

MS16-P17

Pure gyrotropic phase transitions in the arcanite related materials PbMGeO_4 ($M = \text{Ba}, \text{Sr}$)

Gwilherm Nenert¹

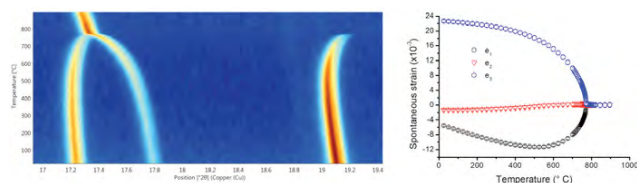
1. Application Competence Center, Almelo, Netherlands (Holland, Europe

email: g.nenert@gmail.com

Gyrotropic phase transitions are characterized by the appearance of a spontaneous optical activity [1]. The appearance of such activity is very common in ferroelectric materials. In such materials, the optical activity is a secondary order parameter and is coupled to the primary order parameter which is the electrical polarization. However, only very rare examples are known of a pure gyrotropic phase transition. Among those, one can cite BiFeO_3 under strain [2], $(\text{C}_5\text{H}_{11}\text{NH}_3)_2\text{ZnCl}_4$ as function of temperature [3]. In both cases, the transition exhibits a change from Pnma to $\text{P2}_1\text{2}_1\text{2}_1$ symmetry.

In this contribution, we have investigated 2 materials belonging to the BaNdGaO_4 structural type, namely PbBaGeO_4 and PbSrGeO_4 using powder X-ray diffraction as function of temperature. While PbBaGeO_4 exhibits a first order phase transition from $\text{P2}_1\text{2}_1\text{2}_1$ to Pnma symmetry. This behaviour is similar to the one reported for $(\text{C}_5\text{H}_{11}\text{NH}_3)_2\text{ZnCl}_4$. However, PbBaGeO_4 exhibits phase coexistence and competition over a wide temperature range of about 200°C . On the contrary, PbSrGeO_4 shows a 2nd order type phase transition towards a Pnma structure with nearly metrically hexagonal cell.

This work demonstrates that both materials are purely gyrotropic and identify BaNdGaO_4 structural type as a new source for such materials. Furthermore, those phase transitions seem unusual in light of the complex behavior reported here for these 2 compounds.



References:

- [1] C. Konak, V. Kopsky, F. Smutny; J. Phys. C: Solid State Physics, 1978, 11, 2493
 [2] S. Prosandeev, I. A. Kornev, L. Bellaiche; Phys. Rev. Lett., 2011, 107, 117602
 [3] A. Gomez Cuevas, J. M. Perez-Mato, M. J. Tello, G. Madariaga, J. Fernandez, L. Echarri, F. J. Zuniga, G. Chapuis; Phys. Rev. B, 1984, 29, 2655

Keywords: gyrotropic, piezoelectric, arcanite

MS16-P18

Structural studies of titanium and zirconium silicate ion-exchange materials for the treatment of nuclear waste

Jennifer Readman¹, Nazesh Sajjad², Reece Hall², Phillippa Patterson²

1. School of Physical Sciences & Computing, University of Central Lancashire, Preston, United Kingdom
 2. Structural studies of titanium and zirconium silicate ion-exchange materials for the treatment of nuclear waste., Preston, United Kingdom

email: jereadman@uclan.ac.uk

Zeolites are commonly used as ion-exchange materials for the remediation of nuclear waste, however, they have certain drawbacks. Unlike zeolites which contain SiO_4 and AlO_4 tetrahedra, microporous Ti-silicates can contain SiO_4 tetrahedra and TiO_6 octahedra and therefore structures are possible which have no traditional aluminosilicate analogues. Microporous Ti-silicates such as sitinakite $\text{KNa}_2\text{Ti}_4\text{Si}_2\text{O}_{13}(\text{OH})\cdot 4\text{H}_2\text{O}$ and the synthetic niobium doped analogue are used for the removal of Cs^+ and Sr^{2+} from nuclear waste [1]. The work presented here will focus on the structures and thermal behaviour of the ion-exchanged Ti- and Zr-silicates. A clear understanding of both is fundamental in determining if these materials have potential as ion-exchangers within the nuclear industry.

Umbite is a naturally occurring small pore microporous Zr-silicate, found in northern Russia and synthetic analogues, $\text{K}_2\text{ZrSi}_3\text{O}_9\cdot\text{H}_2\text{O}$, can be prepared in the laboratory [2]. It has an orthorhombic cell with $a = 10.2977(2)\text{\AA}$, $b = 13.3207(3)\text{\AA}$ and $c = 7.1956(1)\text{\AA}$. Rocha and co-workers found that synthetic umbite undergoes a topotactic transformation when heated 910°C forming a new microporous Zr-silicate with the formula $\text{K}_2\text{ZrSi}_3\text{O}_9\cdot 2\text{H}_2\text{O}$ [2]. In contrast they found that the Na-exchanged analogue transforms to wadeite and the Cs-exchanged form retains the umbite structure when heated to the same temperature. Ion-exchange studies here have shown that umbite has a preference for common radionuclides, such as Cs^+ and Sr^{2+} and Ce^{4+} (as a surrogate for Pu), even in the presence of competing ions. In-situ studies show that these materials behave differently with temperature, indicating that the nature and location of the charge balancing cation plays an important part in determining which high temperature phases are formed and the phases formed do not fit either the AV-15 or wadeite structures previously reported.

Natisite is another material which has interesting ion-exchange chemistry and is a layered Ti-silicate with the formula $\text{Na}_2\text{TiSiO}_5$ [3]. The structure consists of square pyramidal titanium, with the sodium cations located between the layers. This coordination environment is highly unusual for Ti. It crystallises in the tetragonal space group $\text{P4}/nmm$, with $a = b = 6.4967(8)\text{\AA}$ and $c = 5.0845(11)\text{\AA}$. Inclusion of zirconium or vanadium in the framework has a considerable effect on the ion-exchange properties, with changes in the exchange capacity and the rate of uptake for certain ions of interest.

A combination of techniques to probe long and short range order (PDF and XAS) have been used to understand the ion-exchange and thermal behaviour of these materials.

References:

-
- 1) Poojary, D. M., Cahill R. A. and Clearfield, A. (1994). Chem. Mater., 6, 2364.
 - 2) Ferreira, A., Lin, Z., Soares, M. R. and Rocha, J. (2010) J. Solid State Chem., 183, 3067.
 - 3) Ferdov, S., Kostoc-Kytin, V. and Petrov, O. (2002) Powder Diffraction, 17, 234.
-

Keywords: Zeotype, ion-exchange, silicate

MS16-P19

Influence of Microstructure on Symmetry Determination of Piezoceramics

Manuel Hinterstein¹, Henry E. Mgbemere², Markus Hoelzel³, Esmail Adabifiroozjaei⁴, Charles Sorrell⁴, Mark Hoffman⁴

1. Institute for Applied Materials, Karlsruhe Institute of Technology, Karlsruhe, Germany
2. Department of Metallurgical and Materials Engineering, University of Lagos, Lagos, Nigeria
3. Heinz Maier-Leibnitz Zentrum, Technische Universität München, Garching, Germany
4. School of Materials Science and Engineering, UNSW Australia, Sydney, Australia

email: m.hinterstein@kit.edu

Frequently symmetry determination in studies is based on the discussion of agreement factors or the quality of the refinements, rather than on the basis of physical arguments. Especially in the field of piezoceramics this can be observed in the discussion whether monoclinic symmetry can be observed or not.

In this study we could show with temperature-dependent high-resolution X-ray and neutron diffraction that based on agreement factors alone the physical origin of observations cannot be revealed. Only in combination with additional electron microscopy and electron probe microanalysis we could elucidate that a segregation of substituents results in a complex reflection splitting and phase coexistence that can be misinterpreted as monoclinic symmetry. This single-phase monoclinic *Pm* model is able to perfectly reproduce the diffraction patterns and is known from literature [1,2]. A model with phase coexistence of two classical orthorhombic *Amm2* phases can reproduce the diffraction data with equal accuracy.

This demonstrates the need of comprehensive analyses with complementary methods to cover a broad range of length scales as well as considering both average and local structure. The conclusions drawn from this work will have an impact on a broad range of research areas where inhomogeneities cannot be ruled out. The underlying mechanisms of the extraordinary properties of some functional materials originate not just in their structures but also their complex microstructures. Consequently, knowledge of both features of materials may be essential for the exploitation and development of their functionalities as well as improvement of material properties.

References:

-
- [1] H. E. Mgbemere, M. Hinterstein, and G. A. Schneider, J. Eur. Ceram. Soc. 32, 4341 (2012).
 - [2] L. Liu, X. Ma, M. Knapp, H. Ehrenberg, B. Peng, L. Fang, and M. Hinterstein, Europhys. Lett. 118, 47001 (2017).
-

Keywords: piezoelectric,ceramics, ferroelectricity