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Acta Cryst. (2011) A67, C495**Structural features and physical properties of $\text{In}_2\text{Bi}_3\text{Se}_7\text{I}$ and $\text{InBi}_2\text{Se}_4\text{I}$**

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The quaternary compounds $\text{In}_2\text{Bi}_3\text{Se}_7\text{I}$ and $\text{InBi}_2\text{Se}_4\text{I}$ were synthesized via chemical vapor transport. The structures were solved and refined by single crystal X-ray diffraction methods and the thermal behavior was examined by differential thermal analysis and temperature programmed X-ray powder diffraction. The compounds exhibit structural features related to those found in the known semiconductors $\text{InM}_2\text{Se}_4\text{Br}$ ($M = \text{Sb/Bi}$)^[1] and many alkali metal bismuth chalcogenides such as $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ and $\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ which are n-type semiconductors known for their good thermoelectric properties.^[2] All these structures consist of complex partial structures with rocksalt-like and CdI_2 -like fragments and loosely bound anions (selenide halides) or cations (alkali metal selenides), respectively, located in rather large cavities which results in the possibility of phonon scattering by rattling. The total thermal conductivity (κ) of sintered pellets of $\text{In}_2\text{Bi}_3\text{Se}_7\text{I}$ ranges from $0.16 \text{ W K}^{-1} \text{ m}^{-1}$ at 3.5 K to $0.3 \text{ W K}^{-1} \text{ m}^{-1}$ at room temperature, with a maximum of $0.7 \text{ W K}^{-1} \text{ m}^{-1}$ at 22 K . The electrical resistivity of $\text{In}_2\text{Bi}_3\text{Se}_7\text{I}$ and $\text{InBi}_2\text{Se}_4\text{I}$ corresponds to semiconducting behavior ($94 \text{ } \Omega \text{ cm}$ and $3.3 \text{ k}\Omega \text{ cm}$, respectively, at room temperature). The rather high electric resistivity of $\text{In}_2\text{Bi}_3\text{Se}_7\text{I}$ and $\text{InBi}_2\text{Se}_4\text{I}$ is probably a consequence of the different electronegativity of the elements in combination with the balanced valence states. Therefore the ionicity is rather high. In contrast, $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$, which shows slight deviations from the ideal composition, and $\text{K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ are not normal valent, leading to higher conductivity. Therefore, increasing the metallic character by doping e. g. with alkali metals might enhance the thermoelectric properties in the system In-Bi-Se-X ($X = \text{I, Br}$).

[1] L. Wang, S.-J. Hwu, *Chem. Mater.* **2007**, *19*, 6212-6221. [2] D. Y. Chung, K. S. Choi, L. Iordanidis, J. L. Schindler, P. W. Brazis, C. R. Kannewurf, B. X. Chen, S. Q. Hu, C. Uher, M. G. Kanatzidis, *Chem. Mater.* **1997**, *9*, 3060-3071.

Keywords: thermoelectricity, indium bismuth selenide iodides

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Acta Cryst. (2011) A67, C495**Structure analysis of monazite-type ceramics used for nuclear waste management**

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The further development of the conditioning and disposal of nuclear waste poses a major challenge in the near future. In this context, monazite ceramics (LnPO_4 , $\text{Ln} = \text{La, Ce, Nd, Sm, Eu, Gd}$) appear to be promising alternative matrices to borosilicate glasses for the immobilization of actinides like U, Th and Pu.

Monazite is a natural thorium ore, chemically variable and highly radiation resistant [1]. The eldest known monazites including thorium are determined up to 3.2 Ma in age [2]. The high melting temperatures of about $2000 \text{ }^\circ\text{C}$ are a disadvantage of monazite phases and at a first glance this seems to be a drawback.

However, our initial phase is NdPO_4 with a melting temperature of $1975 \pm 20 \text{ }^\circ\text{C}$ [3]. Our intention is to reduce the melting and sintering

temperature of this particular monazite phase, but maintaining the positive properties of monazite simultaneously (high chemical durability and high radiation resistance).

In order to include tetravalent actinides (e.g. Th, U, Pu), a second phase is used for charge balance. We used cheralite ($\text{CaTh}(\text{PO}_4)_2$) and huttonite (ThSiO_4) as solid solution end member. Both phases are isostructural to monazite [4, 5, 6]. Two solid solution series $\text{NdPO}_4\text{-CaTh}(\text{PO}_4)_2$ and $\text{NdPO}_4\text{-ThSiO}_4$ were synthesized by solid state reactions at $T=1400 \text{ }^\circ\text{C}$ and atmospheric pressure for several hours.

The sample properties were analyzed chemically by EDX, structurally by XRD and Raman spectroscopy and thermally by TG-DSC. The analysis by SEM e.g. shows compact conglomerates of crystallites with diameters of $1\text{-}4 \text{ } \mu\text{m}$.

As a first result a complete solid solution along the $\text{NdPO}_4\text{-CaTh}(\text{PO}_4)_2$ join and along the $\text{NdPO}_4\text{-ThSiO}_4$ join does actually exist, respectively. Furthermore cell parameters show a significant shift as a function of chemical composition. Results of detailed rietveld refinements will be presented.

[1] L.A. Boatner, B.C. Sales, In: W. Lutze, R.C. Ewing (Eds.): *Radioactive waste forms for the future*, Amsterdam, North-Holland **1988** [2] B. Rasmussen, I.R. Fletcher, J.R. Muhling, *Geochim. Cosmochim. Acta* **2007**, *71*, 670-690 [3] Y. Hikichi, T. Nomura, *J. Am. Ceram. Soc.* **1987**, *70*, C-252-C-253 [4] P.E. Raison, R. Jardin, D. Bouëxère, R.J.M. Konings, T. Geisler, C.C. Pavel, J. Rebizant, K. Popa, *Phys. Chem. Minerals* **2008**, *35*, 603-609 [5] H.-J. Förster, *American Mineralogist*, **1998**, *83*, 259-272 [6] L. Cartz, F.G. Kariotis, K.A. Gowda, *Radiation Effects* **1981**, *67*, 83-85.

Keywords: powder diffraction, monazite ceramics, nuclear waste

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Acta Cryst. (2011) A67, C495-C496**Characterization of synthetic $\text{Sm}_{1-x}\text{Ce}_x\text{PO}_4$ Ceramics used for Nuclear Waste Management**

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The conditioning of nuclear waste from nuclear power plants is an important issue according to science and society. Therefore the research on an appropriate matrix for the immobilization of e. g. actinides is of great interest.

Beyond the widely used borosilicate glasses, ceramics are promising materials for the conditioning of actinides like U, Th and Pu.

Monazite-type ceramics with compositions $\text{Sm}_{1-x}\text{Ce}_x\text{PO}_4$ ($0 \leq x \leq 1$) represent an important material in this field. To obtain a suitable host matrix for radionuclides, the characterization of monazites of different chemical composition and their thermal and structural behaviour is essential. Monazite was chosen because of its outstanding properties according to radiation resistance and chemical durability [1,2,3].

Our aim is to find a composition with a minimum melting point or an eutectic mixture in order to improve the production design for future industrial synthesis. Therefore we synthesized Samarium-Cerium-monazites as mentioned above, that can be used as simulation phases for radionuclide-doped matrices. Thirteen different compositions of the aforementioned solid solution were prepared by hydrothermal synthesis at $T = 220 \text{ }^\circ\text{C}$, $p \approx 25 \text{ bar}$ following [4].

The sample properties were analysed chemically by electron microscopy (EDX), structurally by powder x-ray diffraction (XRD) and Raman spectroscopy and thermally by TG-DSC. By means of our characterizations we could show that the solid solution with endmembers SmPO_4 and CePO_4 doesn't show ideal behaviour. Accordingly we

assume a minimum of melting point in the compositional range around $\text{Sm}_{0.6}\text{Ce}_{0.4}\text{PO}_4$. First results particularly related to crystal structure analysis of the investigated ceramics will be presented.

[1] G.R. Lumpkin, *Elements* **2006**, 2, 365-372. [2] A. Meldrum, L.A. Boatner, R.C. Ewing, *Physical Review B* **1997**, 56, 13805-13814. [3] E.H. Oelker, F. Poitrasson, *Chemical Geology* **2002**, 191, 73-87. [4] H. Meysamy, K. Riwozki, A. Kornowski, S. Naused, M. Haase, *Advanced Materials* **1999**, 11, 840-844.

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Raman spectra of Synthetic Orthophosphates used for Nuclear Waste Management

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One of the central tasks in nuclear waste management is the safe conditioning of actinides like e.g. U, Th or Pu resulting from the re-processing of nuclear fuel. Besides borosilicate glasses promising candidates to accomplish that task safely are ceramic orthophosphates that own the crystal structure and properties of the mineral monazite. Monazite is monoclinic (SG $P2_1/n$) and exhibits an extraordinary chemical durability and radiation resistance [1,2,3]. For the development of new conditioning matrices orthophosphates with compositions LnPO_4 (Ln = La, Ce, Nd, Sm, Eu) were synthesized as first simulation phases without incorporated actinides. These phases were partly radiated by the bombardment with heavy Kr-ions in order to simulate radiation damage caused by α -emitters (α -recoil effect).

The quality of all phases (radiated and non-radiated) was first characterized by powder x-ray diffraction. The short range order and medium range order was investigated by raman spectroscopy. Using this technique structural changes due to radiation damage can be detected quite easily [4,5,6]. Resulting raman spectra show a high resolution and allow the discrimination of up to 30 different raman frequencies.

As a first result significant correlations between chemical composition, crystal structure, radiation damage and thermodynamic properties of the investigated ceramics can be detected and will be demonstrated in detail.

The findings of our investigation will be the basis for the further development and evaluation of *real* monazite-type conditioning ceramics containing larger amounts of the actinides U, Th, Pu, Am, Cm and Np.

[1] .A. Boatner, B.C. Sales, In: W. Lutze, R.C. Ewing (Eds.): *Radioactive waste forms for the future*, Amsterdam, North-Holland **1988**. [2] G.R. Lumpkin, *Elements* **2006**, 2, 365. [3] W.J. Weber, A. Navrotsky, S. Stefanovsky, E.R. Vance, E. Vernaz, *MRS Bulletin* **2009**, 34, 46. [4] G.M. Begun, G.W. Beall, L.A. Boatner, W.J. Gregor, *J. of Raman Spectroscopy* **1981**, 11, 273. [5] E.N. Silva, A.P. Ayala, I. Guedes, C.W.A. Paschoal, R.L. Moreira, C.-K. Loong, L.A. Boatner, *Optical Materials* **2006**, 29, 224. [6] L. Nasdala, R. Grötzschel, S. Probst, B. Bleisteiner, *Canadian Mineralogist* **2010**, 48, 351.

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XRD analysis of the corrosion products of research reactor fuel elements

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Corrosion experiments of unirradiated $\text{UAl}_x\text{-Al}$ and $\text{U}_3\text{Si}_2\text{-Al}$ research reactor fuel elements were carried out under repository relevant conditions in order to identify and quantify the secondary phases formed by reactions with formation waters being expected in final repositories due to an accidental influx from the enclosing salt formations. This analysis is important for safety assessment issues as such phases quantitatively may act as a barrier against the migration of the released radioactive inventory. In detail the anaerobic experiments were carried out in glass autoclaves at 90°C in repository relevant solutions of defined composition [1]. After termination of the corrosion period WAXS measurements and Rietveld analysis were the major methods being applied for the identification and quantification of the crystalline and amorphous corrosion products which have been subdivided into different grain size fractions previously.

The corrosion products, i. e. the secondary phases of the research reactor fuel elements were identified via "Search/Match" database retrieving. The identified phases were LDH structures, lesukite (aluminium chlorohydrate), elemental iron, residues of uncorroded nuclear fuel, and different iron containing phases like akaganeite, goethite, and lepidocrocite. The quantitative analysis showed that LDH compounds and lesukite are the major crystalline phases which are observed. Rietveld analysis also revealed the content of amorphous phases. To account for an accurate determination of the phase quantities, i. e. for the application of the Brindley [2] correction the average particle diameter has previously determined by REM and image analysis.

For safety assessments the potential for retention of radionuclides has to be focused on the sorption capacities of the major phases as these may additionally applied as a backfilled barrier in order to prevent the migration of radionuclides out of the final repository in deep geological formations.

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Stability and Conductivity of Ce-doped Pyrochlores for SOFCs applications

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Solid Oxide Fuel Cells (SOFCs) are highly efficient and environmentally friendly energy conversion devices with a large variety of potential applications. A SOFC has 3 main components: the cathode, which has to have high electronic/ionic conductivity, to be chemically compatible with other cell components, stable in oxidizing atmospheres and a thermal expansion coefficient similar to other components; the electrolyte that should be ionically conductive, electronically insulating, chemically stable at high temperatures and in reducing and oxidizing environments, free of porosity and with thermal expansion that matches electrodes and finally, the anode which should be electrically conductive, stable in reducing atmosphere and should have high electrocatalytic activity, similar thermal expansion