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SYNTHESIS OF THE DOUBLE ORTHOPHOSPHATE $Ca_3Y(PO_3)_4$

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On the basis of thermal investigations, powder X-ray diffraction and microscopy in reflected light, several methods of obtaining the phase-pure compound $Ca_3Y(PO_4)_3$ in the ternary system Y_2O_3 - CaO - P_2O_5 were determined.

For several years, numerous laboratories have been carrying out investigations on the rare earths, yttrium, scandium and their compounds. The studies are concentrated on the properties, crystal structures and possibilities of their use. However, there is also interest in rare earth phosphates, and mixed phosphates of lanthanides and other metals, as a result of their use as laser and luminophore materials. Examples include the compounds $M^I_3Ln(PO_4)_2$ (M^I = alkali metal, *Ln* = rare earth, Y, Sc) [1-3].

In 1981 the syntheses and structures of this type of double calcium rare earth orthophosphates were reported [4]. $Ca_3Ln(PO_4)_3$ (*Ln* = La-Gd, excluding Pm) are known; they have the eulytite, $Bi_4(SiO_4)_3$, structure.

Experimental

The following commercial starting materials were used: $CaHPO_4$ analytical grade (POCh), $CaCO_3$ analytical grade (POCh), Y_2O_3, 99.99% (ZOCh), and H_3PO_4 85% analytical grade (Xenon). The following compounds were prepared in our laboratory: $Y(PO_3)_3$, YPO_4, $Ca_2P_2O_7$ and $Ca_3(PO_4)_2$. Yttrium metaphosphate, $Y(PO_3)_3$, was obtained from Y_2O_3 and H_3PO_4. The initial components were mixed carefully and sintered in a platinum crucible for 3 days at 200, 300 and 900°. YPO_4 was obtained from and aqueous solution of 0.4 wt% Y_2O_3 and 15 wt% P_2O_5 (from H_3PO_4). The mixture was placed in a round-bottomed flask, brought to the boil under a reflux con-

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denser and held there for 6 h. The precipitated YPO_4 was filtered off, washed several times with hot distilled water and dried at 200°. $Ca_2P_2O_7$ was obtained from $CaHPO_4$ analytical grade by heating at 900 for 1 h. $Ca_3(PO_4)_2$ was prepared from $Ca_2P_2O_7$ and $CaCO_3$. The orginal substances were mixed in stoichiometric quantities, and the mixture was ground in an agate mortar, placed in a platinum crucible and heated at 1350° for 1 h.

The investigations were carried out by means of differential thermal analysis, powder X-ray diffraction and microscopy in reflected light. The thermal analysis was performed with a derivatograph type 3427 (MOM, Hungary) over the temperature range 20 to 1400°, under air, at a heating rate of 10 deg/min, in a platinum cup. The reference material was Al_2O_3. In the thermal investigations, a furnace constructed in this laboratory with platinum or molybdenum winding was used. X-ray analysis was carried out by the powder method in a Guinier camera with CuK_α radiation from an HZG-4 diffractometer.

Results

The phase diagram of the system YPO_4-$Ca_3(PO_4)_2$ was determined and examined in this laboratory. The previously unknown compound with formula $Ca_3Y(PO_4)_3$ was demonstrated by thermal and X-ray investigations. Its melting point was determined and its thermal stability was examined. $Ca_3Y(PO_4)_3$ was discovered to exist only in a particular temperature range. Above this interval, it decomposes into YPO_4 and $Ca_3(PO_4)_2$. Therefore, it was interesting to examine the conditions of obtaining this mixed orthophosphate. The preparation of the phase-pure compound proved to be difficult because specific conditions were necessary, i.e. high temperature (higher than the temperature of $Ca_3Y(PO_4)_3$ decomposition), the presence of liquid phase and the use of a quenching technique.

Attempts to obtain $Ca_3Y(PO_4)_3$ by sintering a stoichiometric mixture of $Ca_3(PO_4)_2$ and YPO_4 at different temperatures, or by melting and then cooling down to room temperature at a rate of 10 deg/min, did not succeed $Ca_3(PO_4)_2$ and YPO_4 (in sinters) and traces of $Ca_3Y(PO_4)_3$ (in alloys) were present in the products.

Several methods of obtaining phase-pure compound $Ca_3Y(PO_4)_3$ were developed as a result of differential thermal, X-ray and microscopic examinations. Some suggestions for the synthesis with the use of various initial materials are presented below.

1. Obtaining $Ca_3Y(PO_4)_3$ from a stoichiometric mixture of the orthophosphates YPO_4 and $Ca_3(PO_4)_2$:

(a) The mixture of these orthophosphates is melted, then sintered at approx. 1600° for 2 h and cooled quickly.

(b) The mixture of orthophosphates is melted and cooled down quickly to room temperature. The molten sample is then transferred to a furnace heated to 1350°, sintered for 1 h and quenched.

2. Obtaining $Ca_3Y(PO_4)_3$ from a 1:3 molar mixture of Y_2O_3 and $Ca_2P_2O_7$:

(a) The mixture is melted and cooled down quickly to room temperature. The sample is then put into a furnace heated to 1350°, sintered for 1 h and quenched.

(b) The mixture os Y_2O_3 and $Ca_2P_2O_7$ is sintered at 1400° for 2 h and quenched in ice.

3. Obtaining $Ca_3Y(PO_4)_3$ from a 1:2:1 molar mixture of YPO_4, $CaHPO_4$ and $CaCO_3$:

(a) The mixture is heated at 900° for 1 h, then melted and cooled down quickly. This preparation is put into a furnace heated to 1350°, sintered for 1 h at this temperature and quenched.

4. Obtaining $Ca_3Y(PO_4)_3$ from a 1:3 molar mixture of $Y(PO_3)_3$ and $CaCO_3$:

(a) The mixture is heated at 900° for 1 h, then melted and cooled down quickly. The product is transferred to a furnace heated to 1350°, sintered at this temperature for 1 h and quenched.

It can be concluded that the least complicated method of synthesizing $Ca_3Y(PO_4)_3$ is that described in point 2b.

References

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Zusammenfassung — Mittels thermischer Untersuchungen, dem Debye-Scherrer-Verfahren und Reflexionslichtmikroskopie wurden einige Methoden zum Erhalt phasenreinem $Ca_3Y(PO_4)_3$ aus dem ternären System Y_2O_3-CaO-P_2O_5 bestimmt.