

Reinvestigation of the Phase Equilibria in the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ System

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The phase equilibria between the solid phases in the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ system were reinvestigated with solid state reaction method. The existence of La_3PO_7 , $\text{La}_7\text{P}_3\text{O}_{18}$, LaPO_4 , and LaP_3O_9 was confirmed. $\text{La}_7\text{P}_3\text{O}_{18}$ can form only at $\sim 1200^\circ\text{C}$ or higher possibly due to kinetic reasons, but it is stable at lower temperatures. On the other hand, three intermediate compounds proposed to exist, $\text{La}_5\text{PO}_{10}$, $\text{La}_4(\text{P}_2\text{O}_7)_3$, and $\text{La}_2\text{P}_4\text{O}_{13}$ were not obtained in this study. Based on the literature, $\text{La}_4(\text{P}_2\text{O}_7)_3$ and $\text{La}_2\text{P}_4\text{O}_{13}$ are considered to be metastable phases, although thermodynamic evidence is still required.

Keywords lanthanum phosphate, phase diagram, solid state reaction

1. Introduction

Various phosphates in the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ system have been studied as proton conductors,^[1-4] laser and luminescent materials,^[5-8] phosphorus diffusion sources for semiconductors,^[9-11] debond materials in oxide composites,^[12] coating materials,^[13] and radioactive waste forms.^[14-16] Two temperature-composition phase diagrams have been reported for the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ system in the literature.^[17,18] In addition, the phase equilibria in the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ system have been studied as a part of ternary systems.^[19-22] However, there are several inconsistencies among these phase diagrams. Table 1 summarizes the intermediate compounds reported to exist in each phase diagram. As indicated in the table, the existences of La_3PO_7 , LaPO_4 , LaP_3O_9 , and $\text{LaP}_5\text{O}_{14}$ have been well established. These compounds were also confirmed to be thermodynamically stable compounds in the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ system by first-principles calculations.^[23] In contrast, the existence of $\text{La}_5\text{PO}_{10}$, $\text{La}_7\text{P}_3\text{O}_{18}$, $\text{La}_4(\text{P}_2\text{O}_7)_3$, and $\text{La}_2\text{P}_4\text{O}_{13}$ has been controversial, and their crystal structures and thermodynamic properties are still unknown. To construct the reliable

phase diagram for the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ system, the existence and stability of these compounds must be verified. In this work, the phase equilibria between the solid phases in the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ system have been reinvestigated with solid state reaction method.

Here, a brief description is given on the compounds whose existence should be confirmed, $\text{La}_5\text{PO}_{10}$, $\text{La}_7\text{P}_3\text{O}_{18}$, $\text{La}_4(\text{P}_2\text{O}_7)_3$, and $\text{La}_2\text{P}_4\text{O}_{13}$. Since the $\text{Nd}_2\text{O}_3\text{-P}_2\text{O}_5$ system has considerable similarity with the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ system in phase equilibrium behaviors,^[20,24-27] the information on analogous compounds in the $\text{Nd}_2\text{O}_3\text{-P}_2\text{O}_5$ system is also presented below.

1.1 $\text{La}_5\text{PO}_{10}$

Kropiwnicka and Znamierowska^[18,28] obtained $\text{La}_5\text{PO}_{10}$ via solid state reaction between La_2O_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ at temperatures above 540°C . By differential thermal analysis, they observed four endothermic effects at 80 , 700 , 860 , and 1180°C and they assigned these effects to four polymorphic transitions. They also determined the congruent melting temperature of $\text{La}_5\text{PO}_{10}$ to be $1870 \pm 10^\circ\text{C}$. However, the formation of $\text{La}_5\text{PO}_{10}$ has not been reported by any other group.

1.2 $\text{La}_7\text{P}_3\text{O}_{18}$

$\text{La}_7\text{P}_3\text{O}_{18}$ has been synthesized by several researchers via solid state reactions, solidification of melts, etc.^[2,16,17,27,29-31] Serra et al.^[30] found that there are low- and high-temperature forms, transforming reversibly at 1650°C , by high-temperature x-ray diffraction analysis. According to Park and Kreidler,^[17] $\text{La}_7\text{P}_3\text{O}_{18}$ does not have a lower temperature limit of stability. However, $\text{La}_7\text{P}_3\text{O}_{18}$ is obtainable only at temperatures above 1300°C and it has not been synthesized at temperatures below 1200°C .^[2,20,27,29,31] The coexistence of La_3PO_7 and LaPO_4 at $1100\text{--}1200^\circ\text{C}$, instead of forming $\text{La}_7\text{P}_3\text{O}_{18}$, was also observed by other authors.^[32,33] Similarly, it was reported that the neodymium analogue, $\text{Nd}_7\text{P}_3\text{O}_{18}$, can be formed at above $\sim 1125^\circ\text{C}$ by Wong and Kreidler^[34] and Tselebrovskaya et al.^[20,27] They attributed this to kinetic reasons.

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Table 1 Compounds in the $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ phase diagrams reported in the literature

Compound	Molar ratio, P/(La + P)	Existence in reported phase diagrams					
		Ref 17 (700-1500 °C)	Ref 18 (R.T.-2000 °C)	Ref 19 (100-500 °C)	Ref 20 (1300 °C)	Ref 21 (650-1300 °C)	Ref 22 (1200-1400 °C)
$\text{La}_5\text{PO}_{10}$	0.167	No	Yes	...	No	No	No
La_3PO_7	0.25	Yes	Yes	...	Yes	Yes	Yes
$\text{La}_7\text{P}_3\text{O}_{18}$	0.3	Yes	No	...	Yes	No	No
LaPO_4	0.5	Yes	Yes	Yes	Yes	Yes	Yes
$\text{La}_4(\text{P}_2\text{O}_7)_3$	0.6	No	No	No	...	Yes	...
$\text{La}_2\text{P}_4\text{O}_{13}$	0.667	Yes	No	No	...	No	...
LaP_3O_9	0.75	Yes	Yes	Yes	...	Yes	...
$\text{LaP}_5\text{O}_{14}$	0.833	Yes	Yes	Yes	...	Yes	...

Ellipses (...) represent “not investigated”

1.3 $\text{La}_4(\text{P}_2\text{O}_7)_3$

Kuznetsov and Vasil'eva^[35] obtained $\text{La}_4(\text{P}_2\text{O}_7)_3$ by heating amorphous $\text{La}_4(\text{P}_2\text{O}_7)_2 \cdot 12\text{H}_2\text{O}$ which was precipitated in aqueous solutions of $\text{La}(\text{NO}_3)_3$ and $\text{M}_4\text{P}_2\text{O}_7$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$).^[36] On heating, an endothermic effect was observed at 80-180 °C corresponding to evaporation of the hydration water. Two exothermic effects were observed at 214-262 and 684-700 °C. They assumed that the amorphous phase starts to crystallize at 260 °C to form $\alpha\text{-La}_4(\text{P}_2\text{O}_7)_3$ and it changes irreversibly into the high-temperature form, $\beta\text{-La}_4(\text{P}_2\text{O}_7)_3$, at 684 °C. Gao et al.^[37] and Zhang et al.^[38] also reported that they obtained $\text{La}_4(\text{P}_2\text{O}_7)_3$ by similar methods. Kropiwnicka^[39] synthesized $\text{La}_4(\text{P}_2\text{O}_7)_3$ by heating $\text{NH}_4\text{LaP}_4\text{O}_{12}$ in a closed system to 280 °C for 5 h, while heating $\text{NH}_4\text{LaP}_4\text{O}_{12}$ in an open system to 700 °C led to the formation of LaP_3O_9 . Shi et al.^[21] obtained $\text{La}_4(\text{P}_2\text{O}_7)_3$ by solid state reaction between $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$.

1.4 $\text{La}_2\text{P}_4\text{O}_{13}$

Park and Kreidler^[17] obtained $\text{La}_2\text{P}_4\text{O}_{13}$ by crystallization from glass. They found that it is stable at temperatures up to 755 °C. However, $\text{La}_2\text{P}_4\text{O}_{13}$ has not been obtained by other methods even at those temperatures.^[19,24,34] The same phenomenon was found for the neodymium analogue, $\text{Nd}_2\text{P}_4\text{O}_{13}$, by Wong and Kreidler.^[34] It was formed by crystallization of a glass, but not formed by direct solid-state reaction. They speculated that $\text{Nd}_2\text{P}_4\text{O}_{13}$ exists in a metastable state.

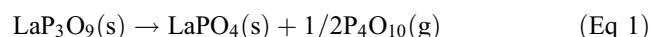
2. Experimental

2.1 Sample Preparation

La_2O_3 (Nacalai Tesque, mass fraction purity 0.9999) and H_3PO_4 (Nacalai Tesque, mass fraction purity 0.85) were used to prepare samples. La_2O_3 was heated overnight at 800 °C prior to use to remove absorbed H_2O and CO_2 .^[40] LaPO_4 and LaP_3O_9 were synthesized by precipitation in

phosphoric acid solutions.^[41] La_2O_3 and H_3PO_4 were mixed at a P/La molar ratio of 15 in a glassy carbon crucible or PFA beaker. The mixture was heated at 190 °C in the air for several days until complete dissolution took place. Then the solution was kept at 120 °C in water vapor (1 atm) for 4 days to precipitate LaPO_4 , or at 230 °C in the air for 2 days to precipitate LaP_3O_9 . The precipitates were separated from the solution, washed well with hot water and dried at ~90 °C. The LaPO_4 precipitates were additionally heated at 800 °C in the air for 100 h to eliminate residual water and phosphoric acid.

For preparing samples with compositions between La_2O_3 and LaPO_4 (“L9P1”, “L8P2”, “L725P275”, “L7P3”, and “L6P4”), La_2O_3 and LaPO_4 powders were mixed in the molar ratios listed in Table 2. The mixtures were then ball-milled for 70-100 h in isopropyl alcohol, dried, and pressed into pellets at ~150 MPa. The sample with a composition slightly poorer in P_2O_5 than LaP_3O_9 , “L25P75- δ ”, was prepared from LaP_3O_9 . The LaP_3O_9 precipitate was ground and pressed into a pellet at ~400 MPa. The pellet was heated at 1050 °C for 3 h, to be partially decomposed according to the following reaction:^[17,42]



The weight loss due to partial decomposition was 1.4 wt.%, while that of 37.8 wt.% was expected if complete decomposition took place.

2.2 Phase Equilibrium Experiments and Sample Characterization

Phase equilibrium experiments were carried out by high-temperature heat treatments and subsequent phase identification. The sample pellets were placed in alumina crucibles, and heated at a predetermined temperature for typically 100 h in the air. Then the samples were cooled down in the furnace. The conditions for each heat treatment, e.g., temperature and duration, are provided in the following section. Phase identification was carried out via x-ray powder diffraction (XRD) analysis on PANalytical X'Pert-Pro MPD using $\text{Cu K}\alpha$ radiation at room temperature.

Table 2 Compositions of samples

Sample	Starting materials	Molar ratio, P/(La + P)	Remarks
L9P1	La ₂ O ₃ and LaPO ₄	0.1	Between La ₂ O ₃ and “La ₅ PO ₁₀ ”
L8P2	La ₂ O ₃ and LaPO ₄	0.2	Between “La ₅ PO ₁₀ ” and La ₃ PO ₇
L725P275	La ₂ O ₃ and LaPO ₄	0.275	Between La ₃ PO ₇ and “La ₇ P ₃ O ₁₈ ”
L7P3	La ₂ O ₃ and LaPO ₄	0.3	Composition of “La ₇ P ₃ O ₁₈ ”
L6P4	La ₂ O ₃ and LaPO ₄	0.4	Between “La ₇ P ₃ O ₁₈ ” and LaPO ₄
L25P75-δ	LaP ₃ O ₉	0.75-δ	Slightly poorer in P ₂ O ₅ than LaP ₃ O ₉

Table 3 Phases detected by x-ray diffraction analysis: after single heat treatments of L9P1, L8P2, L725P275, L6P4, and L25P75-δ samples

Sample	Heat treatment		Phases present after heat treatments
	Temperature, °C	Time, h	
L9P1	1300	100	La ₂ O ₃ + β-La ₃ PO ₇
L8P2	1300	100	La ₂ O ₃ + β-La ₃ PO ₇
L8P2	1000	100	La ₂ O ₃ + β-La ₃ PO ₇
L725P275	1300	100	β-La ₃ PO ₇ + La ₇ P ₃ O ₁₈
L725P275	1000	100	β-La ₃ PO ₇ + LaPO ₄
L6P4	1300	100	La ₇ P ₃ O ₁₈ + LaPO ₄
L6P4	1000	100	β-La ₃ PO ₇ + LaPO ₄
L25P75-δ	1050	3	LaPO ₄ + LaP ₃ O ₉
L25P75-δ	700	100	LaPO ₄ + LaP ₃ O ₉

3. Results and Discussion

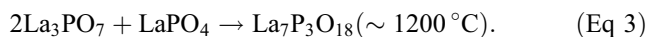
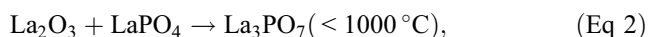
3.1 La₂O₃-LaPO₄ Subsystem

3.1.1 Phase Relationships at 1000 and 1300 °C. The La₂O₃-LaPO₄ subsystem may contain three intermediate compounds, La₅PO₁₀, La₃PO₇, and La₇P₃O₁₈. The phase relationships in this subsystem were investigated at 1000 and 1300 °C using samples L9P1, L8P2, L725P275, and L6P4. The samples were heated at each temperature for 100 h. The samples did not show any sign of melting. The detected phases in each sample after each heat treatment are summarized in Table 3. At both temperatures, intermediate phases were formed by reaction between LaPO₄ and La₂O₃. The coexistence of the initial phases, La₂O₃ and LaPO₄, was not observed after the heat treatments. At 1000 °C, La₃PO₇ was the only intermediate compound formed in the La₂O₃-LaPO₄ subsystem. In contrast, at 1300 °C, La₃PO₇ and La₇P₃O₁₈ were formed. La₅PO₁₀ was not detected at either temperature. It should be noted that although La(OH)₃ was detected in some samples by XRD, it is treated as La₂O₃ in this paper because it should have formed by hydration of La₂O₃ during handling at room temperature. As for La₃PO₇, Park and Kreidler^[17] observed an α-β phase transition at 935 ± 5 °C. The present x-ray diffraction results coincide with the β-phase pattern given by Park and Kreidler.

3.1.2 Formation and Stability of La₇P₃O₁₈. Since La₇P₃O₁₈ was formed at 1300 °C while it was not formed at 1000 °C as described above, the phase evolution behavior at the composition La:P = 7:3 was investigated in the temperature range 1000-1300 °C with long-term heat treatments. The L7P3 samples were subjected to two

temperature programs consisting of successive heat treatments applied in ascending or descending temperature orders, *i.e.* heating and cooling processes. X-ray diffraction analysis was carried out at room temperature between each heat treatment.

Table 4 shows the phases detected by x-ray diffraction during the heating and cooling processes. During the heating process, only La₃PO₇ and LaPO₄ were present both after the heat treatment at 1000 °C for 1000 h and after that at 1100 °C for 200 h. La₇P₃O₁₈ was detected only after the heat treatment at 1200 °C for 100 h. The sequence of reactions occurred during the heating process is expressed as follows:



This indicates that La₇P₃O₁₈ is thermodynamically stable at ~1200 °C or higher. In the cooling process, La₇P₃O₁₈ was formed by the initial heat treatment at 1300 °C for 100 h and it remained unchanged after the heat treatment at 1000 °C for 900 h. Any sign of decomposition, *i.e.* the reverse reaction of Eq 3, was not observed. Based on these results, both single phase La₇P₃O₁₈ and the mixture of La₃PO₇/LaPO₄ are apparently stable at 1000 °C for at least ~1000 h. It indicates that the equilibrium state is difficult to attain at 1000 °C due to kinetic reasons. The similar effect was also observed for the neodymium analogue, Nd₇P₃O₁₈.^[20,34] While the formation of La₇P₃O₁₈ and Nd₇P₃O₁₈ by Eq 3 has been observed by several groups,^[27,29,31,34] the reverse reaction has never been

Table 4 Phases detected by x-ray diffraction analysis: after successive heat treatments of L7P3 samples

Sample	Process	Heat treatment		Phases present after heat treatments
		Temp, °C	Time, h	
L7P3	Heating	1000	1000	β - La_3PO_7 + LaPO_4
		1100	200	β - La_3PO_7 + LaPO_4
		1200	100	$\text{La}_7\text{P}_3\text{O}_{18}$
L7P3	Cooling	1300	100	$\text{La}_7\text{P}_3\text{O}_{18}$
		1000	900	$\text{La}_7\text{P}_3\text{O}_{18}$

reported to occur. Therefore, it is reasonable to assume that $\text{La}_7\text{P}_3\text{O}_{18}$ and $\text{Nd}_7\text{P}_3\text{O}_{18}$ are thermodynamically stable, but the formation of these compounds from solid phases seems to be kinetically inhibited at low temperatures.

With regard to the La_2O_3 - LaPO_4 subsystem, it can be concluded that the present results are completely consistent with the phase diagram given by Park and Kreidler.^[17] $\text{La}_5\text{PO}_{10}$, which appears only in the phase diagrams by Kropiwnicka and Znamierowska,^[18,28] was not obtained in this study. As there is little information available on $\text{La}_5\text{PO}_{10}$, the reason why it did not form is not clear.

3.2 LaPO_4 - LaP_3O_9 Subsystem

The LaPO_4 - LaP_3O_9 subsystem may contain two intermediate compounds, $\text{La}_4(\text{P}_2\text{O}_7)_3$ and $\text{La}_2\text{P}_4\text{O}_{13}$ (decomposes at above 755 °C^[17]). The phase relationships in this subsystem were examined using the sample L25P75- δ . L25P75- δ was synthesized at 1050 °C and then heat-treated at 700 °C for 100 h. The weight loss at 700 °C was negligible (less than 1%). The last two rows of Table 3 give the phases present before and after the heat treatment of L25P75- δ at 700 °C. At both stages, the sample consisted only of LaPO_4 and LaP_3O_9 , and no other phases such as $\text{La}_4(\text{P}_2\text{O}_7)_3$ and $\text{La}_2\text{P}_4\text{O}_{13}$ were detected. Therefore, LaPO_4 and LaP_3O_9 are considered in equilibrium at both 1050 °C (sample preparation temperature) and 700 °C.

A literature survey leads to an idea that $\text{La}_4(\text{P}_2\text{O}_7)_3$ and $\text{La}_2\text{P}_4\text{O}_{13}$ are metastable phases. As described in the Introduction, Kuznetsov and Vasil'eva^[35] proposed an α - β phase transition at 684 °C for $\text{La}_4(\text{P}_2\text{O}_7)_3$. However, the x-ray diffraction pattern for the high-temperature phase (β -phase) given by them indicates that it consists mainly of LaPO_4 . Therefore, it is likely that $\text{La}_4(\text{P}_2\text{O}_7)_3$ decomposes to LaPO_4 and probably LaP_3O_9 at above 684 °C, instead of undergoing a structural phase transition. In addition, since the thermal effect at 684 °C on heating is exothermic and irreversible,^[35] the low-temperature form of $\text{La}_4(\text{P}_2\text{O}_7)_3$ is considered to be in a non-equilibrium (probably metastable) state. According to several reports,^[21,35,38,39] it is supposed that $\text{La}_4(\text{P}_2\text{O}_7)_3$ can form through the dehydration of precursors on heating.

As for $\text{La}_2\text{P}_4\text{O}_{13}$, it has been obtained only by crystallization from glass, and it was reported to decompose into LaPO_4 and LaP_3O_9 at above 755 °C.^[17] Wong and Kreidler remarked that $\text{La}_2\text{P}_4\text{O}_{13}$ and $\text{Nd}_2\text{P}_4\text{O}_{13}$ could not be formed by solid state reaction, and they speculated that $\text{Nd}_2\text{P}_4\text{O}_{13}$

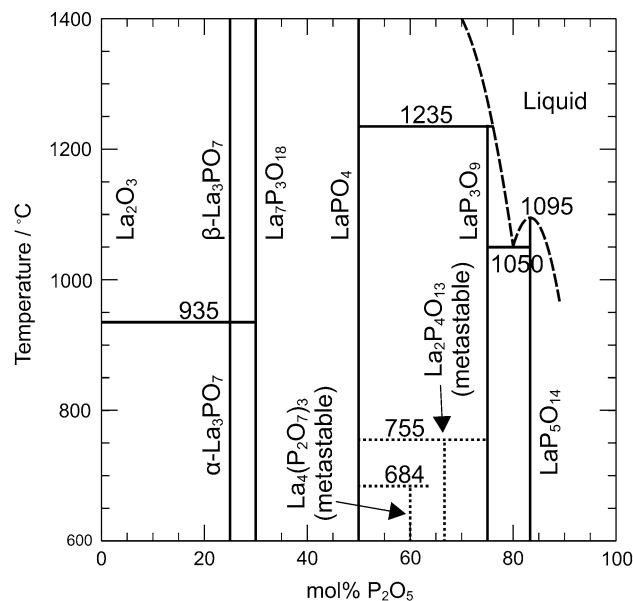


Fig. 1 Phase diagram of the La_2O_3 - P_2O_5 system adapted from Park and Kreidler.^[17] Slight modifications were made to the original diagram so that $\text{La}_2\text{P}_4\text{O}_{13}$ is now shown as a metastable phase and $\text{La}_4(\text{P}_2\text{O}_7)_3$ which was not included in the original diagram is now included as a metastable phase

exists in a metastable state.^[34] In general, it has been shown that intermediate metastable phases tend to form during the crystallization of largely undercooled amorphous phases.^[43,44]

Finally, the above idea is also consistent with the results of solution growth of lanthanum phosphates in phosphoric acid solutions.^[19,41] It has been shown that anhydrous LaPO_4 and LaP_3O_9 can directly be precipitated in homogeneous phosphoric acid solutions at 100-400 °C. If $\text{La}_2\text{P}_4\text{O}_{13}$ and $\text{La}_4(\text{P}_2\text{O}_7)_3$ are also thermodynamically stable phases, equilibria between each phosphate and phosphoric acid solution are expected to exist in this temperature range, based on previously reported phase relations in the La_2O_3 - P_2O_5 - H_2O system.^[19,41] However, the precipitation of $\text{La}_4(\text{P}_2\text{O}_7)_3$ and $\text{La}_2\text{P}_4\text{O}_{13}$ has never been observed at any temperature between 100 and 400 °C, in spite that these experiments were carried out over relatively long periods of time (several days) to allow the equilibrium states to be reached. Thus we currently speculate that $\text{La}_4(\text{P}_2\text{O}_7)_3$ and $\text{La}_2\text{P}_4\text{O}_{13}$ are metastable phases, although thermodynamic evidence is still required.

3.3 Phase Diagram of the La_2O_3 - P_2O_5 System

Figure 1 presents the verified phase diagram of the La_2O_3 - P_2O_5 system which is mainly adopted from Ref 17 and slightly modified to reflect the discussion above. The present results confirm the existence of La_3PO_7 , $\text{La}_7\text{P}_3\text{O}_{18}$, LaPO_4 , and LaP_3O_9 as thermodynamically stable phases in the La_2O_3 - P_2O_5 system. The existence of $\text{LaP}_5\text{O}_{14}$ has also been well established in previous studies. Although $\text{La}_4(\text{P}_2\text{O}_7)_3$ and $\text{La}_2\text{P}_4\text{O}_{13}$ can also form in this system under certain conditions, it is likely that these compounds are metastable. Phase transformation and melting temperatures

of La_3PO_7 , LaP_3O_9 , and $\text{LaP}_5\text{O}_{14}$ shown in Fig. 1 are taken from Ref 17, as they were not investigated in this study. It should be noted that LaP_3O_9 and $\text{LaP}_5\text{O}_{14}$ gradually decompose under atmospheric conditions with the loss of P_4O_{10} even below their melting temperatures as reported in Ref 17, 42.

4. Conclusions

The phase equilibria between the solid phases in the La_2O_3 - P_2O_5 system were reinvestigated with solid state reaction method. The existence of La_3PO_7 , $\text{La}_7\text{P}_3\text{O}_{18}$, LaPO_4 , and LaP_3O_9 was confirmed. $\text{La}_7\text{P}_3\text{O}_{18}$ can form only at $\sim 1200^\circ\text{C}$ or higher possibly due to kinetic reasons, but it is stable at lower temperatures. On the other hand, three intermediate compounds proposed to exist, $\text{La}_5\text{PO}_{10}$, $\text{La}_4(\text{P}_2\text{O}_7)_3$, and $\text{La}_2\text{P}_4\text{O}_{13}$ were not obtained in this study. Based on the literature, $\text{La}_4(\text{P}_2\text{O}_7)_3$ and $\text{La}_2\text{P}_4\text{O}_{13}$ are considered to be metastable phases, although thermodynamic evidence is still required.

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References

1. T. Norby and N. Christiansen, Proton Conduction in Ca- and Sr-Substituted LaPO_4 , *Solid State Ion.*, 1995, **77**, p 240-243
2. K. Amezawa, Y. Tomii, and N. Yamamoto, High-Temperature Protonic Conduction in $\text{La}_7\text{P}_3\text{O}_{18}$, *Solid State Ion.*, 2004, **175**, p 569-573
3. K. Amezawa, Y. Kitajima, Y. Tomii, and N. Yamamoto, High-Temperature Protonic Conduction in LaP_3O_9 , *Electrochem. Solid-State Lett.*, 2004, **7**(12), p A511-A514
4. I. Hammam, K. Horchani-Naifer, and M. Férid, Conduction Properties of Condensed Lanthanum Phosphates: $\text{La}(\text{PO}_3)_3$ and $\text{LaP}_5\text{O}_{14}$, *J. Rare Earths*, 2010, **28**(3), p 321-328
5. R.C. Ropp, Phosphors Based on Rare Earth Phosphates, *J. Electrochem. Soc.*, 1968, **115**(8), p 841-845
6. T.C. Damen, H.P. Weber, and B.C. Tofield, NdLa Pentaphosphate Laser Performance, *Appl. Phys. Lett.*, 1973, **23**(9), p 519-520
7. E.B. Stucchi, A.M. de Castro, M.A. Couto Dos Santos, and P. Melnikov, Synthesis, Characterization and Spectroscopy of the Europium Doped Lanthanum Trimetaphosphate, *J. Alloys Compd.*, 1988, **275-277**, p 86-88
8. S. Lu and J. Zhang, Study on UV Excitation Properties of Eu^{3+} -Doped Rare-Earth Phosphates, *J. Lumin.*, 2007, **122-123**, p 500-502
9. K. Gunjigake, M. Hasegawa, H. Oizumi, and Y. Ogata, United States Patent 4,033,790, 5 July 1977
10. G.R. Pickrell and J.E. Rapp, United States Patent 5,350,460, 27 Sep 1994
11. M. Tao, H. Xiao, T. Sun, and W. Guo, Preparation of $\text{LaP}_5\text{O}_{14}$ Powder by Sol-Gel Method, *J. Chin. Ceram. Soc.*, 2010, **38**(8), p 1553-1557
12. P.E.D. Morgan and D.B. Marshall, Functional Interfaces for Oxide/Oxide Composites, *Mater. Sci. Eng.*, 1993, **A162**, p 15-25
13. S.V. Komarov, S.E. Romankov, S.H. Son, N. Hayashi, S.D. Kaloshkin, S. Ueno, and E. Kasai, Production of LaPO_4 Coatings Using a Novel Ultrasonically-Assisted Plating Technique, *Surf. Coat. Technol.*, 2008, **202**, p 5180-5184
14. G.J. McCarthy, W.B. White, and D.E. Pfoertsch, Synthesis of Nuclear Waste Monazites, Ideal Actinide Hosts for Geologic Disposal, *Mater. Res. Bull.*, 1978, **13**, p 1239-1245
15. A. Meldrum, L.A. Boatner, and R.C. Ewing, Displacive Radiation Effects in the Monazite- and Zircon-Structure Orthophosphates, *Phys. Rev. B*, 1997, **56**(21), p 13805-13814
16. B. Glorieux, M. Matecki, F. Fayon, J.P. Coutures, S. Palau, A. Douy, and G. Peraudeau, Study of Lanthanum Orthophosphates Polymorphism, in View of Actinide Conditioning, *J. Nucl. Mater.*, 2004, **326**, p 156-162
17. H.D. Park and E.R. Kreidler, Phase Equilibria in the System La_2O_3 - P_2O_5 , *J. Am. Ceram. Soc.*, 1984, **67**(1), p 23-26
18. J. Kropiwnicka and T. Znamierowska, Phase Equilibria in the System La_2O_3 - Na_2O - P_2O_5 . Part I. Side System La_2O_3 - P_2O_5 , *Pol. J. Chem.*, 1988, **62**, p 587-594
19. N.N. Chudinova, L.P. Shklover, and G.M. Balagina, Reactions of Lanthanum Oxide with Phosphoric Acids at 100-500 $^\circ\text{C}$, *Inorg. Mater.*, 1975, **11**, p 590-593
20. E.G. Tselebrovskaya, B.F. Dzhurinskii, A.V. Lavrov, and A. Durif, Interaction in the Systems Ln_2O_3 - GeO_2 - P_2O_5 , *Russ. J. Inorg. Chem.*, 1994, **39**(3), p 473-474
21. Y. Shi, J. Liang, Y. Guo, J. Yang, W. Zhuang, and R. Guanghui, Phase Relations in the System La_2O_3 - B_2O_3 - P_2O_5 , *J. Alloys Compd.*, 1996, **242**, p 118-121
22. R. El Ouenzerfi, C. Goutaudier, G. Panczer, B. Moine, M.T. Cohen-Adad, M. Trabelsi-Ayedi, and N. Kbir-Arighuib, Investigation of the CaO - La_2O_3 - SiO_2 - P_2O_5 Quaternary Diagram. Synthesis, Existence Domain, and Characterization of Apatitic Phosphosilicates, *Solid State Ion.*, 2003, **156**, p 209-222
23. K. Toyoura, N. Hatada, Y. Nose, T. Uda, and I. Tanaka, First-Principles Thermodynamics of La_2O_3 - P_2O_5 Pseudobinary System, *Phys. Rev. B*, 2011, **84**(18), p 184301
24. M. Tsuchiko, S. Ikeuchi, T. Matsuo, I. Motooka, and M. Kobayashi, Conditions of the Formation of Rare Earth Phosphates and the Colors of Their Powders, *Bull. Chem. Soc. Jpn.*, 1979, **52**(4), p 1034-1040
25. R.D. Plättner, W.W. Krühler, W.K. Zwickler, T. Kovats, and S.R. Chinn, The Growth of Large, Laser Quality $\text{Nd}_x\text{RE}_{1-x}\text{P}_5\text{O}_{14}$, *J. Cryst. Growth*, 1980, **49**, p 274-290
26. M. Yoshimura, K. Fujii, and S. Somiya, Phase Equilibria in the System Nd_2O_3 - P_2O_5 - H_2O and Growth of $\text{NdP}_5\text{O}_{14}$ Single Crystals under Hydrothermal Conditions, *J. Cryst. Growth*, 1985, **71**, p 333-339
27. E.G. Tselebrovskaya, B.F. Dzhurinskii, G.V. Lysanova, and M.G. Komava, Intermediate and Metastable Phases in the Synthesis of Various Lanthanide Phosphates, *Russ. J. Inorg. Chem.*, 1991, **36**(10), p 1387-1389
28. J. Kropiwnicka, Phase Equilibria in the System La_2O_3 - Na_2O - P_2O_5 The Partial System La_2O_3 - $\text{Na}_4\text{La}_2\text{P}_4\text{O}_{15}$ - LaPO_4 , *J. Therm. Anal.*, 1990, **36**, p 979-990
29. J.J. Serra, J. Coutures, and A. Rouanet, Traitements Thermiques des Orthophosphates de Lanthanides LnPO_4 et Formation de Nouveaux Composés (Oxyphosphates), *High Temp. High Press.*, 1976, **8**, p 337-341
30. J.J. Serra, J. Coutures, A. Rouanet, H. Dexpert, and G. Garon, Etude des Familles d'Oxyphosphates de Lanthanides ($\text{Ln}/\text{P} > 1$): Synthèse, Caractérisation et Stabilité Thermique, *Rev. Int. Hautes Temp. Refract.*, 1978, **15**, p 287-313

31. A. Rouanet, J.J. Serra, K. Allaf, and V.P. Orlovskii, Rare Earth Orthophosphates at High Temperatures, *Inorg. Mater.*, 1981, **17**, p 76-81
32. E. Boakye, R.S. Hay, and M.D. Petry, Continuous Coating of Oxide Fiber Tows Using Liquid Precursors: Monazite Coatings on Nextel 720, *J. Am. Ceram. Soc.*, 1999, **82**(9), p 2321-2331
33. J.R. Mawdsley and J.W. Halloran, The Effect of Residual Carbon on the Phase Stability of LaPO_4 at High Temperatures, *J. Eur. Ceram. Soc.*, 2001, **21**, p 751-757
34. M.-S. Wong and E.R. Kreidler, Phase Equilibria in the System Nd_2O_3 - P_2O_5 , *J. Am. Ceram. Soc.*, 1987, **70**(6), p 396-399
35. V.G. Kuznetsov and V.P. Vasil'eva, Thermographic and X-ray Studies of Lanthanum Pyrophosphates, *Inorg. Mater.*, 1967, **3**(2), p 316-321
36. I.V. Tananaev and V.P. Vasil'eva, Lanthanum Pyrophosphates, *Russ. J. Inorg. Chem.*, 1964, **9**(9), p 1141-1144
37. X. Gao, G. Hong, W. Wang, H. Cui, and Y. Li, Preparation and Spectroscopic Properties of $\text{La}_4(\text{P}_2\text{O}_7)_3$:Ce, Gd, Tb Phosphors, *Chin. J. Lumin.*, 1993, **14**(1), p 25-31
38. Z. Zhang, J. Li, and X. Yang, Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime over Rare Earth Pyrophosphates, *Catal. Lett.*, 2007, **118**, p 300-305
39. J. Kropiwnicka, Phase Equilibrium in the System LaP_3O_9 - NaPO_3 - P_2O_5 : The New Compounds $\text{NH}_4\text{LaP}_4\text{O}_{12}$ and $\text{La}_4(\text{P}_2\text{O}_7)_3$, *J. Therm. Anal.*, 1995, **44**, p 725-731
40. S. Bernal, J.A. Díaz, R. García, and J.M. Rodríguez-Izquierdo, Study of Some Aspects of the Reactivity of La_2O_3 with CO_2 and H_2O , *J. Mater. Sci.*, 1985, **20**, p 537-541
41. N. Hatada, Y. Nose, A. Kuramitsu, and T. Uda, Precipitation Behavior of Highly Sr-Doped LaPO_4 in Phosphoric Acid Solutions, *J. Mater. Chem.*, 2011, **21**, p 8781-8786
42. O.A. Serra and E. Giesbrecht, Lanthanum, Cerium and Praseodymium Trimetaphosphates, *J. Inorg. Nucl. Chem.*, 1968, **30**, p 793-799
43. K.N. Ishihara, M. Maeda, and P.H. Shingu, The Nucleation of Metastable Phases from Undercooled Liquids, *Acta Metall.*, 1985, **33**(12), p 2113-2117
44. S.-Y. Chung, Y.-M. Kim, J.-G. Kim, and Y.-J. Kim, Multiphase Transformation and Ostwald's Rule of Stages During Crystallization of a Metal Phosphate, *Nat. Phys.*, 2009, **5**, p 68-73