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Original Article

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

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ABSTRACT

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 8 h. 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.

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^- 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

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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 ($NaPO_3$) was synthesized by heating sodium dihydrogen phosphate (NaH_2PO_4), followed by quenching. This salt is a known inorganic phosphate polymer that has about 110 of polymerization degree [19]. $La(NO_3)_3$ and $Eu(NO_3)_3$ solutions (0.038 and 0.002 mol/L, respectively) were mixed with 0.12 P-mol/L of $NaPO_3$ solution at mole ratios of P/(La + Eu) = 3. This mixed ratio was the same as obtained with $La_{0.95}Eu_{0.05}(PO_3)_3$. It was stirred for 24 h, and placed in an airtight 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

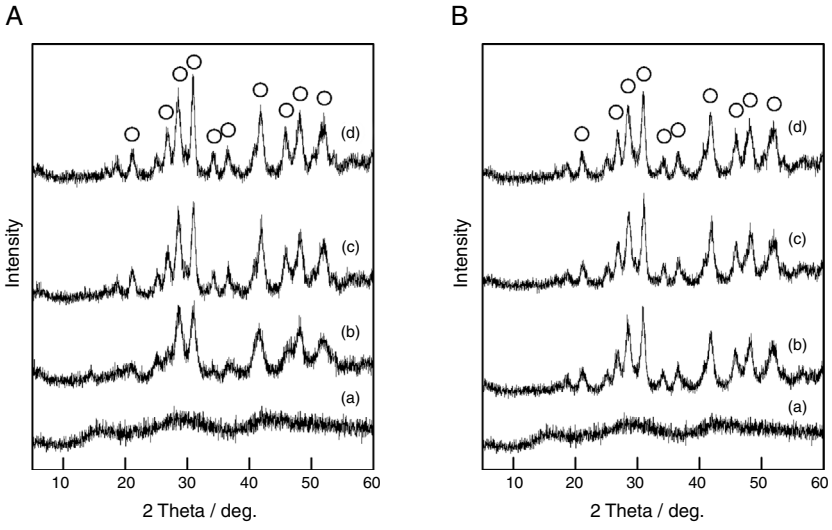

Fig. 1 – X-ray diffraction patterns of samples prepared by hydrothermal process (A, 120 °C; B, 160 °C) for: (a) 0, (b) 2, (c) 4, and (d) 8 h; ○, $LaPO_4$.