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Sanjuanite,  $\text{Al}_2(\text{PO}_4)(\text{SO}_4)\text{OH}\cdot 9\text{H}_2\text{O}$ , is a fibrous mineral found in Carboniferous slates at the Pocito Department, San Juan province, Argentina. This phase was first described in [1] and is chemically related to other hydrated aluminium phosphate-sulphate minerals like kribergite  $\text{Al}_5(\text{PO}_4)_3(\text{SO}_4)(\text{OH})_4\cdot 2\text{H}_2\text{O}$  [2] and hotsonite  $\text{Al}_{11}(\text{PO}_4)_2(\text{SO}_4)_3(\text{OH})_{21}\cdot 16\text{H}_2\text{O}$  [3]. Unfortunately, the structural relationship among these minerals is difficult to establish, since no specimens suitable for single-crystal experiments are available, and no isostructural materials are known. To increase the knowledge on these compounds, the crystal structure of sanjuanite was solved and refined from intensity data collected on a conventional powder diffractometer (Bragg-Brentano geometry, scintillation detector, secondary graphite monochromator,  $\text{CuK}\alpha_{1,2}$  radiation). The first necessary step was the indexing of the powder pattern. Unlike the triclinic unit cell previously proposed in [4], the new monoclinic cell  $a=14.3719(3)$ ,  $b=17.2381(4)$ ,  $c=6.1110(2)$  Å,  $\beta=106.617(21)^\circ$ ,  $V\cong 1452$  Å<sup>3</sup> indexes all reflections and hence was used for extracting the integrated intensities down to a  $d$ -spacing of 1.30 Å. This data set was further processed with S-FFT based direct methods [5]. With the exception of one O atom, all non-H atoms clearly showed up in the Fourier synthesis computed with the refined phases from the best direct methods solution. Once the crystal structure model was completed, it was optimized by restrained Rietveld refinements to an effective  $\chi^2$  value of 2.08 [6]. During the refinement the slight preferred orientation along  $[-2\ 0\ 3]$  detected in the flat sample was treated with the March-Dollase correction. The structure of sanjuanite (space group  $P2_1/a$ ,  $Z=4$ ) is composed of infinite alumino-phosphate chains running parallel to  $c$ . Isolated  $(\text{SO}_4)^{2-}$  groups and  $\text{H}_2\text{O}$  molecules connect the groups of chains. Hydrogen bonding plays a key role in the stabilization of the structure.

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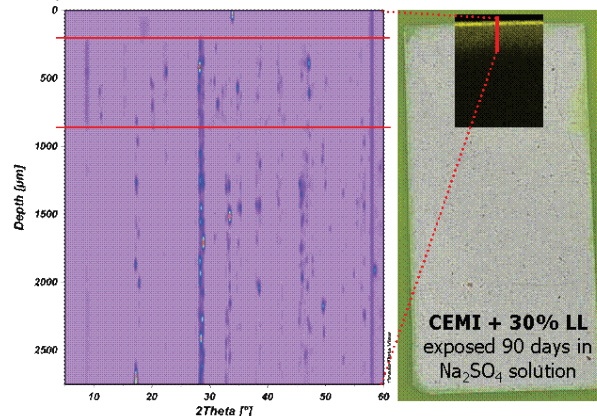
**Keywords:** sanjuanite, ab-initio solution, powder diffraction

#### FA2-MS16-P14

**High resolution phase analyses and early crystallization processes of cement.** Moritz-C. Schlegel<sup>a</sup>, Urs Mueller<sup>a</sup>, Ulrich Panne<sup>a</sup>, Franziska Emmerling<sup>a</sup>. <sup>a</sup>BAM Federal Institute of Materials Research and Testing, Berlin, Germany *Materials Science, Technical University Darmstadt, Germany*. E-mail: [moritz-caspar.schlegel@bam.de](mailto:moritz-caspar.schlegel@bam.de)

Cementitious building materials are a substantial part of our built environment. Due to the nature of the cementitious binder those materials can be described as multi component nano composite materials. Furthermore, for studying degradation mechanisms spatial chemical or phase analytical data are needed, which can be linked to the microstructure of the cementitious paste. The objectives of this work are the

observation of the early crystallization of cement during the hydration and the analysis of the phase assemblage of chemical attacked mortar and concrete including synchrotron methods. Both objectives were examined by diffraction with synchrotron radiation in transmission geometry ( $\lambda=1.0656$  Å,  $\mu$ -spot beamline, BESSY II, HZB, Berlin). The latter one is performed using an ultrasonic trap. That was provided the contact free analysis of a sample and ensures a constant water cement ratio. This is a tremendous improvement since former studies using capillaries coupled with water injection system could not guarantee a homogeneous dispersion of water within the cement suspension. The integration time for a single diffraction pattern was about 30 sec and allowed a detailed view into the dynamics of the crystallization processes at early stages. The spatial phase analysis was performed on cement paste and mortar specimens, which were exposed to sulphate and chloride solutions. The reaction fronts of sulphur and chloride were localised by elemental mapping with a micro X-ray fluorescence analysis. Synchrotron X-ray diffraction was used in-situ for the identification of the phase composition (Fig. 1). The primary focussing optics established a spatial resolution of 10  $\mu\text{m}$  for thick section samples with a thickness of ca. 200  $\mu\text{m}$ . That means phase analysis can be performed in-situ with a high local resolution and within the intact micro structure of the sample. First results show patterns with a good peak to background ratio. The measurement of sulphate content exposed cement paste samples reveal a phase composition, determined by synchrotron XRD which corresponds well to the chemical profile measured by micro XRF.



**Keywords:** cement, time-resolved, space-resolved

#### FA2-MS16-P15

**Elastic anomalies and electromechanical properties of tourmalines.** Chandra Shekhar Pandey, Jürgen Schreuer. *Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Germany*. E-mail: [schreuer@ruhr-uni-bochum.de](mailto:schreuer@ruhr-uni-bochum.de)

Tourmalines exhibit a broad variability in chemical composition and are a promising piezoelectric material for acoustic-electronic devices operating at high-temperatures. In contrast to  $\alpha$ -quartz,  $\text{LiNbO}_3$  and materials of the langasite family, the application of tourmaline at temperatures up to its melting point is not limited by phase transitions, electrical conductivity or strong ultrasound dissipation effects.

Here we report the full set of elastic and piezoelectric constants of five natural single crystal tourmalines of gem quality between room temperature and 903 K as determined

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.

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**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<sup>1\*</sup>, Ali Akbar Khandar<sup>a</sup>, Amin Salem<sup>b</sup>, Leila Kafi –Ahmadi<sup>c</sup>. <sup>a</sup>*Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, IRAN.* <sup>b</sup>*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  $\text{In}_2\text{O}_3$ – $\text{Na}_2\text{B}_4\text{O}_7$  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.

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**Keyword :** Borate, Glass ceramic, Incorporation

#### FA2-MS16-P17

**Crystal chemistry of silicofluorides.** Tonci Balić-Zunić<sup>a</sup>, Anna Garavelli<sup>b</sup>, Donatella Mitolo<sup>b</sup>, Pasquale Acquafredda<sup>b</sup>, Erik Leonardsen<sup>c</sup>, Sveinn Peter Jakobsson<sup>d</sup>. <sup>a</sup>*Natural History Museum, University of Copenhagen, Denmark.* <sup>b</sup>*Dipartimento Geomineralogico, University of Bari, Italy.* <sup>c</sup>*St. Karlsmindevej 46, Hundested, Denmark.* <sup>d</sup>*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 ( $\text{Na}_2\text{SiF}_6$ ) [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  $\text{XF}_6$  sites are occupied in ratio  $1\text{SiF}_6:2\text{NaF}_6$ . 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 ( $\text{KNaSiF}_6$ ) [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  $\text{Na}_2\text{SiF}_6$  and  $\text{K}_2\text{SiF}_6$  polymorphs suggest absence of solid solution in the pseudo-binary phase field  $\text{Na}_2\text{SiF}_6$ - $\text{K}_2\text{SiF}_6$  which is confirmed by the field observations on the type locality for this mineral, Hekla volcano on Iceland [4].

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**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  $\text{CaTiSiO}_5$  consists of corner linked  $\text{TiO}_6$ -octahedra,  $\text{SiO}_4$ -tetrahedra and sevenfold coordinated Ca