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The System $LaPO_4 – Ca_3(PO_4)_2 – Ca_2P_2O_7$

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The phase diagram of the ternary system $LaPO_4 – Ca_3(PO4)_2 – Ca_2P_2O_7$ has been determined by thermal, X–ray and microscopic examinations. The system contains only one double phosphate $Ca_3La(PO_4)_3$ which is formed at the 1:1 molar ratio $LaPO_4$:$Ca_3(PO_4)_2$.

Key words: phase diagram, DTA, X-ray, phosphates

Phase diagrams of the three binary side systems: $LaPO_4 – Ca_3(PO_4)_2$, $Ca_3(PO_4)_2 – Ca_2P_2O_7$, $LaPO_4 – Ca_2P_2O_7$ are known. According to [1], the system $LaPO_4 – Ca_3(PO_4)_2$ contains a double orthophosphate $Ca_3La(PO_4)_3$, which exists above 1230°C, transforms at 1270°C and melts congruently at 1890 ± 20°C. Below 1230°C, $Ca_3La(PO_4)_3$ decomposes to $LaPO_4$ and a solid solution of a rhombohedral β-$Ca_3(PO_4)_2$ structure. This limited solid solution with the formula $Ca_{3-x}La_{2x/3}(PO_4)_2$ ($0 \le x \le 3/7$) was found to exist between 20 to approximately 1450°C. The phosphates $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$ form an eutectic system [2–5]. A limited solid solution (10 wt % $Ca_2P_2O_7$ [5], 40 wt % $Ca_2P_2O_7$ [2]) occurs in this system. The system $LaPO_4 – Ca_2P_2O_7$ is a simple eutectic system. Parameters of the eutectic mixture are: 82 wt % $Ca_2P_2O_7$ and 18 wt % $LaPO_4$ at 1310°C [6].

EXPERIMENTAL

The following ready-made parent substances were used: 85% H_3PO_4, $CaCO_3$, $CaHPO_4 \cdot 2H_2O$ (all of analytical grade), La_2O_3 of 99.99% purity, and $La(NO_3)_3$ (Fluka). Additionally, $LaPO_4$ [7], $Ca_2P_2O_7$ [8], $Ca_3(PO_4)_2$ [8] and $Ca_3La(PO_4)_3$ [1] were synthesized in our laboratory. The double orthophosphate $Ca_3La(PO_4)_3$ was obtained by sintering a mixture of $Ca_2P_2O_7$ and La_2O_3 (molar ratio 1:3) at 1400°C for 2 hours and then quenching in ice. The phase equilibria in the system $LaPO_4 – Ca_3(PO_4)_2 – Ca_2P_2O_7$ were examined by DTA of cooling, powder X-ray diffraction and light microscopy. The DTA of heating could not be used, because of thermal instability of the double orthophosphate $Ca_3La(PO_4)_3$, which decomposes at 1230°C to $LaPO_4$ and the β solid solution. The DTA of cooling was carried out in a home-made resistance furnace with a PtRh30 winding. 3g-mass samples in platinum crucibles in air atmosphere were used. Temperature was measured by a Pt/PtRh10 thermocouple, calibrated against the melting points of NaCl (801°C), K_2SO_4 (1070°C) and $Ca_2P_2O_7$ (1353°C). Thermal examination above 1400°C was carried out in argon in a vertical resistance furnace with a molybdenum winding. 1–2 g tablet-shaped samples were fused in platinum boats. Temperature was read with an accuracy of ± 20°C by an optical pyrometer calibrated against the melting point of Na_3PO_4 (1583°C) and $Ca_3(PO_4)_2$ (1810°C). A quenching technique was also used for the phase determination: 1g-mass samples were sintered, followed by quenching in crushed ice. Phases were identified by X-ray analysis using an HZG-4 diffractometer (Guinier camera, CuKα radiation, Ni filter) and a Siemens D 5000 diffractometer (CuKα radiation, Ni filter, scintillation counter). The system was also examined microscopically. Microsections from molten samples were prepared and examined in reflected light.

RESULTS AND DISCUSSION

The system $LaPO_4$ – $Ca_3(PO_4)_2$ – $Ca_2P_2O_7$ was examined by the thermal and X-ray methods in the entire composition range. A previously unknown binary section $Ca_3La(PO_4)_3$ – $Ca_2P_2O_7$ was found to occur in the region under investigation. Fig. 1 shows the phase diagram of this system, constructed based on DTA of cooling and X-ray examinations. Because of decomposition of the double orthophosphate $Ca_3La(PO_4)_3$ at 1230°C, the samples for thermal analysis, consisting of the two initial phosphates, were placed in the furnace at 1450°C, and then analysed during cooling. The liquidus curve in the composition range 0–50 wt % $Ca_2P_2O_7$ was determined by

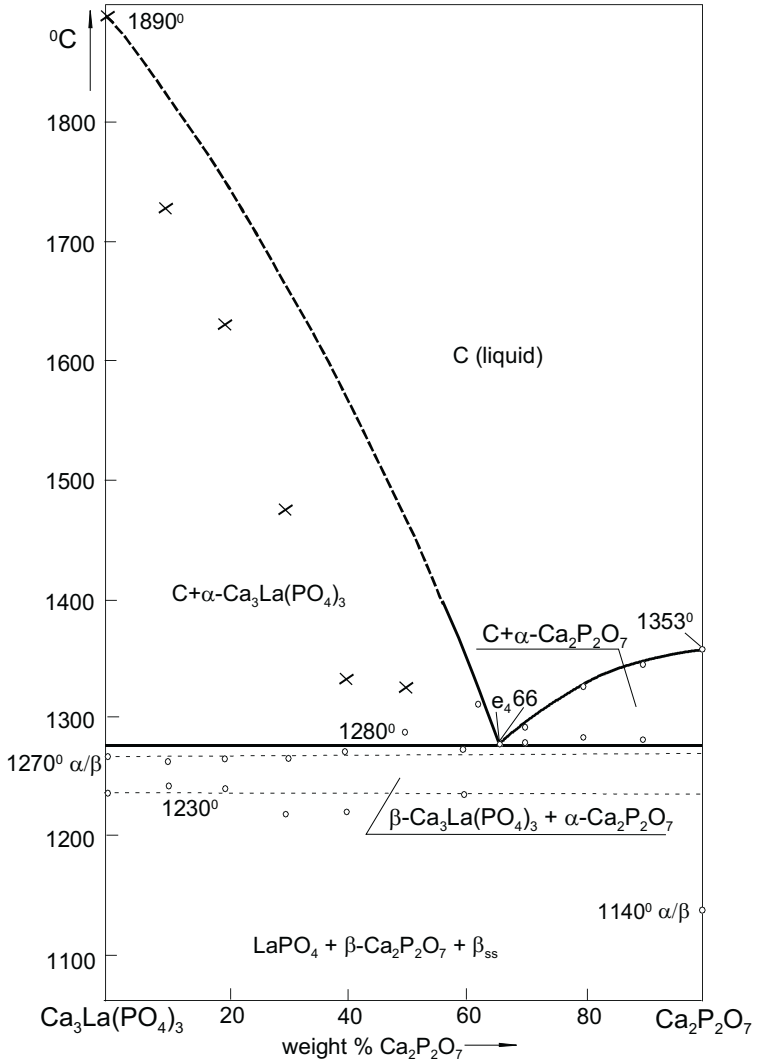

Figure 1. Phase diagram of the system $Ca_3La(PO_4)_3$ – $Ca_2P_2O_7$; x – thermal analysis of cooling, o – optical; $\beta_{ss} = \beta$ – solid solution.

observing the samples during their melting in a vertical furnace. Mixtures of appropriate amounts of $Ca_2P_2O_7$ and La_2O_3 were ground, pressed into pellets and placed in platinum boats in the furnace. These samples were heated at 1400°C for 2 hours (the suitable conditions for the synthesis of $Ca_3La(PO_4)_3$ to proceed), and then melted. The temperature was determined by the optical pyrometry method, hence the course of the liquidus curve in the diagram has been marked with the dashed line. It is seen from Fig. 1 that the system $Ca_3La(PO_4)_3 – Ca_2P_2O_7$ has a binary character only above 1230°C. The initial phosphates form an eutectic of the composition 66 wt % $Ca_2P_2O_7$ and 34 wt % $Ca_3La(PO_4)_3$ at 1280°C. Below 1230°C, as a result of $Ca_3La(PO_4)_3$ decomposition to $LaPO_4$ and a solid solution of the β-$Ca_3(PO_4)_2$ structure, the system is a ternary one.

DTA curves of the samples in the system $Ca_3La(PO_4)_3 – Ca_2P_2O_7$ did not exhibit any thermal effect connected with a polymorphic transition of $Ca_2P_2O_7$, i.e α/β at 1140°C and β/γ at 627°C. It is probable that the α/β $Ca_3La(PO_4)_3$ transformation effect and the eutectic effect merge and yield a joint thermal effect on the DTA curve, to which corresponds a temperature of about 1280°C.

The phase diagram of the ternary system $LaPO_4 – Ca_3(PO_4)_2 – Ca_2P_2O_7$, together with solidification isotherms, is presented in Fig. 2. Further ternary compounds have not been found in the composition range examined. Four primary crystallization

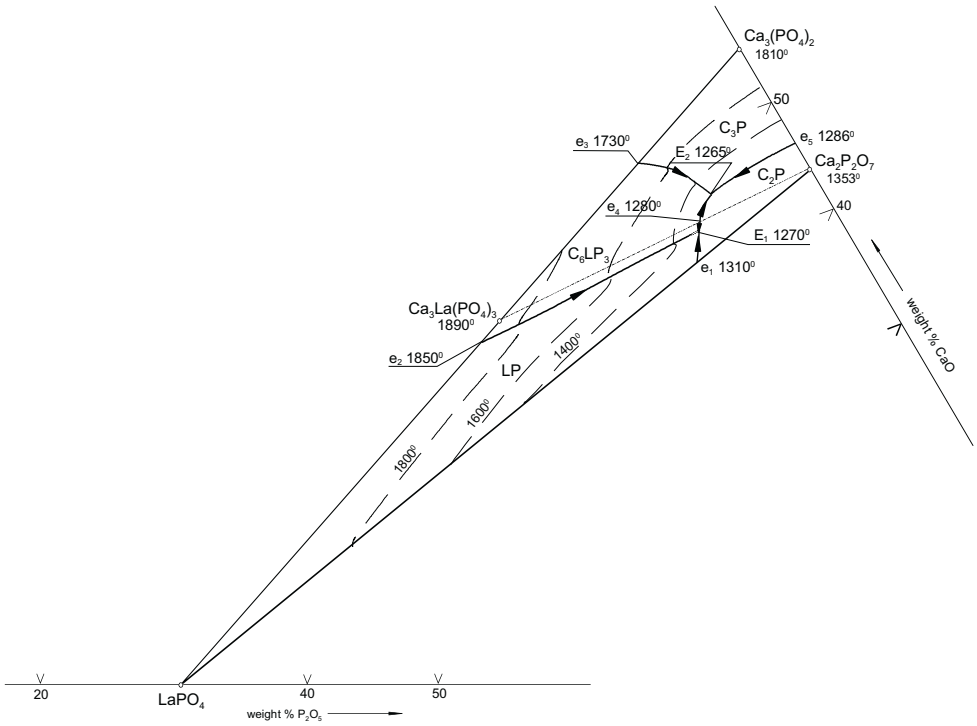

Figure 2. Phase diagram of the system $LaPO_4 – Ca_3(PO_4)_2 – Ca_2P_2O_7$; LP = $LaPO_4$, C_2P = $Ca_2P_2O_7$, C_3P = $Ca_3(PO_4)_2$, C_6LP_3 = $Ca_3La(PO_4)_3$.

fields of phosphates are separated by suitable eutectic curves. Phase equilibrium of Fig. 2 exists only above 1230°C. In this temperature range the system $LaPO_4$ – $Ca_3(PO_4)_2$ – $Ca_2P_2O_7$ is divided into two partial ternary eutectic systems: (i) $LaPO_4$ – $Ca_3La(PO_4)_3$ – $Ca_2P_2O_7$ and (ii) $Ca_3La(PO_4)_3$ – $Ca_3(PO_4)_2$ – $Ca_2P_2O_7$. The first of these contains a ternary eutectic, E_1, of the composition 50.2 wt % P_2O_5, 11.5 wt % La_2O_3, 38.3 wt% CaO and a temperature of 1270°C. In the second partial system, the ternary eutectic E_2 contains 49.1 wt % P_2O_5, 8.7 wt % La_2O_3, 42.2 wt % CaO at a temperature of 1265°C.

An isothermal section of the system $LaPO_4$ – $Ca_3(PO_4)_2$ – $Ca_2P_2O_7$ at room temperature is shown in Fig. 3. In the side systems: $LaPO_4$ – $Ca_3(PO_4)_2$ and $Ca_3(PO_4)_2$ – $Ca_2P_2O_7$, the limited solid solutions exist in the subsolidus regions. These solutions are stable down to room temperature; in the ternary system $LaPO_4$ – $Ca_3(PO_4)_2$ – $Ca_2P_2O_7$ they are reflected in the form of the limited solid solution β. Because of the thermal instability of the double orthophosphate $Ca_3La(PO_4)_3$, this compound does not exist under equilibrium conditions at room temperature.

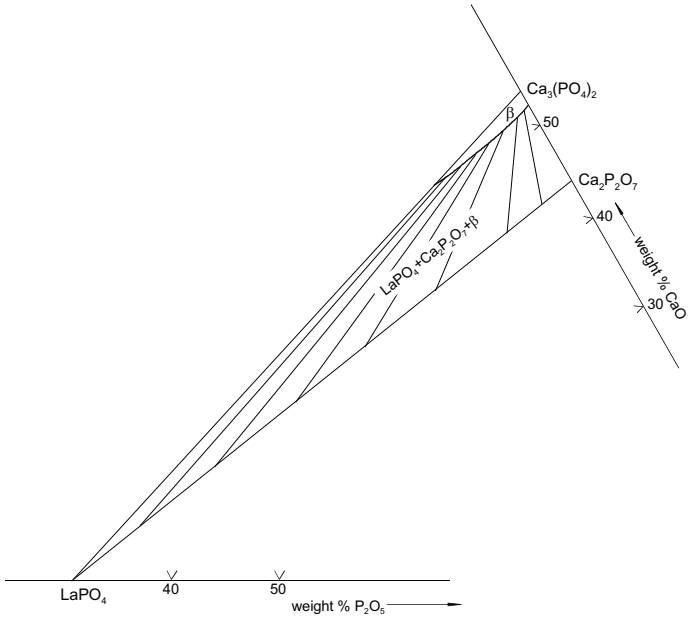

Figure 3. Isothermal section at room temperature; β = β – solid solution.

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