Characterization of Sm- & Tb-Orthophosphates used for Nuclear Waste Management

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Introduction

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 and fission products is of great interest. Ceramics are promising materials for conditioning. Monazite-type ceramics with compositions LnPO$_4$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb), represent an important material in this field because of its outstanding properties according to radiation resistance and chemical durability. With a view to future industrial syntheses it is important to find a composition with a melting point minimum or an esthetic mixture.

Experimental

Sm,Ce-Orthophosphates of six different chemical compositions were prepared by hydrothermal synthesis using Ln(NO$_3$)$_3$$\cdot$6 H$_2$O ($n$ = Sm, Ce) (aq), (NH$_4$)$_2$HPO$_4$ (aq) as phosphorous-component and NaOH for an alkaline environment. The chosen $\text{Sm}_{1-x}\text{Ce}_x$ ratio in the mixture was 10:1. The mixture was heated to 120 °C. After synthesis the product was mixed with an aqueous solution of nitric acid ($c = 1$ mol 1$^{-1}$) and stirred for three hours to make, could not recover the original from linear behavior. Crystallizing again after three days, the product was washed three times with distilled water, afterward oversaturated at 80 °C and ground in an agate mortar.

Tb-orthophosphate (monoclinic) was synthesized by annealing hydrated TbPO$_4$ which has been obtained by precipitation using Tb(NO$_3$)$_3$$\cdot$5 H$_2$O and H$_3$PO$_4$ as initial materials.

Analytical Methods

- Chemical Analyses: EDX-Quanta 200F by FEI, (60 Pa, 30 kV) and ESI CA/XPS ESCALAB 250 by VG Vigo Scientific, using Al K$_\alpha$_ monochromator, GmbH. Münster.
- Thermal Analyses by coupled TG-DSC Netzsch STA 449 C Jupiter, (10 K min$^{-1}$, $T_{\text{max}}$ = 1000 °C).
- X-ray powder diffraction by D8-Enertab/OK by Bruker AXS GmbH, using Cu K$_\alpha$. LynxEye detector running in continuous mode ($\Delta 2 \theta = 0.022$, $\omega = 10 = 100^\circ$, $L = 2$ s/step).
- Raman Spectroscopy by Horiba HR 800 by HORIBA Scientific, using a He-Ne laser, $\lambda = 632.81$ nm.

Results and Discussion

Sm$_{1-x}$Ce$_x$PO$_4$:

- The thermal analyses showed a non-linear behaviour of the system.
- A minimum of three exothermic lambda peaks was observed, which indicates the total recrystallization of the phase.
- This non-linear thermal behaviour of Sm$_{1-x}$Ce$_x$PO$_4$ is descried for the first time.
- The corresponding antisymmetric vibrations $v_1$ ($\text{Sm}_2$PO$_4$).

Conclusions

- New experimental data for Sm$_{1-x}$Ce$_x$PO$_4$ could be generated and so far unknown properties be determined.
- Reference data do only exist for the pure endmembers SmPO$_4$ and CePO$_4$.
- Synthesis and characterization of synthetic Orthophosphate solid solutions have rarely been described so far.
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