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A PARTIAL SYSTEM $LaPO_4$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$La(PO_3)_3$

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Abstract

The system $LaPO_4$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$La(PO_3)_3$ was investigated by means of thermal and X-ray analyses. Three binary systems were found to occur in this region: $LaPO_4$–$Ca(PO_3)_2$, $LaPO_4$–$Ca_4P_6O_{19}$ and $LaPO_4$–$CaLa(PO_3)_5$. Their phase diagrams, and also that for the system $LaPO_4$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$La(PO_3)_3$, were obtained.

Keywords: binary system, thermal analysis, phase equilibria

Introduction

This paper presents the results of an investigation of part of the ternary system La_2O_3–CaO–P_2O_5, inclusive of the range $LaPO_4$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$La(PO_3)_3$.

The partial system $LaPO_4$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$La(PO_3)_3$ was previously unknown. However, the phase diagrams of the side systems, i.e. $Ca_2P_2O_7$–$Ca(PO_3)_2$ [1–3], $La(PO_3)_3$–$Ca(PO_3)_2$ [4], $LaPO_4$–$La(PO_3)_3$ [5, 6] and $LaPO_4$–$Ca_2P_2O_7$ [7], have been reported. In the system $Ca_2P_2O_7$–$Ca(PO_3)_2$, a compound called tremelite occurs. In [1], the formula $7CaO\cdot 5P_2O_5$ was ascribed to tremelite. It was also reported that tremelite occurs within the temperature range 915–985°C and that it forms a solid solution with $Ca_2P_2O_7$ and $Ca(PO_3)_2$. In contrast, tremelite has also been reported to be calcium hexaphosphate with the formula $Ca_4P_6O_{19}$ [2]. This was confirmed in [3], where it was found that $Ca_4P_6O_{19}$ melts incongruently at 1000°C, is stable at room temperature and does not form a solid solution. In the system $La(PO_3)_3$–$Ca(PO_3)_2$, a binary metaphosphate with the formula $CaLa(PO_3)_5$ occurs. It melts incongruently at 900°C [4]. According to [5], an intermediate compound with formula $La_2P_4PO_{13}$ exists in the system $LaPO_4$–$La(PO_3)_3$. It is stable in the solid phase only up to 755°C. Our previous examinations did not confirm the presence of $La_2P_4O_{13}$ in this system [6]. The phosphates $LaPO_4$ and $Ca_2P_2O_7$ have been found to form a eutectic system [7]. The position of the eutectic point is 82 wt% $Ca_2P_2O_7$, 18 wt% $LaPO_4$, at 1310°C.

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Experimental

The following original substances were used: 99.99% La_2O_3, 85% H_3PO_4, $CaHPO_4$ p.a., $Ca(H_2PO_4)_2{\cdot}H_2O$ p.a., $CaCO_3$ p.a. and $NH_4H_2PO_4$ p.a. Additionally, $Ca_4P_6O_{19}$ [3], $LaPO_4$ [6], $La(PO_3)_3$ [8], $Ca(PO_3)_2$ [9] and $Ca_2P_2O_7$ [10] were synthesized in our laboratory. The investigations were carried out by using differential thermal analysis (DTA) on heating and X-ray diffraction. Test samples were presynthesized by reaction in the solid phase. The mixtures of initial substances were pressed into pellets and sintered at different temperatures, depending on the composition of the samples. DTA was performed with a 3427 derivatograph (MOM, Hungary) over the temperature range 20–1350°C. Samples of 250–450 mg were used in an air atmosphere, in platinum crucibles, with the standard substance Al_2O_3 p.a. Temperature was measured with a Pt/Pt Rh 10 thermocouple, which was standardized by using the melting points of NaCl (801°C), K_2SO_4 (1073°C) and $Ca_2P_2O_7$ (1353°C) and the polymorphic transition temperature of K_2SO_4 (583°C). A vertical resistance furnace with molybdenum winding on a corundum tube was used for high-temperature thermal studies above 1400°C. Temperatures were read by means of an optical pyrometer, which was calibrated against the melting points of $Ca_2P_2O_7$, Na_3PO_4 and $Ca_3(PO_4)_2$. A quenching technique was also used for the phase determination. Samples were quenched in air or ice. The phase purities of the reagents and the phase structures of the products were controlled by powder X-ray analysis with an HZG-4 diffractometer (Guinier camera, CuK_α radiation, Ni filter) and a Siemens D5000 diffractometer.

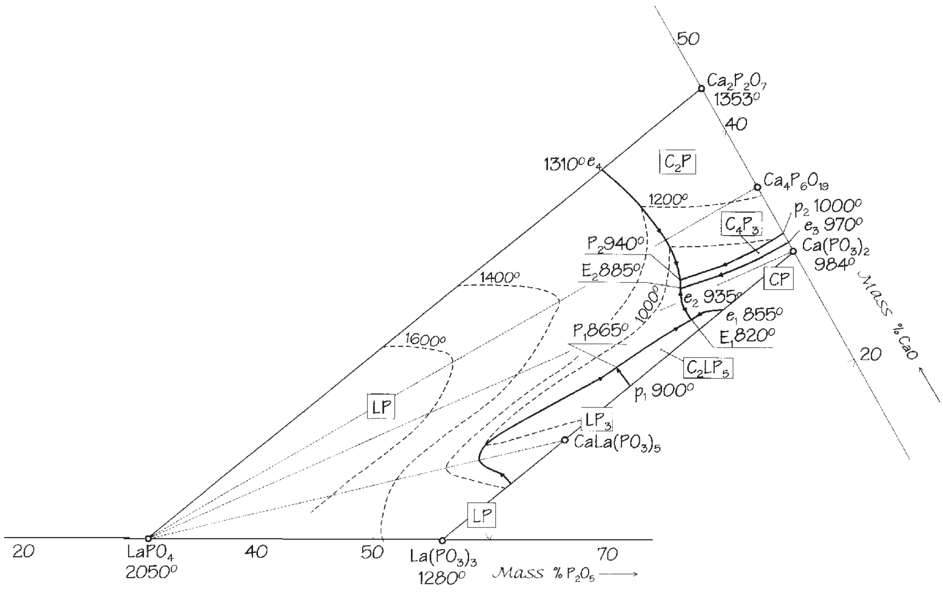

Fig. 1 Phase diagram of the system $LaPO_4$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$La(PO_3)_3$. $LaPO_4$=LP, $La(PO_3)_3$=LP_3, $Ca_2P_2O_7$=C_2P, $Ca_4P_6O_{19}$=C_4P_3; $Ca(PO_3)_2$=CP, $CaLa(PO_3)_5$=C_2LP_5

Results and discussion

The results of DTA on heating and X-ray analysis of the samples were used to construct the previously unknown phase diagram for the system $LaPO_4$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$La(PO_3)_3$. This is presented in Fig. 1. Samples for examination were presynthesized from the initial compounds by sintering within the temperature range 800–900°C for 20 h. Mainly DTA on heating was used during the investigations. The use of DTA on cooling was disadvantageous because of the probability of decomposition of the samples at higher temperature.

It has been found that three previously unknown binary systems occur in the field under investigation: $LaPO_4$–$Ca_4P_6O_{19}$, $LaPO_4$–$Ca(PO_3)_2$ and $LaPO_4$–$CaLa(PO_3)_5$.

Figure 2 presents the phase diagram of the system $LaPO_4$–$Ca_4P_6O_{19}$. The samples for examination were presynthesized from the initial phosphates by sintering at 850°C. Our results confirm that $Ca_4P_6O_{19}$ is formed peritectically, is stable up to room temperature and forms no solid solution. The majority of the samples in the system $LaPO_4$–$Ca_4P_6O_{19}$ melt at a temperature above 1300°C. Their melting points were determined by means of an optical pyrometer. This technique of measurement gives values of temperature that are too low. For this reason, the course of the liquidus curve is only proposed. The system $LaPO_4$–$Ca_4P_6O_{19}$ is ternary in its upper part. At high temperatures, above 940°C, four phases appear: liquid C and the phosphates $LaPO_4$, $Ca_4P_6O_{19}$ and $Ca_2P_2O_7$. As a result of the peritectic reaction, liquid C and the phosphate $Ca_2P_2O_7$ are used up to form tremelite. Hence, below 940°C this section has a binary nature and only two phases occur: $LaPO_4$ and $Ca_4P_6O_{19}$.

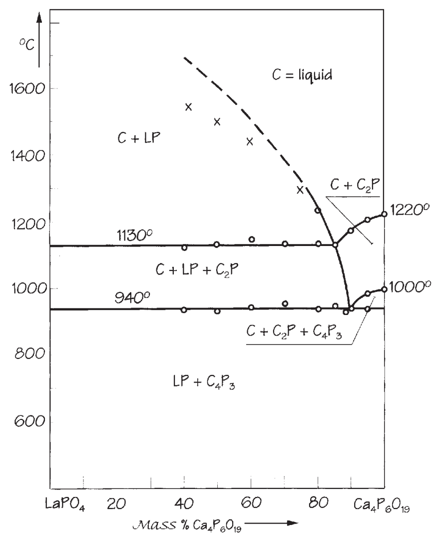

Fig. 2 Phase diagram of the system $LaPO_4$–$Ca_4P_6O_{19}$; o – thermal analysis; x – optical; $Ca_2P_2O_7$=C_2P, $Ca_4P_6O_{19}$=C_4P_3, $LaPO_4$=LP

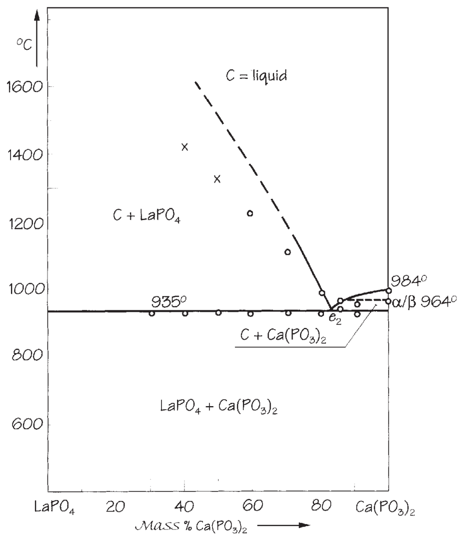

Fig. 3 Phase diagram of the system $LaPO_4$–$Ca(PO_3)_2$; o – thermal analysis; x – optical

Figure 3 presents the phase diagram of the system $LaPO_4$–$Ca(PO_3)_2$, determined on the basis of DTA on heating and X-ray diffraction. Samples for investigation were synthesized from the initial phosphates by sintering at 800°C. Additionally, some of the samples presynthesized from $La(PO_3)_3$ and $CaCO_3$ or $Ca_2P_2O_7$ were prepared for X-ray examination. X-ray phase analysis of the samples sintered at different temperatures or melted showed the presence only of $LaPO_4$ and $Ca(PO_3)_2$. We find that the section $LaPO_4$–$Ca(PO_3)_2$ is a simple eutectic system with the eutectic composition 83 wt% $Ca(PO_3)_2$, 17 wt% $LaPO_4$ at 935°C.

The phase diagram of the system $LaPO_4$–$CaLa(PO_3)_5$ is presented in Fig. 4. The binary metaphosphate $CaLa(PO_3)_5$ is formed peritectically according to the reaction: liquid C+$La(PO_3)_3$→$CaLa(PO_3)_5$. Because of difficulties in obtaining the phase-pure form of $CaLa(PO_3)_5$ [4], the samples for investigation were prepared from $LaPO_4$, $La(PO_3)_3$ and $Ca(PO_3)_2$. A few samples for X-ray analysis were prepared from $La(PO_3)_3$ and $CaCO_3$ or $Ca_2P_2O_7$ or $Ca_4P_6O_{19}$. The samples were sintered at several temperatures, up to 820°C. On the basis of DTA on heating, visual observation and X-ray diffraction, the phase diagram of the system $LaPO_4$–$CaLa(PO_3)_5$ was constructed (Fig. 4). The thermal effects that resulted from the melting of the samples were very weak, and almost unnoticeable, in the DTA heating curves. The temperatures of melting determined by means of the optical pyrometer (for the $LaPO_4$-rich samples) were too low. Therefore, only the direction of the run of the liquidus curve is determined in Fig. 4. The system $LaPO_4$–$CaLa(PO_3)_5$ is ternary in its upper, high-temperature part. Above 856°C, four phases occur: liquid C and $LaPO_4$, $La(PO_3)_3$ and $CaLa(PO_3)_5$. As a result of the peritectic reaction, liquid C and $La(PO_3)_3$ are used up to form $CaLa(PO_3)_5$. Under equilibrium conditions, below 856°C, only the phases $LaPO_4$ and $CaLa(PO_3)_5$ should occur. Under our experimental conditions, the samples

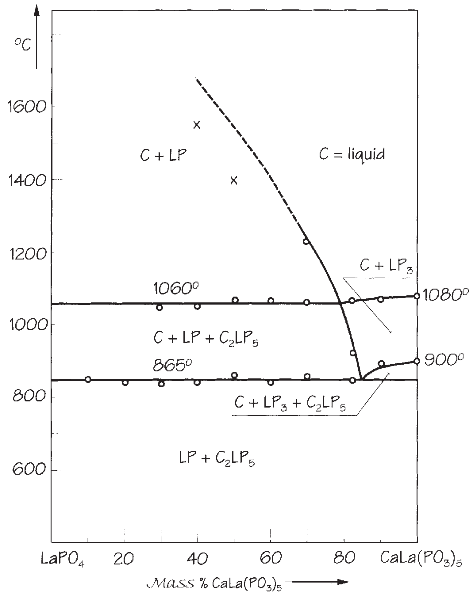

Fig. 4 Phase diagram of the system $LaPO_4$–$CaLa(PO_3)_5$; o – thermal analysis; x – optical; $La(PO_3)_3$=LP_3, $LaPO_4$=LP, $CaLa(PO_3)_5$=C_2LP_5

were mixtures of $LaPO_4$, $CaLa(PO_3)_5$ and a considerable amount of $La(PO_3)_3$. The presence of $La(PO_3)_3$ was caused by the difficulties mentioned above in obtaining phase-pure $CaLa(PO_3)_5$.

In the partial system $LaPO_4$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$La(PO_3)_3$, there are six primary crystallization fields of binary and ternary compounds (Fig. 1). They are separated by eutectic or peritectic curves. The curve p_1P_1 corresponds to a binary peritectic reaction according to the network $C(p_1P_1)+La(PO_3)_3 \rightarrow CaLa(PO_3)_5$ ($C(p_1P_1)$ denotes a liquid with the composition corresponding to the points in the line p_1P_1). During the solidification of alloys from the field $LaPO_4$–P_1–$CaLa(PO_3)_5$–$La(PO_3)_3$ (triple peritectic quadrangle), a ternary peritectic reaction proceeds: $C(P_1)+La(PO_3)_3 \rightarrow LaPO_4+CaLa(PO_3)_5$ ($C(P_1)$ denotes a liquid with the composition of point P_1). This reaction proceeds at a constant temperature of 865°C. Along the p_2P_2 curve a binary peritectic reaction proceeds: $C(p_2P_2)+Ca_2P_2O_7 \rightarrow Ca_4P_6O_{19}$ ($C(p_2P_2)$ denotes a liquid with the composition corresponding to the points in the line p_2P_2). During the solidification of alloys from the field $LaPO_4$–$Ca_2P_2O_7$–$Ca_4P_6O_{19}$–P_2, the ternary peritectic reaction takes place: $C(P_2)+Ca_2P_2O_7 \rightarrow LaPO_4+Ca_4P_6O_{19}$ ($C(P_2)$ denotes a liquid with the composition of point P_2). The reaction proceeds at a constant temperature of 940°C. In the field $LaPO_4$–$Ca_2P_2O_7$–$Ca(PO_3)_2$–$La(PO_3)_3$, two ternary eutectics occur: E_1 at 820°C and E_2 at 885°C.

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