Synthesis and characterization of lanthanum phosphate sol for fibre coating

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Various routes to synthesize lanthanum phosphate sols ($LaPO_4$) were explored. Prepared lanthanum phosphate sols were characterized using differential thermal analysis/thermogravimetric analysis (DTA/TGA) and powder X-ray diffraction (XRD) after heat treatments. Appreciable crystallization of lanthanum phosphate was observed above 400 °C and the average crystallite sizes were calculated to be 15 nm and 46 nm after heat treatment at 700 and 1100 °C, respectively. Sapphire fibres were dip coated in $LaPO_4$ sol, and subsequently heated to 1100 °C. The thickness of the coating ranged from 60 to 150 nm depends upon the sol concentration and the number of times of dip coatings. XRD of coated fibres revealed the formation of $LaPO_4$ after heat treatment above 700 °C.

1. Introduction

To achieve tough behaviour of ceramic matrix composites (CMC), the fibre/matrix interlayer should be weak to promote crack deflection and fibre pull-out [1, 2]. Various interlayers have been employed to achieve this goal: *in situ* formed carbon interlayer, fugitive carbon or molybdenum coating, easily cleavable oxides such as beta alumina and mica, etc. [3–12]. Another requirement for CMC is that the composite constituents, as well as the interlayer(s), should not only be compatible with each other but should also be oxidation resistant at elevated temperatures.

Recently, Morgan and Marshall [7] studied potential interfacial coating materials for sapphire/alumina composites, with mechanical weakness, high temperature chemical compatibility and stability in oxidizing environments criteria. SnO_2, $LaPO_4$, CaF_2, and various aluminates having the magnetoplumbite-b-alumina structure were studied. They used the candidate interlayer materials as matrices for sapphire fibres or plates. Based upon the observations of their preliminary assessment study, they concluded $LaPO_4$ would be a good candidate for coating material. Synthesis of $LaPO_4$ sol, which is suitable for fibre coating, was not reported.

The objective of the present research effort is to study various routes to synthesize lanthanum phosphate ($LaPO_4$) sols that are suitable for continuous single fibre and fibre tow coating [13, 14], and characterize these samples by various techniques including differential thermal analysis/thermogravimetric analysis (DTA/TGA), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. Experiments

2.1. Synthesis and characterization of lanthanum phosphate sol

Lanthanum phosphate ($LaPO_4$, Monazite) can be synthesized through various reactions and/or combinations of them [15–24]. Several of these reaction routes were investigated in this study and the experimental details of each route were as follows.
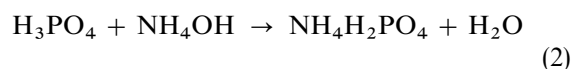
2.1.1. Method A

The first method involves using an equal molar ratio of $LaPO_4$ and H_3PO_4 [24]

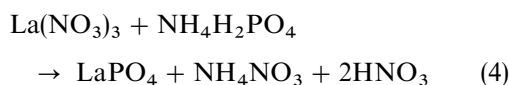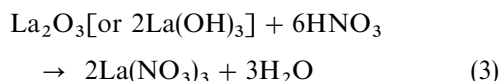$$LaCl_3 + H_3PO_4 \rightarrow LaPO_4 + 3HCl \qquad (1)$$

An approximately 20 wt % phosphoric acid solution was reacted with lanthanum chloride. White precipitates were immediately formed. The precipitates were washed with water three times and dried at room temperature.

2.1.2. Method B

Lanthanum phosphate precipitates were prepared by the neutral reaction of lanthanum nitrate with ammonium phosphate at room temperature (reaction 4). It was reported that large, high purity $LaPO_4$ crystals could be produced by this reaction [25]. Disadvantages of this reaction include the cumbersome procedures and the various by-products that are formed

$$H_3PO_4 + NH_4OH \rightarrow NH_4H_2PO_4 + H_2O \qquad (2)$$

$$\text{La}_2\text{O}_3[\text{or } 2\text{La}(\text{OH})_3] + 6\text{HNO}_3$$
$$\rightarrow \ 2\text{La}(\text{NO}_3)_3 + 3\text{H}_2\text{O} \qquad (3)$$
$$\text{La}(\text{NO}_3)_3 + \text{NH}_4\text{H}_2\text{PO}_4$$
$$\rightarrow \ \text{LaPO}_4 + \text{NH}_4\text{NO}_3 + 2\text{HNO}_3 \qquad (4)$$

The ammonium phosphate was prepared by gradually adding 85 wt % phosphoric acid to ammonium hydroxide and water solution until a pH of $7 \sim 8$ was reached. It was then cooled to allow $\text{NH}_4\text{H}_2\text{PO}_4$ to crystallize and then vacuum filtered.

The lanthanum nitrate was prepared by dropwise addition of concentrated nitric acid into a solution of lanthanum oxide and water. The mixture was stirred until all the solids disappeared. The pH of the solution was measured between 6 and 7. Since lanthanum nitrate is extremely difficult to crystallize, due to its high solubility in water [26], the resulting solution was allowed to cool at $4\,^{\circ}\text{C}$ to crystallize. The crystals were separated by vacuum filtration and recrystallized again to obtain purified lanthanum nitrate. The crystals were then dried in air before use.

Equimolar amounts of lanthanum nitrate and ammonium phosphate were dissolved into water to make 0.1 M solutions. During the vigorous mixing of these solutions, white insoluble LaPO_4 precipitates were formed. These precipitates were separated using a centrifuge, washed with water three times and finally dried in air.

2.1.3. Method C
The direct reaction between lanthanum oxide and phosphoric acid is a clean reaction with no by-products other than water.

$$\text{La}_2\text{O}_3 + 2\text{H}_3\text{PO}_4 \ \rightarrow \ 2\text{LaPO}_4 + 3\text{H}_2\text{O} \qquad (5)$$
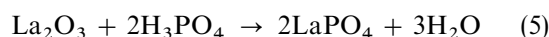
Due to the hygroscopic nature of lanthanum oxide [27], the starting powder was calcined at $700\,^{\circ}\text{C}$ for 2 h. The La_2O_3 powder was slowly added to 85 wt % H_3PO_4. The reaction was vigorous and exothermic. Large precipitates were immediately formed at the reaction site, and then gradually broke into fine particles. The sol was extremely dense and stable and did not separate for a long period of time. If the sol concentration was less than 0.1 M, visible separation between the sol and water was observed. The sol was stirred for 30 min and then separated by centrifuging. Traces of excess H_3PO_4 were removed by washing samples three times with water.

2.1.4. Method D
The synthesis of LaPO_4 by the reaction of $\text{La}(\text{OH})_3$ and H_3PO_4 has been studied and is reproducible

$$\text{La}(\text{OH})_3 + \text{H}_3\text{PO}_4 \ \rightarrow \ \text{LaPO}_4 + 3\text{H}_2\text{O} \qquad (6)$$
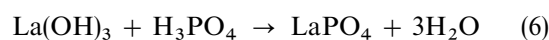
An approximately 20 wt % H_3PO_4 solution was used to prepare a lanthanum phosphate sol. The reaction did not complete within several hours when the concentration of phosphoric acid used was less than 10 wt %. The reaction was initiated by slowly adding $\text{La}(\text{OH})_3$ powder into a 20 wt % H_3PO_4 solution. The sample was stirred for 10 h to ensure the completion of the reaction. This was followed by centrifugal separation and washing the sample with water three times. A large-scale batch (2 moles of LaPO_4) of the sol was easily prepared using this reaction route. The coating experiments were performed using this sol (diluted to various concentrations).

The ratio between phosphate and lanthanum in the reaction mixture is important in terms of the final lanthanum phosphate formed [28]. An experiment was carried out to confirm the formation of LaP_3O_9 according to the following reaction equation

$$\text{La}(\text{OH})_3 + 3\text{H}_3\text{PO}_4 \ \rightarrow \ \text{LaP}_3\text{O}_9 + 6\text{H}_2\text{O} \quad (7)$$
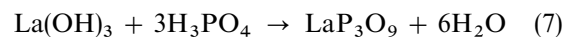
In this case, the sol was prepared with a molar ratio of 1:3 instead of 1:1. The dried sol was heat treated for 2 h at $700\,^{\circ}\text{C}$ before examination using XRD.

2.2. Fibre dip coating process
The coating experiments were carried out using similar technique reported in the literature [29–31]. The sapphire fibres, obtained from Advanced Crystal Products Corporation, Woburn, MA, was used for the dip coating experiments. The fibres were cut into 7.62-cm long pieces and cleaned with a 85% H_3PO_4 solution. After the acid cleaning, the surface of the fibre was rinsed with water.

Four different concentrations (0.1, 0.05, 0.01 and 0.001 M LaPO_4) were prepared using the sol obtained by Method D, reaction 6. The cleaned sapphire fibres were dip coated 20 times with drying (30 s) using an infrared lamp between each coating cycle. The coated fibres were calcined at $700\,^{\circ}\text{C}$ and $1100\,^{\circ}\text{C}$ for 2 h. The coated fibre surfaces were examined using polarized light microscopy and SEM.

3. Results and discussion
It was found from the current study that LaPO_4 can be synthesized through four chemical reaction routes described in the experimental section. However, methods A and B are abandoned at the early stage of this work due to the formation of HCl as a by-product and the cumbersome multiple step reactions, respectively.

The DTA/TGA curves of the room temperature dried LaPO_4 sol, prepared through reaction 6 are shown in Fig. 1. Most of the weight loss takes place below $300\,^{\circ}\text{C}$ and no further weight loss was observed between 400 and $1100\,^{\circ}\text{C}$. More weight loss was observed between 1100 and $1200\,^{\circ}\text{C}$, which corresponds to an endothermic peak in TGA curve. The exothermic peak around $400\,^{\circ}\text{C}$ corresponds to the crystallization of LaPO_4. The XRD pattern of the sol calcined at $700\,^{\circ}\text{C}$ for 2 h is shown in Fig. 2. All the peaks in the diffraction pattern matched with those of LaPO_4 (JCPDS file #32-0493). The XRD pattern of the LaPO_4 sol calcined at $1100\,^{\circ}\text{C}$ for 2 h is similar to Fig. 2, except the peaks became much sharper. Despite the weight loss between 1100 to $1200\,^{\circ}\text{C}$, the XRD pattern (Fig. 3) of the sol after the calcination at $1200\,^{\circ}\text{C}$ for 2 h show only peaks for LaPO_4. The
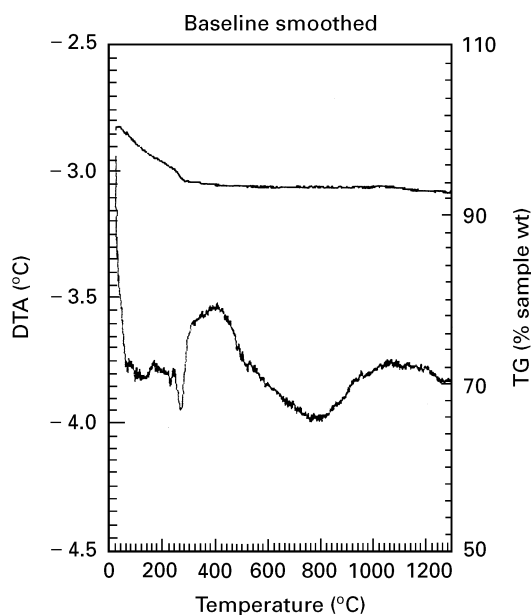
Figure 1 DTA/TGA curves of the dried $LaPO_4$ sol at 1200 °C.
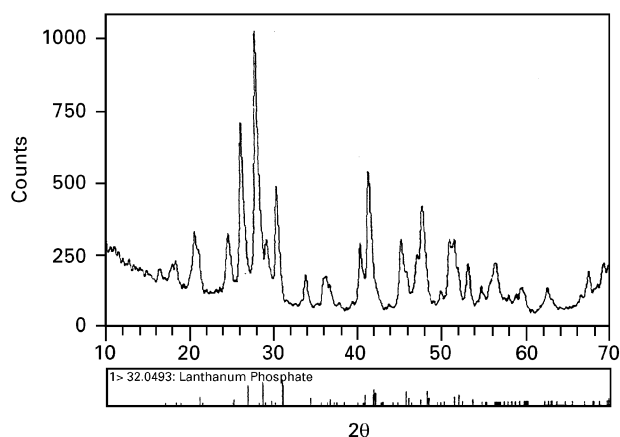

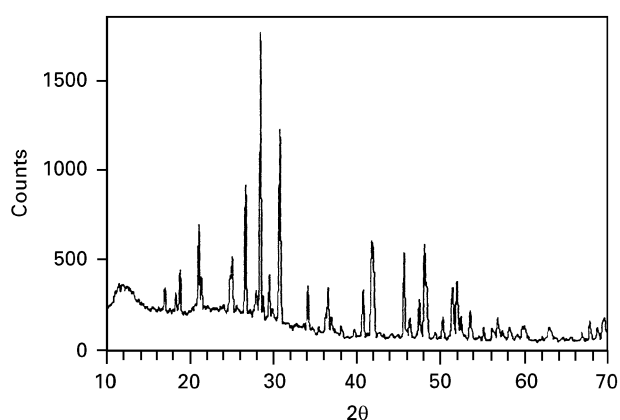*Figure 2* XRD pattern of $LaPO_4$ after 700 °C calcination, below is the JCPDS file.

Figure 3 XRD pattern of $LaPO_4$ sol after 1200 °C calcination.

reasons for the weight loss and the endothermic reaction between 1100 to 1200 °C are not clear at this moment.

The crystallite sizes of the calcined sols were calculated according to the Scherrer formula [32],

$t = 0.9\lambda/\{B\cos\theta_B\}$, where t is particle size, λ is wavelength of X-ray used ($\lambda = 0.154$ nm), B is the line width to half the maximum intensity, in radians, and θ_B is a half of 2θ in degrees. The calculated particle sizes after 700 and 1100 °C calcinations were about 15 nm and 46 nm, respectively.

The molar ratio between lanthanum and phosphate during the reaction is important in terms of the formation of final products. As listed in reactions 6 and 7, the La to P ratio has to be 1:1 in order to achieve $LaPO_4$ as a final product. When the reactant molar ratio was 1:3, LaP_3O_9 (JCPDS #33-717) was the only crystalline phase observed by powder XRD after 700 °C calcination (Fig. 4). When the molar ratio was adjusted between 1:1 and 1:3, mixtures of $LaPO_4$ and La_3PO_9 were observed. This effect was also observed in the fibre coatings.

Four concentrations of the $LaPO_4$ sols were prepared (0.1, 0.05, 0.01 and 0.001 M) for fibre coating experiments. The concentration variation was two orders of magnitude, which provides a wide range of sol concentration for good fibre coatings. The coating was not easily described by light microscopy on the fibres coated with the 0.001 M $LaPO_4$ sol. The coating was too thick and showed signs of cracking when the 0.1 M $LaPO_4$ sol was used. Reasonably good coatings were obtained for the 0.01 and 0.05 M $LaPO_4$ sols. SEM micrographs of the fractured sapphire fibre (with the 0.01 M sol coating) are shown in Fig. 5. The top micrograph (Fig. 5a) shows secondary electron image (SEI) and back-scattered electron (BSE) images of the fractured fibre. Since the fibre and the coating have vastly different average atomic weights, the coating was easily detectable by BSE imaging (Fig. 5a, right). The higher magnification micrograph (Fig. 5b) of the periphery of the fibre shows the coating with a uniform thickness of about 60 nm. For the same dip coating and heat treatment, the coating thickness increased to ~150 nm when the 0.05 M $LaPO_4$ sol was used (Fig. 6).

As in the case of the monolithic powder, the coatings on the sapphire fibres were crystalline $LaPO_4$ after heat treatment at 1100 °C for 2 h. The XRD pattern of the coated fibre surface is shown in Fig. 7. A strong (1 1 0) reflection of corundum is shown along with the $LaPO_4$ diffraction peaks. The intensities
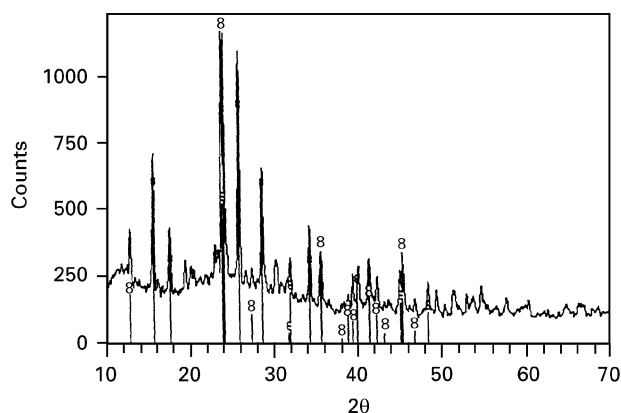

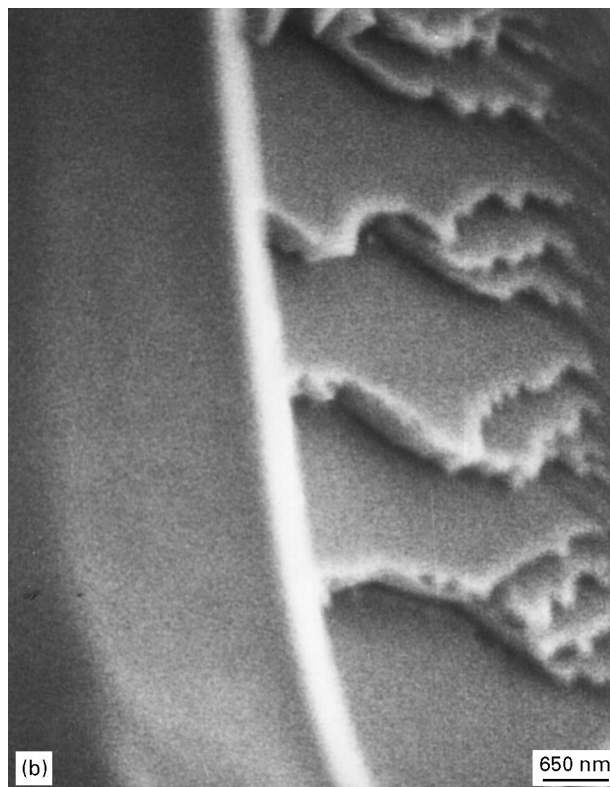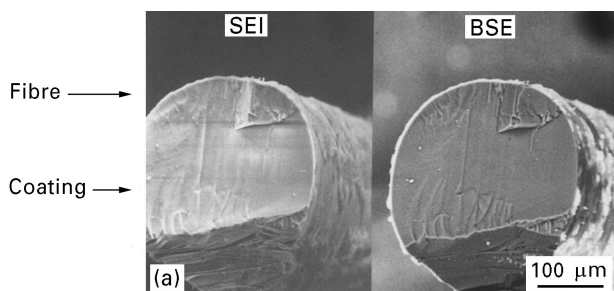*Figure 4* XRD pattern of LaP_3O_9 sol after 700 °C calcination.

Figure 6 SEM photomicrograph of LaPO$_4$ sol (0.05 M) dip-coated sapphire fibre after 1100 °C calcination.

Figure 5 SEM photomicrograph of LaPO$_4$ sol (0.01 M) dip-coated sapphire fibre after 1100 °C calcination.

Figure 7 XRD pattern of LaPO$_4$ sol (0.01 M) coated sapphire fibre after 1100 °C calcination. The strongest peak is (1 1 0) reflection of corundum.

match reasonably well with the powder XRD pattern, which implies that the LaPO$_4$ crystals in the coating are not strongly textured.

4. Conclusions

Various routes to synthesize lanthanum phosphate sols for potential CMC interlayer coatings were studied. It was relatively simple to synthesize stoichiometric LaPO$_4$ sol by the reaction of lanthanum oxide or lanthanum hydroxide and phosphoric acid, with water as the only by-product. It was found that any excess phosphoric acid over the stoichiometric reaction led to the formation of another lanthanum phosphate (LaP$_3$O$_9$) phase, along with LaPO$_4$. The as-reacted sol could be diluted to a wide range of concentrations and the resulting sols were stable.

The crystallization behaviour of the LaPO$_4$ sol was studied using DTA/TGA. The crystallization of LaPO$_4$ started around 400 °C and well-developed cry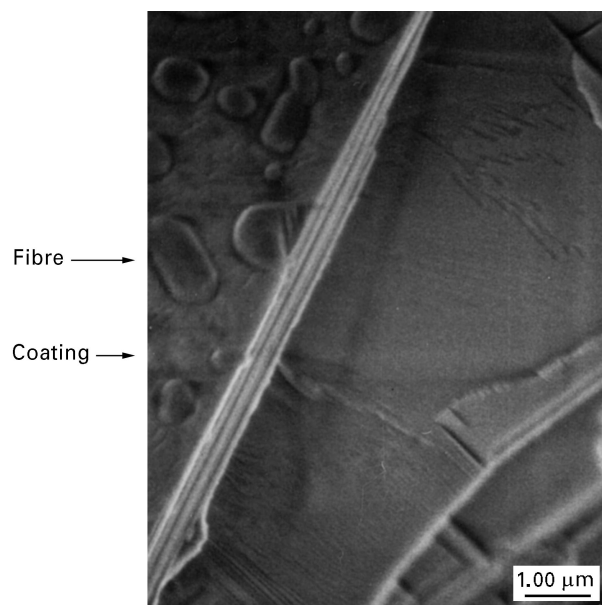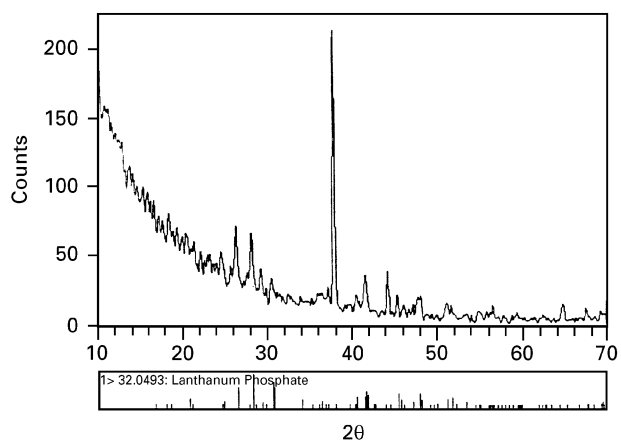stals were observed by XRD after a 700 °C, 2 h heat treatment. The endothermic reaction accompanied by weight loss between 1100 to 1200 °C can not be explained at present. The calculated crystallite sizes of the sols after 700 and 1100 °C calcinations were about 15 and 46 nm, respectively.

Coating experiments on sapphire fibres were carried out using various sol concentrations. Based upon the dip coating technique used in this study, the average coating thicknesses were 60 and 150 nm for the sol concentrations of 0.01 and 0.05 M LaPO$_4$, respectively. The XRD analysis of the coated fibre surface confirmed that the coating was LaPO$_4$.

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