

Phase relations of the Solid Solutions $\text{Sm}(\text{Ca,Ce})\text{PO}_4$ and $\text{La}(\text{Sr,Ce})\text{PO}_4$

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Monazite-type ceramics are considered as an alternative matrix for high level nuclear waste. Besides an extensive chemical flexibility, long-term stability, and durability natural monazites can accommodate considerable amounts of Th and U [1,2]. Using the monazite-types LaPO_4 and SmPO_4 as endmembers, solid solutions were prepared, replacing 2 Sm^{3+} by Ca^{2+} and Ce^{4+} , and 2 La^{3+} by Sr^{2+} and Ce^{4+} . $\text{Ca}^{2+}/\text{Sr}^{2+}$ have similar radii like Sm/La and hence were considered as suitable earth alkaline replacements for these Lanthanoides, focussing on Ce^{4+} as non-radioactive surrogate for actinoides. The samples were characterised by XRD, SEM/EDS, and IR.

The solid solutions of $\text{Sm}_{1-x}(\text{Ca,Ce})_x\text{PO}_4$ were synthesised at 1000 °C. With increasing (Ca,Ce)-amount, $\text{Ca}_2\text{P}_2\text{O}_7$ was observed. This result was in good accordance with the work by Pepin and Vance [3] using trivalent Nd/Gd. On heating $\text{Sm}_{0.85}(\text{Ca,Ce})_{0.15}\text{PO}_4$, at 1200 °C for 24 h we observed the formation of $\text{Ca}_3(\text{PO}_4)_2$. At 1400 °C, $\text{Ca}_3(\text{PO}_4)_2$ was not stable and in addition to monazite the eulytite-type $\text{Ca}_3(\text{Sm,Ce})(\text{PO}_4)_3$ was formed.

Considering solid solutions $\text{La}_{1-y}(\text{Sr,Ce})_y\text{PO}_4$ ($y=0-0.3$), prepared at 1400 °C, the Sr(La,Ce)-eulytite-type was observed for $y=0.05$ to 0.3. Solid solution series which were prepared at 1000 °C with 10 and 20 wt% $\text{NH}_4\text{H}_2\text{PO}_4$ excess showed that LnP_3O_9 or $\text{Sr}_3\text{P}_4\text{O}_{13}$ were formed. The solid solutions with 10 wt% excess phosphate were only pure for $y=0.10$ and 0.15. These findings could be relevant for adjusting parameters for future experiments with Sm,(Ca,Th) and for sintering suitable waste forms.

We gratefully acknowledge the DFG (RO 2055/7-1) and BMBF (02 NUK 021E) for financial support.

[1] N. Clavier, R. Podor, N. Dacheux, *Journal of the European Ceramic Society* **31**, pp. 941–976, 2011, [2] R. Ewing, L. Wang, Phosphates as nuclear waste forms in *Reviews in Mineralogy and Geochemistry*, 2002, [3] J. Pepin, E. Vance, *Mat. Res. Bull.*, Vol. **16**, pp. 627–633, 1981