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THE SYNTHESIS AND THERMAL STABILITY OF CERIUM ULTRAPHOSPHATE CeP_5O_{14}

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The synthesis and thermal stability of cerium ultraphosphate CeP_5O_{14} were examined by differential thermal analysis, powder X-ray diffraction, microscopy (electron microscope) and IR spectroscopy.

There are many literature reports on alkali metal-lanthanide phosphates, where *Ln*: La, Nd, Y, Sm, Gd, and quite few on connections of cerium phosphate with alkali metals. The published data deal mainly with methods of synthesis, crystal structure and the stability of these compounds. Ce(III) phosphates such as: CeP_5O_{14}, CeP_3O_9, $CePO_4$ are known [1, 2], as well as mixed metaphosphates: $NaCe(PO_3)_4$, $KCe(PO_3)_4$, $K_2Ce(PO_3)_5$ [3, 4]. Cerium ultraphosphate can be obtained quite easily as a result of the reaction of CeO_2 with phosphoric acid H_3PO_4, but the conditions of synthesis reported by various authors are different [2, 5, 6]. CeP_5O_{14} crystallizes in a monoclinic system [5, 7], however its triclinic modification is also known [8].

There are few publications on phase examinations in alkali metallanthanide phosphates systems. For Ce(III), only phase diagrams of binary systems: CeP_3O_9 - KPO_3, CeP_3O_9 - $NaPO_3$ are known [3, 4] and the phase diagram of the ternary system Ce_2O_3 - Na_2O - P_2O_5 in the part richer in P_2O_5 [9].

Experimental

Cerium ultraphosphate CeP_5O_{14} was obtained from CeO_2 (99.9%) and H_3PO_4 (85%). A mixture of CeO_2 and H_3PO_4 of molar ratio P/Ce = 10 was vaporized slowly until a thick, transparent mass was obtained. The mass was then sintered in a gold crucible at 700° for 24 h. The product was ground in

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agate mortar and then washed several times with distilled water and dried at 200°.

The experiment were performed with differential thermal analysis, powder X-ray diffraction, microscopy and IR spectroscopy. The thermal analysis was performed using a derivatograph Type 3427 (MOM, Hungary) within the temperature range 20-1200°; heating rate 10 deg/min, platinum cup, under air. As reference material Al_2O_3 was used. Powder X-ray analysis was performed with a HZG-4 diffractometer using $CuK_{\bar{\alpha}}$ radiation. The crystallized samples were microscopically examined (electron microscope, Cambridge Instruments). Phase identification was made with IR absorption spectroscopy using a Specord IR - 75 spectrophotometer.

Results

Within the investigations of phase equilibria of the ternary system Ce_2O_3 - Na_2O - P_2O_5 in the part richer in P_2O_5, the temperature of congruent CeP_5O_{14} formation, its thermal stability and behaviour in the presence of sodium metaphosphate $NaPO_3$ at higher temperatures were determined. Figure 1 presents the thermal curves of pure CeP_5O_{14}. There is a strong endothermic effect which begins at approx. 900° on DTA curve. The effect is accompanied by a two-stage mass decrement which amounts to approx. 4% (TG curve) at the first stage. To examine the course of reaction of CeP_5O_{14} decomposition, isothermal measurement of mass decrement at 900° was performed. Powder X-ray examinations showed that CeP_5O_{14} sintered at 900° for approx. 150 h decomposes completely according to the reaction: $CeP_5O_{14} \rightarrow Ce(PO_3)_3 + P_2O_5$. Therefore cerium ultraphosphate is unstable at higher temperatures and the mass decrement on TG curve is connected with the evaporation of P_2O_5. While examining the preparations forming the mixture of phosphates CeP_5O_{14} and $NaPO_3$ with changing composition, cerium ultraphosphate was found to behave in different ways according to the content of $NaPO_3$ and thermal treatment. Two variants of thermal treatment were used:

(1) the sintering of samples over the temperature range 450-700° (according to composition),

(2) the melting of samples and their crystallization with grafting.

In sintered samples containing small quantities of $NaPO_3$, after cooling, mixed metaphosphate $NaCe(PO_3)_4$ was found to be present X-ray analysis. The content of $NaCe(PO_3)_4$ increases in proportion to the content of $NaPO_3$, and thus the 40% addition of $NaPO_3$ causes a complete decomposi-

tion of CeP_5O_{14} to $NaCe(PO_3)_4$. Figure 2 presents the thermal curves of a sample containing 10 wt.% of $NaPO_3$. A strong thermal effect at approx. 770° can be noticed on DTA curve. It results from a lowered temperature of peritectic decomposition of $NaCe(PO_3)_4$.

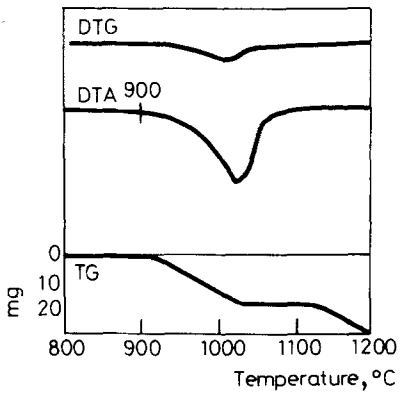

Fig. 1 TG, DTG and DTA curves of CeP_5O_{14}

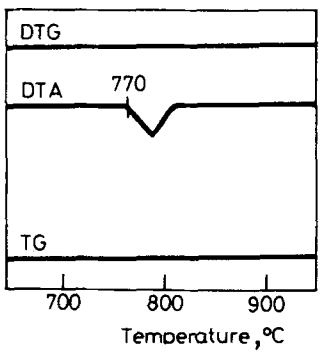

Fig. 2 TG, DTG and DTA curves of the mixture of 90 wt.%CeP_5O_{14} with 10 wt.% $NaPO_3$

Preparations containing CeP_5O_{14} with the addition of $NaPO_3$, which were melted and crystallized with grafting, changed their phase composition as well. By X-ray analysis $Ce(PO_3)_3$ or $NaCe(PO_3)_4$ were found to be present in reaction products. The course of the process and the phase com-

position of molten preparations depend on the proportional content of $NaPO_3$. The addition up to 40 wt.% of $NaPO_3$ was discovered to cause the decomposition of CeP_5O_{14} to CeP_3O_9. In preparation containing over 40% of $NaPO_3$, CeP_5O_{14} is decomposed to mixed metaphosphate $NaCe(PO_3)_4$.

Therefore, it can be concluded that pure cerium ultraphosphate CeP_5O_{14} is more stable. The addition of $NaPO_3$ reduces the temperature range of CeP_5O_{14} stability and a direction of the decomposition depends on the conditions of thermal treatment which was used.

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Zusammenfassung — Mittels DTA, Debye-Scherrer-Untersuchungen, Mikroskopie (Elektronenmikroskopie) und IR-Spektroskopie wurde die Synthese und thermische Stabilität von Zer-ultraphosphat CeP_5O_{14} untersucht.