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Structural features and physical properties of $In_2Bi_3Se_7I$ and $InBi_2Se_4I$

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The quaternary compounds $In_2Bi_3Se_7I$ and $InBi_2Se_4I$ 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 InM_2Se_4Br (M = Sb/Bi)[1] and many alkali metal bismuth chalcogenides such as β-$K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$ 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 In_2BiSe_4I ranges from 0.16 W K^{-1} m^{-1} at 3.5 K to 0.3 W K^{-1} m^{-1} at room temperature, with a maximum of 0.7 W K^{-1} m^{-1} at 22 K. The electrical resistivity of $In_2Bi_3Se_7I$ and $InBi_2Se_4I$ corresponds to semiconducting behavior (94 Ω cm and 3.3 kΩ cm, respectively, at room temperature). The rather high electric resistivity of $In_2Bi_3Se_7I$ and In_2BiSe_4I 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, β-$K_2Bi_8Se_{13}$, which shows slight deviations from the ideal composition, and $K_{2.5}Bi_{8.5}Se_{14}$ 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 = I, Br).

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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 ($LnPO_4$, *Ln* = 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 °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±20 °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 ($CaTh(PO_4)_2$) and huttonite ($ThSiO_4$) as solid solution end member. Both phases are isostructural to monazite [4, 5, 6]. Two solid solution series $NdPO_4$-$CaTh(PO_4)_2$ and $NdPO_4$-$ThSiO_4$ were synthesized by solid state reactions at T=1400 °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 1-4 µm.

As a first result a complete solid solution along the $NdPO_4$-$CaTh(PO_4)_2$ join and along the $NdPO_4$-$ThSiO_4$ 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.

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Characterization of synthetic $Sm_{1-x}Ce_xPO_4$ 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 $Sm_{1-x}Ce_xPO_4$ ($0 \le x \le 1$) 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 °C, $p \approx 25$ 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