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Conduction properties of condensed lanthanum phosphates: $La(PO_3)_3$ and LaP_5O_{14}

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Abstract: Single crystals of $LaP_3O_9 \cdot 3H_2O$ were prepared using a classical method of aqueous chemistry whereas those of the ultraphosphate LaP_5O_{14} were obtained by flux method. Thermal treatment of $LaP_3O_9 \cdot 3H_2O$ up to 700 °C allowed us to obtain the lanthanum polyphosphate $La(PO_3)_3$. The conductivity as well as the vibrational study of the lanthanum ultraphosphate and polyphosphate were analysed in order to explain the mechanism of conduction. Activation energies of 0.45 and 0.84 eV, deduced from the Arrhenius relation, were respectively found for the polyphosphate and the ultraphosphate. Taking into account the structural features of these materials we linked the origin of their electrical properties to the incorporation of atmospheric humidity. Thus, it was a proton conduction phenomenon which took place as a result of the establishment of hydrogen bonds as well as the reorganisation of water molecules already incorporated into these structures. Referring to the Grotthuss mechanism, a proton transfer model inside the polyphosphate's structure was suggested.

Keywords: condensed lanthanum phosphates; electrical conductivity; Grotthuss mechanism; rare earths

Because of their potential to reduce the environmental impact and geopolitical consequences of the use of fossil fuels, fuel cells have attracted worldwide attention. Low and high temperature fuel cells, which have their own specific advantages and disadvantages, have been developed[1].

Intermediate temperature fuel cells are of particular interest as this temperature range may allow for the use of non-noble catalysts, and may enable *in situ* reforming of liquid biofuels, such as methanol or ethanol. At the same time, this temperature range facilitates management, and reduces material problems that complicate higher temperature systems[2].

So, it is highly desired to develop ion-conductive electrolytes that have high conductivity at intermediate temperatures.

Proton-conducting materials are used as the electrolyte for low- and intermediate temperature fuel cells (i.e., polymer electrolyte membrane or proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), phosphoric acid fuel cells (PAFCs), and alkaline fuel cells (AFCs))[3]. Several solids inherently without protons such as oxides, sulfates and phosphates exhibit significant protonic conduction at elevated temperatures in the presence of hydrogen containing gases[4]. However, the proton-transfer mechanism is still poorly understood. Recent works have shown $LaPO_4$ to be a proton conductor in the 500–700 °C range[5–8]. Conductivity values for 'pure' $LaPO_4$ range approximately 2.5×10^{-7} to 9.7×10^{-9} S/cm[8–11].

Earlier studies had demonstrated that conductivities of rare earth phosphates enhance considerably by substituting divalent metal (acceptor) for the rare earth element[5–13]. In such phosphates, protons were considered as extrinsic defects that were incorporated into the materials in order to compensate the effective negative charge of the acceptor substituents[6]. It was concluded that the total conductivity is dominantly protonic at the temperature range 500–900 °C and took place by the so-called Grotthuss mechanism[9,11]. In recent study[14], Gabriel Harley et al. mentioned that the formation of grain boundary films as result of the addition of alkaline earth elements to the rare earth phosphates contribute as well to the conductivity's increase since the grain boundary conductivity is calculated to be ~2.5×10^{-3} S/cm.

Proton transport within rare earth phosphates remains incompletely characterized and there are no mechanisms reported for these non-substituted materials[14].

In this work, the electrical conductivity of undoped lanthanum condensed phosphates LaP_5O_{14} and $La(PO_3)_3$ was investigated at the temperature range 100–300 °C in order to propose a model of proton-transfer process into their structures, therefore, explaining the origin of their electric properties.

1 Experimental

1.1 Synthesis

The synthesis of $LaP_3O_9 \cdot 3H_2O$ single crystals consists in slowly mixing $LaCl_3 \cdot 6H_2O$ and $Na_3P_3O_9$ 0.1 mol/L aqueous

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solutions in a 1:1 ratio under mechanical stirring at room temperature. The chemical reaction is as follows:

$Na_3P_3O_9+LaCl_3·6H_2O \rightarrow LaP_3O_9·3H_2O+3H_2O+3NaCl$

Two days later, single crystals were isolated from the resulting precipitate after being filtered, washed with water and dried in the air.

Single crystals of LaP_5O_{14} were prepared by flux method. At room temperature, 0.5 g of La_2O_3 was slowly added to 10 ml of phosphoric acid H_3PO_4 (85%). The mixture was then slowly heated to 400 °C and kept at this temperature for seven days. Washing the product in boiling water led to the separation of the obtained colourless crystals from the phosphoric acid excess.

1.2 Measurements

The X-ray powder diffraction (XRD) patterns of all samples were recorded on an X'PERT Pro PANAnalytical diffractometer with Cu Kα radiation (λ=0.15418 nm). Thermal analysis (DTA and TGA) were performed on a SETSYS Evolution 1750 SETRAM at a heating rate of 10 (°)/min. Infrared spectra were recorded on a NICOLET 560 spectrometer using KBr pellets in the region of 4000–400 cm^{-1}. The electrical conductivity measurements were performed as a function of both temperature (100 to 300 °C) and frequency (100 Hz to 13 MHz) employing a Hewlett-Packard 4192 A LF automatic bridge monitored by a HP Vectra microcomputer.

2 Results

2.1 X-ray diffraction

The X-ray pattern of $LaP_3O_9·3H_2O$ is presented in Fig. 1(a). The compound crystallizes in the hexagonal system with space group P-6. The TREOR program refinement reveals the following lattice parameters: $a=b=0.6780$ (1) nm; $c=0.6105(2)$ nm; $\gamma=120°$; $Z=1$ and $V=0.24305$ nm^3.

The X-ray powder diffraction pattern of the ultraphosphate shows that this compound is well crystallized. As shown in Fig. 1(b), the lanthanum phosphate LaP_5O_{14}, isostructural with NdP_5O_{14}[15], exhibited a monoclinic structure with space group $P2_1/c$. Unit cell parameters refined by the TREOR program are as follows: $a=0.878(1)$ nm; $b=0.904(1)$ nm; $c=1.308(2)$ nm; $\beta=91.00°(3)$; $Z=4$ and $V=1.03840$ nm^3.

2.2 Thermal behaviour

We used thermal analysis (DTA and TGA) and X-ray powder diffraction technique in order to study how the hydrated phosphate of lanthanum evolved with temperature. Fig. 2 shows the thermogram and the change in weight obtained during the heating process in the 42–600 °C range. The TGA curve shows two dehydration domains: the first occurs at the 42–199 °C range and the second between 199–428 °C. In fact, the first endothermic peak appearing in the DTA curve is related to the elimination of residual water adsorbed by the studied compound and having as origin atmospheric humidity. Thus, the first dehydration of $LaP_3O_9·3H_2O$ starts really at 145 °C and corresponds to a weight loss of 5.242% which is equivalent to 1.15 mole of structure water. Whereas, the weight loss associated to the second dehydration is equal to 8.266% which means the removal of 1.88 mole of structure water. The stoichiometry of the hydrated phosphate $LaP_3O_9·3H_2O$ was so confirmed.

In addition, each step of weight loss in the TGA curve is accompanied in the thermogram by an endothermic peak which is due to crystalline transformations of the $LaP_3O_9·3H_2O$. These transformations were studied more accurately by X-ray powder diffraction and infrared spectroscopy after thermal treatment of the lanthanum hydrated phosphate at different temperatures (Figs. 3 and 4).

The X-ray diffractogram of $LaP_3O_9·3H_2O$ heated at 300 °C shows a destruction of the hexagonal structure of the initial

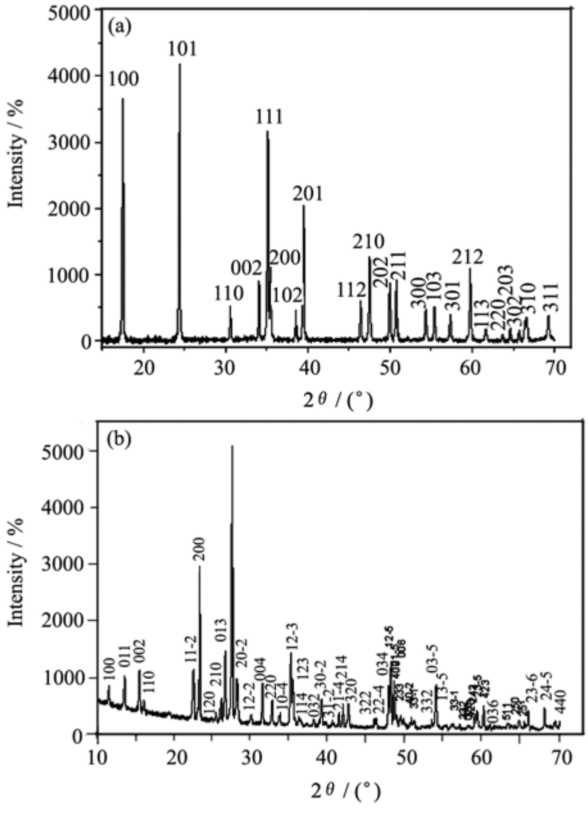

Fig. 1 X-ray powder diffraction pattern of $LaP_3O_9·3H_2O$(a) and LaP_5O_{14} (b)

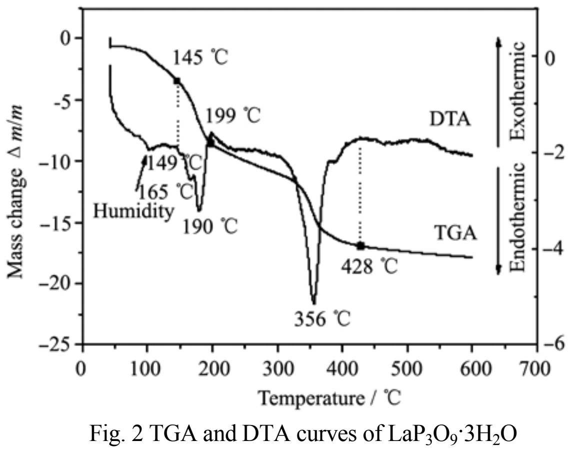

Fig. 2 TGA and DTA curves of $LaP_3O_9·3H_2O$