SYNTHESIS AND CHARACTERIZATION OF LANTHANUM PHOSPHATE: EFFECT OF STARTING PRECURSORS

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Abstract Three powder samples of lanthanum phosphate were prepared via the precipitation method. La_2O_3 , LaCl_3 , $(\text{NH}_4)_3\text{PO}_4$ and H_3PO_4 were used as precursor materials. Chemical and thermal analyses, infrared spectra, X-ray diffraction and particle size techniques were used for characterization. The results of chemical analysis indicated that the three samples are in non-stoichiometric state which attributed to the solubility of the products in the aqueous medium and/or to the partial precipitate of HPO_4^{2-} and H_2PO_4^- species. The results of infrared spectra exhibited the specific bands of phosphate salts such OH, $\text{O}=\text{P}-\text{O}$, $\text{P}-\text{O}$ and $\text{O}-\text{P}-\text{O}$. A band at 1380 cm^{-1} corresponding to PO_2^{2-} is observed in sample I and II which may due to make complexation species between the phosphates and the metal ions.

The X-ray diffraction indicated the formation of lanthanum phosphates of hexagonal structure of rhabdophane $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$. DTA/TGA curves show that the prepared samples remain thermally stable at high temperatures.

INTRODUCTION

Owing to the great importance of metal phosphates particularly in electronics industry, non-linear optics, biocompatible materials, super-ionic conductors and ion exchangers, different trials for preparation of some specific phosphates were done¹⁻⁴. Among the metal phosphates, the rare earth phosphates have a variety of potentially beneficial properties, including very low solubility in water, high thermal stability and high index of refraction. Guo et al⁵ succeeded in producing rare earth orthophosphate ($\text{RE}-\text{PO}_4$) using a sol-gel technique based on the reaction between their salts and phosphoric acid in aqueous or ethanolic media. Allal et al⁶ found that the prepared rare earth phosphates and their substitution with Ag from mixtures of AgNO_3 , $(\text{NH}_4)_2\text{HPO}_4$ and La_2O_3

Received August 5, 2002; Accepted October 18, 2002

crystallized in a triclinic system. LaPO_4 powder was synthesized by using the precipitation method⁷. Depending on synthesis conditions, the $\text{La PO}_4 \cdot 0.5\text{H}_2\text{O}$ powder has the monoclinic structure or hydrated hexagonal structure.

Some metal phosphates, AlPO_4 , FePO_4 , Na-phosphates and $\text{Zr}_3(\text{PO}_4)_2$ were previously synthesized by the classical and the sol-gel methods in our laboratory⁸⁻¹². As continuous, the present work is aimed to synthesize LaPO_4 by different methods depending on various precursor materials.

EXPERIMENTAL

La_2O_3 , HNO_3 , $(\text{NH}_4)_3\text{PO}_4$, LaCl_3 and H_3PO_4 (85%) of analar grade were used as the starting materials. Depending on the precursor material, LaPO_4 was prepared by using three precipitation methods.

Method (I) depends on the dissolution of La_2O_3 in nitric acid solution and using triammonium phosphate as precipitating agent according to the following equations.

Method (II) precipitation of LaPO_4 from its chloride (0.1M solution),

Method (III) by the reaction between (1 M) H_3PO_4 and (0.05 M) LaCl_3 , in this case phosphoric acid was added dropwise to avoid formation of other phosphates.

In all cases , the precipitates were separated, washed and dried at $\sim 80^{\circ}\text{C}$. The products were characterized by chemical and thermal analyses, infrared spectra and X-ray diffraction. Also, the specific surface area were measured by BET method (micromeritics ASAP 2000).

The chemical analysis was carried out by inductively coupled plasma (ICP). Infrared spectra were performed using JASCO FT/CR-3000 E infrared spectrophotometer (Japan). X-ray diffraction analysis was carried out for the samples by means of a chart recording Philips PW, 1790, X-ray diffractometer (Holland) using copper ($\text{Cu}\alpha$) radiation. The identification of the constituents has been accomplished through the use of the ASTM cards by determining the d-values of the different atomic planes and their relative intensities. DTA and TGA were performed in air with heating rate $5^{\circ}\text{C}/\text{m}$ by using Shimadzu DTA-50 and TGA-50 and Perkin-Elmer 7- series.

RESULTS AND DISCUSSION

The chemical analysis of the prepared samples shows that $\text{La}=0.32$, 0.33 and $0.33 \times 10^2 \text{ mole g}^{-1}$ for samples I, II and III respectively , while $\text{P}= 0.39 \text{ mole g}^{-1}$. This results indicated that the three samples are in non-stoichiometric state where $\text{La}/\text{P}= \sim 0.9$. This may due to the solubility of some products in aqueous medium (0.014 mg/l) and/or to the partial precipitate of HPO_4^{2-} and H_2PO_4^- species leading to chemical composition that could be written as⁷ ,

The IR spectra of LaPO_4 prepared by the three methods are shown in Fig. 1. In all cases, residual OH absorption around $\sim 3500 \text{ cm}^{-1}$ is observed. The observed bands around $1610\text{-}1620 \text{ cm}^{-1}$ are probably associated with the water bending mode . The main peaks which

FIGURE 1 IR spectra of lanthanum phosphate.

FIGURE 2 XRD patterns of lanthanum phosphate.

characterized the phosphate groups were observed at 1040 cm^{-1} specified P-O stretch, $610/630$ corresponding to O= P-O bend and O-P-O at 540 cm^{-1} . A band at 1380 cm^{-1} corresponding to PO_2^{2-} which observed in samples I and II only indicating the substitution of PO_4^{3-} by $\text{H}_2\text{PO}_4^{2-}$ ion during the precipitation process especially at low pH value¹³. This finding is in agreement with Byrne et al, where they observed that trivalent rare earth elements tend partially to make complexation species according to the following equilibrium states¹⁴.

These complexes may cause the departure of La/ P mole ratio than unity . In case of sample III, the peak (1380cm^{-1}) was not observed which may be due to step-wise addition of H_3PO_4 .

XRD patterns of the three prepared phosphates Fig.2 show that all the processes lead to single phase lanthanum phosphates of hexagonal structure of rhabdophane $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$ according to ASTM card (4-0635). In addition a peak corresponding to ammonium phosphate is appeared in case of samples I and II.

Fig. 3 represents the thermogravimetric analysis of the prepared samples. The results showed two endothermic peaks at ~ 130 and $\sim 246^\circ\text{C}$. The first peak is attributed to the loss of physisorbed water and the second one is related to the loss of the hydration water of the rhabdophane phosphates $\text{La PO}_4 \cdot 0.5\text{ H}_2\text{O}$ as detected from the X-ray patterns. DTA/TGA curves beyond $\sim 300^\circ\text{C}$ up to $\sim 1000^\circ\text{C}$ did not appear any additional observation. This indicate, that La PO_4 prepared by the three methods remain thermally stable at the high temperatures¹⁵.

Specific surface area of the powders issued from the three methods

FIGURE 3 TG and DTA of lanthanum phosphate.

I, II and III are nearly similar where it equals to 35.65, 40.22 and 37.51 m²/g respectively.

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