Original Article

Hydrothermal treatment for preparation of europium-lanthanum phosphates and exploration of their fluorescence properties

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Europium-substituted lanthanum phosphates (Eu; 5 mol%) were prepared from lanthanum nitrate, europium nitrate, and sodium polyphosphate solutions by a hydrothermal process at 120 and 160 °C up to 8h. The obtained phosphates were studied using XRD, IR spectroscopy, TG–DTA, and SEM. UV–vis absorbance and reflectance, as well as fluorescence, were estimated as functional properties of these phosphate materials. We found that samples prepared without hydrothermal treatment were amorphous (as indicated by their XRD patterns), whereas those prepared by a hydrothermal treatment contained peaks corresponding to lanthanum orthophosphate, indicating that the hydrothermal process caused the polyphosphate(s) to decompose into orthophosphate(s). The TG–DTA curves of the samples prepared by a hydrothermal treatment were different from those of the samples prepared without hydrothermal treatment. All samples reported herein had no specified shape despite using prolonged hydrothermal treatment times. Although the samples prepared without hydrothermal treatment showed only weak fluorescence peaks, those prepared by a hydrothermal treatment showed strong peaks at 556, 590, 615, and 690 nm. These peaks corresponded to transitions from $^5D_0$ to $^7F_0$, $^7F_1$, $^7F_2$, and $^7F_4$, respectively. Collectively, these results indicate that the hydrothermal treatment is a useful method of obtaining europium-substituted lanthanum phosphates with fluorescence properties.

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1. Introduction

Phosphates can be transformed into its various forms by undergoing hydrolysis and dehydration reactions at elevated temperatures [1,2]. Polyphosphate and ultraphosphate are known as “condensed phosphates” the former has a chain structure in which the PO$_4^{3-}$ unit shares two oxygen atoms and the latter has a network structure [1]. Formation of these condensed phosphates is known to be affected by a number of factors such as the ratio of phosphorus/cation, heating temperature, time, and atmosphere [3–5]. Thus, obtaining these condensed phosphates in high yield can be difficult, and therefore, their study has been limited. Orthophosphate-based materials have been used as ceramic materials, catalysts, fluorescent materials, dielectric substances, metal-surface...
treatments, detergents, food additives, fuel cells, pigments, and so on [6,7]. Because the properties of condensed phosphates are different from those of orthophosphates, they can be used as novel functional materials [8–11].

Rare-earth phosphates have high melting points and large specific surface areas than conventional phosphate materials [12,13]. Rare-earth orthophosphates, which are the main components of rare-earth ores, are phosphate groups that are stable under acidic and/or basic conditions, making them ideal for incorporation into other phosphate-based materials [14]. Moreover, the incorporation of rare-earth elements into a material is known to affect the fluorescence properties of that material. In particular, the addition of europium is known to improve the fluorescence properties of many materials [15]. In previous work, europium-substituted lanthanum condensed phosphates were synthesized from lanthanum oxide, europium oxides, and phosphoric acid [16], and the resulting europium-substituted lanthanum polyphosphate and ultraphosphate were found to be more suitable materials for obtaining red luminescence than those based on orthophosphate.

The synthetic process used to fabricate a material affects the resulting functional properties of that material. Therefore, a hydrothermal process is generally used to control the powder properties of inorganic phosphate materials [17,18], and factors such as temperature, reactant concentration, and pH values play key roles in the process.

In the study reported herein, europium-substituted lanthanum phosphates were synthesized by a hydrothermal process, and the chemical compositions and particle shapes of the resulting products were evaluated. The absorbance and fluorescence properties of these phosphate materials were then evaluated.

2. Experimental

Sodium polyphosphate (NaPO₃) was synthesized by heating sodium dihydrogen phosphate (NaH₂PO₄), followed by quenching. This salt is a known inorganic phosphate polymer that has about 110 of polymerization degree [19]. La(NO₃)₃ and Eu(NO₃)₃ solutions (0.038 and 0.002 mol/L, respectively) were mixed with 0.12 P·mol/L of NaPO₃ solution at mole ratios of P/(La + Eu) = 3. This mixed ratio was the same as obtained with La₀.₉₅Eu₀.₀₅(PO₄)₃. It was stirred for 24 h, and placed in an air-tight container whose inner tube was composed of Teflon and the outer part was composed of stainless steel. This container was heated at either 120 or 160 °C for 2, 4, or 8 h (hydrothermal treatment) at 0.20 and 0.62 MPa, respectively. The samples were centrifuged, decanted, and then dried at 60 °C. A portion of each sample was heated at 800 °C for 3 h to compare them with the nonheated samples. All chemicals, obtained from Wako Chemical Industries Ltd., were of commercial purity and used without further purification.

The chemical composition of the samples was analyzed using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and thermogravimetry–differential thermal analysis (TG–DTA). The XRD patterns were recorded on a model MiniFlex Rigaku X-Ray diffractometer using monochromated CuKα-radiation. The IR spectra were recorded on JASCO FT-IR 4200 with a KBr disk method. The TG and DTA curves were measured with Shimadzu DTG-60A at a heating rate of 10 °C/min. The particle shapes of phosphate powders were observed using a JEOL JGM-5510LV scanning electron microscope (SEM). The light absorbance of the phosphate materials was estimated using ultraviolet–visible (UV–vis) reflectance spectra with a UV2100 spectrometer, supplied by Shimadzu Corp. The fluorescence properties were measured using a Perkin-Elmer LS55 luminescence spectrometer.

3. Results and discussion

3.1. Chemical compositions and powder properties of europium-substituted lanthanum polyphosphates

Fig. 1 shows the XRD patterns of samples prepared by a hydrothermal process (various times). Samples prepared
without hydrothermal treatment were shown to be amorphous, whereas those prepared by a hydrothermal treatment showed peaks corresponding to lanthanum orthophosphate (LaPO₄). Polyphosphates decomposed to orthophosphates when treated with the hydrothermal process for 2 h, according to Eq. (1).

$$\text{La(PO}_3)_2 \rightarrow \text{LaPO}_4 + 2\text{H}_3\text{PO}_4 \quad (1)$$

The phosphoric acid formed in this reaction was removed by decantation. Samples treated at 160 °C for 2 h showed XRD patterns similar to those treated at 120 °C for 4 h. This result indicates that conducting the hydrothermal treatment at a higher temperature is an effective method of reducing the reaction time.

Fig. 2 shows the XRD patterns of samples prepared by a hydrothermal process (various times) and then heated at 800 °C. Samples prepared without hydrothermal treatment showed peaks corresponding to lanthanum polyphosphate (La(PO₄)₃). Polyphosphate did not decompose under aqueous conditions. From this result, samples prepared without hydrothermal treatment were determined to be amorphous lanthanum polyphosphate, whereas those prepared by a hydrothermal treatment showed strong peaks corresponding to lanthanum orthophosphate. Differences in the hydrothermal time (2, 4, and 8 h) did not affect the XRD patterns of the resulting materials. Fig. 3 shows the IR spectra of samples prepared by a hydrothermal process (various times) and then heated at 800 °C. Samples prepared without hydrothermal treatment showed spectra different from those prepared by a hydrothermal treatment. These IR results were in accordance with the abovementioned XRD results.

Fig. 4 shows the DTA curves of samples treated by a hydrothermal process (various times). Samples prepared
without hydrothermal treatment showed a large endothermic peak at 130 °C and an exothermic peak at 660 °C (Fig. 4(A-a)). This exothermic peak was due to the crystallization of lanthanum polyphosphate, as indicated by the XRD results. The exothermic peak at 660 °C disappeared upon hydrothermal treatment because the polyphosphate decomposed into orthophosphate. Samples prepared by conducting the hydrothermal treatment for 2 h showed an endothermic peak at 260 °C (Fig. 4(A-b)). The presence of this peak is typical for Rhabdophane-type lanthanum phosphate species. In contrast, samples treated for 4 and 8 h showed no such peak around 260 °C (Fig. 4(A-c) and (A-d)). These samples changed to Monazite-type lanthanum phosphates, which are much more stable than the Rhabdophane-type ones. Samples treated at 160 °C for 2 h (Fig. 4(B-b)) showed DTA curves similar to those treated at 120 °C for 4 h (Fig. 4(A-c)). Fig. 5 shows the TG curves of samples treated by a hydrothermal process (various times). Samples prepared without hydrothermal treatment showed two steps, from room temperature to 200 °C and over 200 °C, in the TG curve (Fig. 5(A-a)). These steps became smaller by conducting the hydrothermal treatment at 120 °C for 2 h (Fig. 5(A-b)). Samples prepared by conducting the hydrothermal treatment at 120 °C for 4 and 8 h (Fig. 5(A-c) and (A-d)) showed smaller weight losses than those prepared without hydrothermal treatment (Fig. 5(A-a)). Sample treated at 160 °C for 2 h (Fig. 5(B-b)) had smaller weight loss than that treated at 120 °C for 2 h (Fig. 5(A-b)), because of the transition to Monazite-type lanthanum phosphate. At >800 °C, the samples showed small weight losses because lanthanum polyphosphate decomposed to lanthanum orthophosphate (by losing phosphorus oxide according to Eq. (2)), and lanthanum orthophosphate decomposed to lanthanum oxide (by losing phosphorus oxide according to Eq. (3)).

$$\text{La}(\text{PO}_3)_3 \rightarrow \text{LaPO}_4 + \text{P}_2\text{O}_5$$

(2)

$$2\text{LaPO}_4 \rightarrow \text{La}_2\text{O}_3 + \text{P}_2\text{O}_5$$

(3)

Fig. 6 depicts the SEM images of samples treated by a hydrothermal process (120 °C, various times). None of the samples

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**Fig. 4** – Differential thermal analysis curves of samples prepared by hydrothermal process (A, 120 °C; B, 160 °C) for: (a) 0, (b) 2, (c) 4, and (d) 8 h.

**Fig. 5** – Thermogravimetry curves of samples prepared by hydrothermal process (A, 120 °C; B, 160 °C) for: (a) 0, (b) 2, (c) 4, and (d) 8 h.
had a specified shape, regardless of the time spent undergoing the hydrothermal process. In previous work, the particles had a faceted surface at samples synthesized by heating [16]. The europium-substituted lanthanum polyphosphate had different particle shape by using the various synthetic methods.

3.2. Fluorescence properties of phosphate materials

Fig. 7 shows the UV–vis reflectance spectra of samples prepared by a hydrothermal process (various times). All the samples showed high reflectance at 350–800 nm. Samples prepared without hydrothermal treatment showed smaller absorption at 200–350 nm compared to those prepared by a hydrothermal treatment. By heating at 800 °C, the absorption at 200–350 nm became smaller in samples prepared by the hydrothermal process. Samples treated at 160 °C showed little difference in the UV–vis reflectance spectra compared to those treated at 120 °C.

Fig. 8 shows the excitation and emission spectra of samples prepared by conducting the hydrothermal process for several hours (emission; 592 nm, excitation; 254 nm) [20]. Samples prepared by the hydrothermal process strongly adsorbed the excitation radiation at 250–260 nm and weakly at 390–400 nm. Amorphous phosphates (i.e., samples prepared without hydrothermal treatment) showed minimal absorption at 250–260 nm.

Samples prepared without hydrothermal treatment showed weak fluorescence peaks, corresponding to the absorption at 250–260 nm. This sample had a large amount of water (as determined from the TG curves; Fig. 5(A-a)), and samples containing large quantities of water typically exhibit minimal fluorescence [21]. Furthermore, XRD analysis

![Fig. 6 - Scanning electron microscopy images of samples prepared by hydrothermal process (120 °C) for: (a) 0, (b) 2, (c) 4, and (d) 8 h.](image)

![Fig. 7 - UV–vis reflectance spectra of samples prepared by hydrothermal process (A, 120 °C; B, 160 °C) for: (a) 0, (b) 2, (c) 4, and (d) 8 h.](image)
Fig. 8 – Excitation spectra (em. 592 nm) and emission spectra (ex. 254 nm) of samples prepared by hydrothermal process (A, 120 °C; B, 160 °C) for: (a) 0, (b) 2, (c) 4, and (d) 8 h.

(Fig. 1(A-a)) showed that this material was amorphous. It should be noted that the weak fluorescence shown by this material could also be due to lattice vibration [22].

In contrast, samples prepared by a hydrothermal treatment showed strong fluorescence peaks. Owing to the hydrothermal treatment, these materials changed to Monazite-type lanthanum phosphate. Because these materials contained only small amounts of water, strong fluorescence was observed. The fluorescent peaks at 556, 590, 615, and 690 nm corresponded to the transitions from $^5D_0$ to $^7F_0$, $^7F_1$, $^7F_2$, and $^7F_4$, respectively, with some peaks divided in two because of the symmetry of the phosphate structure. Samples prepared by a hydrothermal treatment at 160 °C showed fluorescence spectra identical to those prepared by a hydrothermal treatment at 120 °C.

4. Conclusions

Europium-substituted lanthanum phosphates were synthesized from lanthanum nitrate, europium nitrate, and sodium polyphosphate solutions by a hydrothermal process. Samples prepared without hydrothermal treatment were amorphous (as indicated by their XRD patterns). In contrast, samples prepared by a hydrothermal treatment, at 120 and 160 °C for up to 8 h, exhibited peaks indicating the presence of lanthanum orthophosphate, showing that polyphosphate decomposed to orthophosphate during the hydrothermal process. The TG–DTA curves of the samples prepared by a hydrothermal treatment were different from those of the samples prepared without hydrothermal treatment. None of the samples in this study had any specified shape despite using prolonged hydrothermal treatment times. Samples prepared without hydrothermal treatment showed only weak fluorescence peaks, whereas those prepared by a hydrothermal treatment showed strong peaks at 556, 590, 615, and 690 nm. These peaks corresponded to the transitions from $^5D_0$ to $^7F_0$, $^7F_1$, $^7F_2$, and $^7F_4$, respectively. Collectively, these results show that hydrothermal treatment is important for obtaining europium-substituted lanthanum phosphates with fluorescence properties.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES

[5] Rathan SV, Govindaraj G. Thermal and electrical relaxation studies in Li$_{13/4}$Ti$_3$Nb$_9$_3$\cdot$ $P_2$O$_{12}$ ($0.0 \leq x \leq 1.0$) phosphate glasses. Solid State Sciences 2010;12:790–5.


[15] Bettinelli M, Piccinelli F, Speghini A, Ueda J, Tanabe S. Exited state dynamics and energy transfer rates in \( \text{Sr}_3\text{Ti}_{0.5}\text{O}_{4} \cdot 10\text{Eu}_{0.1} \cdot \text{PO}_{4}_{3} \). Journal of Luminescence 2012;132:27–9.


