

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 ~ 1200 °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 ± 10 °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 1100-1200 °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 ~ 1125 °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 La₂O₃-P₂O₅ 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)
La ₅ PO ₁₀	0.167	No	Yes	...	No	No	No
La ₃ PO ₇	0.25	Yes	Yes	...	Yes	Yes	Yes
La ₇ P ₃ O ₁₈	0.3	Yes	No	...	Yes	No	No
LaPO ₄	0.5	Yes	Yes	Yes	Yes	Yes	Yes
La ₄ (P ₂ O ₇) ₃	0.6	No	No	No	...	Yes	...
La ₂ P ₄ O ₁₃	0.667	Yes	No	No	...	No	...
LaP ₃ O ₉	0.75	Yes	Yes	Yes	...	Yes	...
LaP ₅ O ₁₄	0.833	Yes	Yes	Yes	...	Yes	...

Ellipses (...) represent “not investigated”

1.3 La₄(P₂O₇)₃

Kuznetsov and Vasil’eva^[35] obtained La₄(P₂O₇)₃ by heating amorphous La₄(P₂O₇)₂·12H₂O which was precipitated in aqueous solutions of La(NO₃)₃ and M₄P₂O₇ (M = Li, Na, 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 α-La₄(P₂O₇)₃ and it changes irreversibly into the high-temperature form, β-La₄(P₂O₇)₃, at 684 °C. Gao et al.^[37] and Zhang et al.^[38] also reported that they obtained La₄(P₂O₇)₃ by similar methods. Kropiwnicka^[39] synthesized La₄(P₂O₇)₃ by heating NH₄LaP₄O₁₂ in a closed system to 280 °C for 5 h, while heating NH₄LaP₄O₁₂ in an open system to 700 °C led to the formation of LaP₃O₉. Shi et al.^[21] obtained La₄(P₂O₇)₃ by solid state reaction between La₂(CO₃)₃·8H₂O and NH₄H₂PO₄.

1.4 La₂P₄O₁₃

Park and Kreidler^[17] obtained La₂P₄O₁₃ by crystallization from glass. They found that it is stable at temperatures up to 755 °C. However, La₂P₄O₁₃ has not been obtained by other methods even at those temperatures.^[19,24,34] The same phenomenon was found for the neodymium analogue, Nd₂P₄O₁₃, by Wong and Kreidler.^[34] It was formed by crystallization of a glass, but not formed by direct solid-state reaction. They speculated that Nd₂P₄O₁₃ exists in a metastable state.

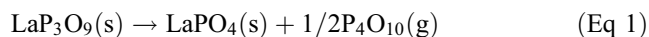
2. Experimental

2.1 Sample Preparation

La₂O₃ (Nacalai Tesque, mass fraction purity 0.9999) and H₃PO₄ (Nacalai Tesque, mass fraction purity 0.85) were used to prepare samples. La₂O₃ was heated overnight at 800 °C prior to use to remove absorbed H₂O and CO₂.^[40] LaPO₄ and LaP₃O₉ were synthesized by precipitation in

phosphoric acid solutions.^[41] La₂O₃ and H₃PO₄ 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 LaPO₄, or at 230 °C in the air for 2 days to precipitate LaP₃O₉. The precipitates were separated from the solution, washed well with hot water and dried at ~90 °C. The LaPO₄ 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 La₂O₃ and LaPO₄ (“L9P1”, “L8P2”, “L725P275”, “L7P3”, and “L6P4”), La₂O₃ and LaPO₄ 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 P₂O₅ than LaP₃O₉, “L25P75-δ”, was prepared from LaP₃O₉. The LaP₃O₉ 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 Cu Kα 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

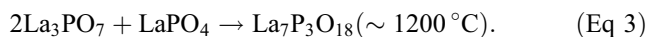
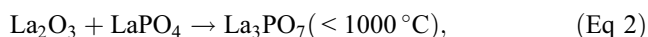
3.1 La₂O₃-LaPO₄ Subsystem

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 ₃ PO ₇ + LaPO ₄
		1100	200	β -La ₃ PO ₇ + LaPO ₄
		1200	100	La ₇ P ₃ O ₁₈
L7P3	Cooling	1300	100	La ₇ P ₃ O ₁₈
		1000	900	La ₇ P ₃ O ₁₈

reported to occur. Therefore, it is reasonable to assume that La₇P₃O₁₈ and Nd₇P₃O₁₈ are thermodynamically stable, but the formation of these compounds from solid phases seems to be kinetically inhibited at low temperatures.

With regard to the La₂O₃-LaPO₄ subsystem, it can be concluded that the present results are completely consistent with the phase diagram given by Park and Kreidler.^[17] La₅PO₁₀, 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 La₅PO₁₀, the reason why it did not form is not clear.

3.2 LaPO₄-LaP₃O₉ Subsystem

The LaPO₄-LaP₃O₉ subsystem may contain two intermediate compounds, La₄(P₂O₇)₃ and La₂P₄O₁₃ (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 LaPO₄ and LaP₃O₉, and no other phases such as La₄(P₂O₇)₃ and La₂P₄O₁₃ were detected. Therefore, LaPO₄ and LaP₃O₉ are considered in equilibrium at both 1050 °C (sample preparation temperature) and 700 °C.

A literature survey leads to an idea that La₄(P₂O₇)₃ and La₂P₄O₁₃ are metastable phases. As described in the Introduction, Kuznetsov and Vasil'eva^[35] proposed an α - β phase transition at 684 °C for La₄(P₂O₇)₃. However, the x-ray diffraction pattern for the high-temperature phase (β -phase) given by them indicates that it consists mainly of LaPO₄. Therefore, it is likely that La₄(P₂O₇)₃ decomposes to LaPO₄ and probably LaP₃O₉ 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 La₄(P₂O₇)₃ is considered to be in a non-equilibrium (probably metastable) state. According to several reports,^[21,35,38,39] it is supposed that La₄(P₂O₇)₃ can form through the dehydration of precursors on heating.

As for La₂P₄O₁₃, it has been obtained only by crystallization from glass, and it was reported to decompose into LaPO₄ and LaP₃O₉ at above 755 °C.^[17] Wong and Kreidler remarked that La₂P₄O₁₃ and Nd₂P₄O₁₃ could not be formed by solid state reaction, and they speculated that Nd₂P₄O₁₃

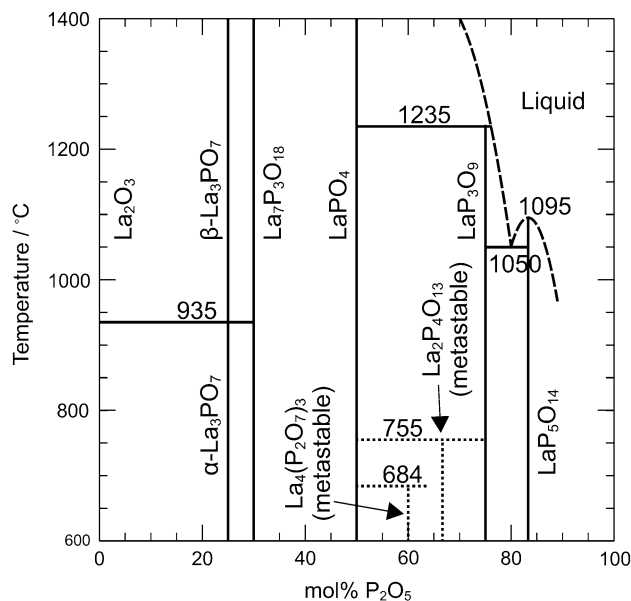


Fig. 1 Phase diagram of the La₂O₃-P₂O₅ system adapted from Park and Kreidler.^[17] Slight modifications were made to the original diagram so that La₂P₄O₁₃ is now shown as a metastable phase and La₄(P₂O₇)₃ which was not included in the original diagram is now included as a metastable phase

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 LaPO₄ and LaP₃O₉ can directly be precipitated in homogeneous phosphoric acid solutions at 100-400 °C. If La₂P₄O₁₃ and La₄(P₂O₇)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 La₂O₃-P₂O₅-H₂O system.^[19,41] However, the precipitation of La₄(P₂O₇)₃ and La₂P₄O₁₃ 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 La₄(P₂O₇)₃ and La₂P₄O₁₃ are metastable phases, although thermodynamic evidence is still required.

3.3 Phase Diagram of the La₂O₃-P₂O₅ System

Figure 1 presents the verified phase diagram of the La₂O₃-P₂O₅ system which is mainly adopted from Ref 17 and slightly modified to reflect the discussion above. The present results confirm the existence of La₃PO₇, La₇P₃O₁₈, LaPO₄, and LaP₃O₉ as thermodynamically stable phases in the La₂O₃-P₂O₅ system. The existence of La₅O₁₄ has also been well established in previous studies. Although La₄(P₂O₇)₃ and La₂P₄O₁₃ 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 $\text{La}_2\text{O}_3\text{-P}_2\text{O}_5$ 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.

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