elastic and piezoelectric properties of tourmalines.

On first heating four samples showed an unexpected irreversible softening of all resonance frequencies. These anomalies are most likely related to an increase of configurational entropy caused by order/disorder processes on certain cation sites. The onset temperature of the softening depends on chemical composition.

The well reproducible spectra collected in the second and subsequent heating/cooling cycles were used for the calculation of elastic and piezoelectric constants and of their temperature derivatives. Both elastic and piezoelectric constants behave almost linearly in the investigated temperature interval. Size and anisotropy of the electromechanical properties are closely related to chemical composition and structural features, respectively.

[1] Migliori A. and Sarrao J., *Resonant ultrasound spectroscopy* (John Wiley & Sons, New York), 1997. [2] Schreuer J., *IEEE Transactions on UFFC*, 2002, 49, 1474.

Keywords: tourmaline, order/disorder transition, elasticity

FA2-MS16-P16

Synthesis and characterization of Indium– borate glass-ceramics containing $\text{Ho}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ nanorods via incorporation method. Alemi Abdolali^{1*}, Ali Akbar Khandar^a, Amin Salem^b, Leila Kafi –Ahmadi^c. ^a*Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, IRAN.* ^b*Chemical Engineering Department, Sahand University of Technology, Tabriz, Iran.*
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Glass ceramics materials are polycrystalline solids containing nanometers to micrometers size crystals embedded in a residual glass matrix[1]. Glass ceramics derive particular interest for several end applications, such as thermal, chemical, biological and dielectric ones, because these systems provide great possibilities to manipulate their properties, such as transparency, strength, resistance to abrasion and coefficient of thermal expansion by selecting the suitable constituent oxides[2]. The purpose of this work was synthesis of Indium–borate glass-ceramics containing $\text{Ho}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ nanocrystals with "incorporation method" and characterization with XRD, FT-IR, SEM and DTA analysis. Glasses in the system In_2O_3 – $\text{Na}_2\text{B}_4\text{O}_7$ were fabricated via melt quenching technique. The amorphous nature of the quenched glasses was confirmed by X-ray powder diffraction studies. The infrared spectra of the glasses show no boroxol ring formation in the structure of these glasses. A cerium–zirconium mixed oxides ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and $\text{Ho}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$) were obtained by solid-state method. Glass powder and $\text{Ho}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ were mixed. The mixture was heated in a crucible. The glass-ceramic sample was obtained by pouring the melts on stainless steel. Obtained samples were annealed at 450°C for 1h to remove thermal strain. DTA analysis of the glass and glass-ceramic samples show an endotherm corresponding to the glass transition and an exotherm corresponding crystallization temperature. The difference between T_g and T_x (i.e. $\Delta T = T_x - T_g$) in curves DTA is larger for the $\text{Ho}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ containing specimen, indicating that the thermal stability of glass-ceramic is higher than that of the glass without crystal. The scanning electron microscopy study for glass-ceramic indicates that the crystallized glass consists of rod-like

crystals with average diameter of about 38 nm dispersed in the glassy regions.

[1] A. Arora, A. Goel, E.R. Shaaban, K. Singh, O.P. Pandey, J.M.F. Ferreir, *Physica B* 403(2008) 173. [2] K. Cheng, *J. Phys. Chem. B* 103(1999) 8272.

Keyword : Borate, Glass ceramic, Incorporation

FA2-MS16-P17

Crystal chemistry of silicofluorides. Tonci Balić-Zunić^a, Anna Garavelli^b, Donatella Mitolo^b, Pasquale Acquafredda^b, Erik Leonardsen^c, Sveinn Peter Jakobsson^d. ^a*Natural History Museum, University of Copenhagen, Denmark.* ^b*Dipartimento Geomineralogico, University of Bari, Italy.* ^c*St. Karlsmindevej 46, Hundested, Denmark.* ^d*Icelandic Institute of Natural History, Reykjavik, Iceland.*
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The family of silicofluorides includes compounds of alkaline metals or ammonium with silicium and fluorine. Their common structural characteristic is the presence of isolated $[\text{SiF}_6]$ octahedra. There is a major difference between the coordination of sodium compared with that of potassium and ammonium. As a result, the crystal structure of malladrite (Na_2SiF_6) [1][2] is significantly different from those of potassium or ammonium compounds. In malladrite fluorine atoms form a hexagonal eutaxy. In this arrangement half of vacant octahedrally-coordinated XF_6 sites are occupied in ratio 1 SiF_6 :2 NaF_6 . On the contrary, the structures of potassium or ammonium silicofluorides are based on eutactic arrangements where both fluorine and potassium/ammonium partake and silicon atoms fill isolated octahedral holes surrounded exclusively by fluorine atoms. Structures with both cubic-eutaxy and hexagonal-eutaxy stackings can be found in this part of the family, as well as with a special ...ABCBABC... stacking of layers. In the structure of the new mineral heklaite (KNaSiF_6) [3][4] the eutactic arrangement of fluorine and Na/K atoms is not present, due to distortion of K coordination. It is a peculiarity of this structure that the cation with shorter bond lengths (Na) has a larger coordination number (10) than the cation with the longer bond lengths (K; CN 9) [3]. The fundamental differences between the Na and K coordinations in heklaite, plus the difference between its structure and those of Na_2SiF_6 and K_2SiF_6 polymorphs suggest absence of solid solution in the pseudo-binary phase field Na_2SiF_6 - K_2SiF_6 which is confirmed by the field observations on the type locality for this mineral, Hekla volcano on Iceland [4].

[1] Zahlkin A., Forrester J.D., Tempelton D.H. *Acta Cryst.*, 1964, 17, 1408. [2] Schäfer G.F. *Zeitschrift Krist.*, 1986, 175, 269. [3] Fischer J., Krämer V. *Mat. Res. Bulletin*, 1991, 26, 925. [4] Garavelli A., Balić-Zunić T., Mitolo D., Acquafredda P., Leonardsen E., Jakobsson S.P. *Min. Mag.*, in print.

Keywords: crystal chemistry, silicofluorides, minerals

FA2-MS16-P18

Metamict Titanite. Tobias Beirau, Ulrich Bismayer, Carsten Paulmann. *Universität Hamburg, Germany.*
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The structure of the pure mineral titanite with chemical composition CaTiSiO_5 consists of corner linked TiO_6 -octahedra, SiO_4 -tetrahedra and sevenfold coordinated Ca

positions. A well studied phase transition from $A2/a - P2_1/a$ occurs near 500 K. In nature titanite often incorporates various impurities like the radiogenic elements U and Th. Through the resulting structural damage induced by α - and β -decay the titanite becomes metamict. This means over geological time scales recoil processes due to alpha radiation change the originally periodically structured material into a quasi-amorphous state with persisting short-range order but destroyed long-range order. We present IR and Raman spectra as well as X-ray diffraction data of metamict and heat treated titanite from the Cardiff mine in Canada. The Raman and IR modes are strongly broadened in the metamict material and became sharper on annealing. The OH-stretching mode at 3486 cm^{-1} indicates strong changes in the local environment of OH⁻ in metamict titanite. Between 620 and 750 cm^{-1} Raman excitations appear in the metamict material, which in IR spectra result from Ti-O stretching excitations of the TiO₆ octahedra. This indicates the breakdown of the Raman selection rules and points to the breaking of the octahedral symmetry of TiO₆ polyhedra.

[1] Bismayer U., Paulmann C., Groat L., Zhang M., *Acta Phys. Pol. A*, 2010, 117, 74.

Keywords: titanite, metamict, x-ray diffraction

FA2-MS16-P19

Crystal chemistry of synthetic semiconductors

Pb₅Sb₄S_{11-m}X_m (X=Te,Se). Klaus Bente^a, Gerald Wagner^a, Ronny Kaden^a, Sven Gerhardt^a, Sandra Lobe^a.

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Inspired by the natural semiconductor boulangerite, Pb₅Sb₄S₁₁, the sulfosalts Pb₅Sb₄S_{11-m}Se_m and Pb₅Sb₄S_{11-m}Te_m of varying compositions ($0.0 < m < 11$, step width of $m = 1$) were synthesized by solid state reaction.

The chemical composition was determined by powder X-ray diffraction and electron microprobe analysis. If the Se and/or Te content is increased the Pb(Pb+Sb) ratio decreases. X-ray powder diffraction was used to determine lattice parameters related to the composition.

The synthesized powders were used as starting material for single crystal growth via chemical vapour transport. Iodine was used as transporting agent.

To determine the composition of the as-grown single crystals both REM-EDX and TEM-EDX were applied. The electrical conductivity of these needle-shaped single crystals improves with increasing selenium and/or tellurium content.

Keywords: semiconductor, lattice parameters, boulangerite

FA2-MS16-P20

Comparative study of the stability of various crystallographic phases with composition and stress in the multiferroic BiFeO₃-xPbTiO₃ system.

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BiFeO₃ (BF) is an attractive multiferroic material, exhibiting antiferromagnetic [G-type, having an incommensurate cycloidal spin structure] transition at $T_N \sim 643\text{ K}$ and a ferroelectric transition at $T_C \sim 1103\text{ K}$. BiFeO₃ forms a continuous solid solution with PbTiO₃ and shows a morphotropic phase boundary (MPB) region. There is considerable controversy in literature about the location, width and constituting crystallographic phases of the MPB in the (1-x)BiFeO₃-xPbTiO₃ (BF-xPT) system^{1,2}. Also in this system applied external stress can induce a tetragonal phase in the Bi rich side of MPB and this effect can effectively alter the width of the MPB³. We have studied the stability of various crystallographic phases of (1-x)BiFeO₃-xPbTiO₃ (BF-xPT) as a function of composition and applied stress and have established accurately the room temperature phase diagram for this solid solution^{4,5,6}. It is shown that the structure of BF-xPT is tetragonal for $x > 0.31$ in the P4mm space group and monoclinic for $0.10 \leq x \leq 0.27$ in Cc space group, whereas the two phases coexist in the MPB region $0.27 < x < 0.31$.^{4,5}. The composition width, $\Delta x \sim 0.03$, for the MPB observed by us is the narrowest reported so far in the literature for this system. We have shown that the very high c/a ratio in the tetragonal phase of this system is linked with the covalency effects for bonding between both A and B site cations with oxygen, by comparing the observed bond lengths between oxygen and other cations, obtained from Rietveld analysis of the room temperature powder x-ray diffraction data with expected ionic bond lengths. We have studied the nature of stress induced phase transition for compositions on the BiFeO₃ rich side and shows that the width of the MPB region is extended as a result of external stress. It has been found that this effect is most prominent for compositions close to the MPB, reduces with increasing BiFeO₃ content and for $x=0.9$ the effect is practically absent. But there is no similar effect on the tetragonal side of the MPB. A high temperature x-ray diffraction study carried out on $x=0.27$ composition (which has a monoclinic structure with Cc space group symmetry) with stress induced tetragonal phase shows that the stress induced tetragonal phase and the parent monoclinic phase both transform to paraelectric cubic phase simultaneously.

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Keywords: Multiferroic, Perovskites, Rietveld refinement.

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Environmental Aspects of Mineral Synthesis Through Interaction of Smoke Gases from Biomass Burning and Low Grade MnO₂ Ores.

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The biomass burning results a mixture of gases and particulate matter [1] causing hazardous air pollution as the so called black clouds left behind rice straw. In this study, low grade lumps and dust of manganese oxides capture effectively the evolved gases from the rice straw burning. The rice straw