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Preparation and characterisation of $La_{10-x}Ge_{5.5}Al_{0.5}O_{26\pm\delta}$ apatites by freeze-drying precursor method

D. Marrero-López [a,b,*], M.C. Martín-Sedeño [c], J.C. Ruiz-Morales [b], P. Núñez [b], J.R. Ramos-Barrado [a]

[a] Dpto. de Física Aplicada I, Laboratorio de Materiales y Superficies (Unidad Asociada al C.S.I.C.), Universidad de Málaga, 29071 Málaga, Spain
[b] Dpto. de Química Inorgánica, Universidad de La Laguna, 38200 La Laguna, Tenerife, Spain
[c] Dpto. de Química Inorgánica, Universidad Málaga, 29071 Málaga, Spain

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ABSTRACT

Nanocrystalline powders of $La_{10-x}Ge_{5.5}Al_{0.5}O_{26\pm\delta}$ ($x = 0$–0.5) with an average crystallite size of 50 nm were prepared by a freeze-drying precursor method. These powders were used to obtain dense ceramic materials at rather low temperature as 1100–1200 °C for 1 h and to study the transport properties by impedance spectroscopy. The composition with the highest La-content ($x = 0$) exhibits a second-order phase transition from triclinic ($P\bar{1}$) to hexagonal ($P6_3/m$) space groups around 750 °C, whereas for $x \geq 0.2$ the materials presents hexagonal structure in the whole temperature range studied. The thermal properties of these materials were investigated by high temperature X-ray diffraction (XRD), thermal analysis (TG/DTA) and impedance spectroscopy. These results confirmed the incorporation of water in the germanate-apatite structure. However, the conductivity resulted to be independent on the gas atmosphere used, which seems to indicate that the proton contribution to the overall conductivity is negligible in these materials.

1. Introduction

Materials with oxide and/or proton ion conductivity have been widely studied as potential electrolyte for fuel cells, sensors, electrochemical pumps, electrochemical micro-reactors, etc. [1–3]. New ion conducting materials have been identified during the last few years and one of the most promising are those with apatite-type structure, because they present high ionic conductivity compared to the state-of-the-art yttria stabilised zirconia (YSZ) in the intermediate temperature range [4–9].

Different rare-earth apatites with composition $RE_{10-x}\square_x(MO_4)_6O_{3-3x/2}$ (M = Si, Ge) have been reported without and with substitutions on the La and Si sites [7,8,10–18]. The dominant ion conduction mechanism in these materials is via interstitial oxide ions, in contrast to fluorite (e.g. ZrO_2 and CeO_2) and perovskite (e.g. $LaGaO_3$)-based electrolytes, where the conduction occurs via oxygen vacancies [1,19]. Although proton conductivity was recently observed for germanate apatites at low temperature [20].

The conductivity of Ge-based apatites has been reported to be higher compared to the analogous silicates [16,17]. Nevertheless, silicates have been most widely studied in comparison to germanates, due to several problems related to Ge volatility at temperatures above 1300 °C. These high temperatures are usually necessary to obtain dense ceramic materials for electrical characterisation [17,21,22].

The main synthesis method in the preparation of germanate-based apatites has been the conventional solid state reaction method, although alternatives synthesis routes, such as sol–gel and mechanosynthesis were also used [23,24]. The conventional ceramic method, which usually requires high sintering temperatures to obtain a pure phase and densification, has disadvantages; such as the formation of undesirable phases, chemical inhomogeneities and relatively large grain ceramic sizes. In the case of germanate-based materials, the Ge evaporation is an additional drawback, so that reducing the sintering temperature is particularly important in these materials. In this sense, the synthesis routes based on precursors are useful to prepare materials, which are no stable at high temperature. It should be also noted that the preparative route plays also a critical role in the materials properties, controlling the structure, morphology and grain size of the synthesised materials. In addition, the transport properties of the ceramic materials are also depending on ceramic microstructure and specially the grain boundary contribution. Thus, alternative synthesis routes could improve both the microstructure and conductivity of these materials. In this context, the use of

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* Corresponding author at: Dpto. de Física Aplicada I, Laboratorio de Materiales y Superficies (Unidad Asociada al C.S.I.C.), Facultad de Ciencias, Campus de Teatinos, Universidad de Málaga, 29071 Málaga, Spain. Tel.: +34 952137057; fax: +34 952132382.
E-mail address: damarre@uma.es (D. Marrero-López).

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precursors obtained by freeze-drying processing of the appropriate aqueous metal salts has proved to be a very versatile method for obtaining stoichiometrically controlled complex polymetallic systems [25–27].

In the present contribution $La_{10-x}\Box_x(GeO_4)_6O_{3-3x/2}$ materials were prepared by a freeze-dried precursor method. Aluminium has been used as doping because it improves the stability of the silicates and a similar effect is expected for germanate-based apatites [28,29]. The phase formation, structure, densification, microstructure and conductivity under different atmospheres of the sintered ceramics have been studied in the present report.

2. Experimental

Polycrystalline powders of $La_{10-x}Ge_{5.5}Al_{0.5}O_{26\pm\delta}$ (x = 0, 0.2, 0.4 and 0.5) have been prepared by a freeze-drying precursor method. Starting materials used as reagents were: La_2O_3 (99.99%), amorphous GeO_2 (99.99%) and $Al(NO_3)_3\cdot9H_2O$ (>98%), all of them supplied from Sigma–Aldrich. Lanthanum oxide was precalcined at 1000 °C for 2 h in order to archive dehydration and decarbonation. Aluminium nitrate and germanium oxide, which are hygroscopic, were previously studied by thermogravimetric analysis to determine the correct cation composition of these reagents. Cation solutions were prepared separately by dissolving GeO_2 and $Al(NO_3)_3\cdot9H_2O$ in distilled water, whereas La_2O_3 was dissolved in diluted nitric acid. These solutions were mixed in stoichiometric amounts and ethylenediaminetetraacetic acid (EDTA) (99.5% Aldrich) was added as complexing agent in a 1.5:1 ligand:metal molar ratio. The volume of the resulting stoichiometric cation solution was 200 ml and the cation concentration was about 0.12 M of La^{3+}. The solution pH was adjusted to 7 by adding ammonia solution. Droplets of this solution were subsequently flash frozen in liquid nitrogen, retaining the cation homogeneity of the starting solution, and then freeze-dried in a HetoLyolab freeze-dryer for 3 days. The amorphous precursor powders, obtained in this way, were immediately calcined at 300 °C to prevent rehydration and finally fired at 700 °C for 1 h to remove the residual organic species and for achieving crystallisation. The samples will be hereafter denoted according to the lanthanum content in $La_{10-x}Ge_{5.5}Al_{0.5}O_{26\pm\delta}$ as, La10 − x.

X-ray powder diffraction (XRD) patterns were recorded using a Philips X'Pert Pro diffractometer, equipped with a Ge(1 1 1) primary monochromator, the X'Celerator detector and a high temperature Anton Paar HTK-16 camera. The scans were collected in the 2θ range (5–120°) with 0.016° step for 1–3 h. The high temperature XRD patterns were collected during heating and cooling processes with stabilisation time of 30 min between consecutive measurements. The Rietveld refinements were performed using the Fullprof and X'Pert HighScore Plus v.2.2d software using the ICSD database for the structural models [30–32]. The usual parameters (scale factors, background coefficients, zero-points, pseudo-Voigt and asymmetry parameters for the peak-shape) were refined. The atomic parameters were fixed and not refined.

TG–DTA curves were collected with a PerkinElmer TG/DTA instrument (mod. Pyris Diamond) in different dry/wet gases (air, Ar and 5%H_2–Ar mixture) at a rate of 10 °C min^{-1}.

The morphology of sintered pellets was monitored using a scanning electron microscope (SEM) (Jeol LTD, mod. JSM-6300) combined with energy dispersive spectroscopy (EDS). All samples were covered with a thin film of sputtered gold or carbon to avoid charging problems.

For the electrical characterisation, ceramic pellets were prepared by pressing the nanocrystalline powders into disks of 10 mm of diameter and 1–2 mm of thickness at 125 MPa without any previous mechanical treatment (e.g. ball-milling) to avoid a possible contamination during the milling process due to zirconia/silica balls and vessel. The resulting pellets were sintered between 1000 and 1250 °C in air for 1 h. Symmetrical Pt-paste electrodes were painted on each side of the pellet and then fired at 800 °C for 10 min to ensure good electrical contact with the electrochemical cell. Impedance spectra were recorded on a 1260 Solartron FRA in air flow and dry/wet gases (Ar and 5%H_2–Ar mixtures) in the 0.1 Hz to 1 MHz frequency range with an ac signal of 150 mV. Gases were humidified by bubbling through a gas-washer at a temperature of 20 °C to ensure a constant water content of about 3%. The spectra were acquired on heating and cooling processes from 200 to 950 °C with a rate of 5 °C min^{-1} and stabilisation time of 30 min between consecutive measurements. Data were analysed by non-linear least squares fitting using equivalent circuits with ZView v2.8 software [33].

3. Results and discussions

3.1. Phase formation and structure

The TG curve confirmed that the complete decomposition of the amorphous precursor powder occurs at around 600 °C (not shown), so that the powders were fired slightly above this temperature. Fig. 1 shows the X-ray diffraction patterns for some compositions after firing at 700 °C for 1 h. As can be observed, single phase materials are obtained at only 700 °C with no additional diffraction peaks. The average crystallite size estimated by the Scherrer's equation, which was corrected for the instrumental broadening, was around 50 nm. For further structural and thermal characterisation, the polycrystalline powders were calcined at 1100 °C for 1 h to improve crystallisation. The room temperature XRD patterns are shown in Fig. 2. All the materials were single phases in the compositional range studied ($0 \leq x \leq 0.5$). The composition La10 (x = 0) is triclinic (s. g. $P\bar{1}$), while that for $0.2 \leq x \leq 0.5$ the phases are hexagonal (s. g. $P6_3/m$). It should be mentioned that these results are somewhat different than those reported by León-Reina et al. [22]. These authors reported that the triclinic phase is stabilised at room temperature for $x \leq 0.33$ and the single phase existence is in the range $0.25 \leq x \leq 0.55$. The single phase domain is also extended in the

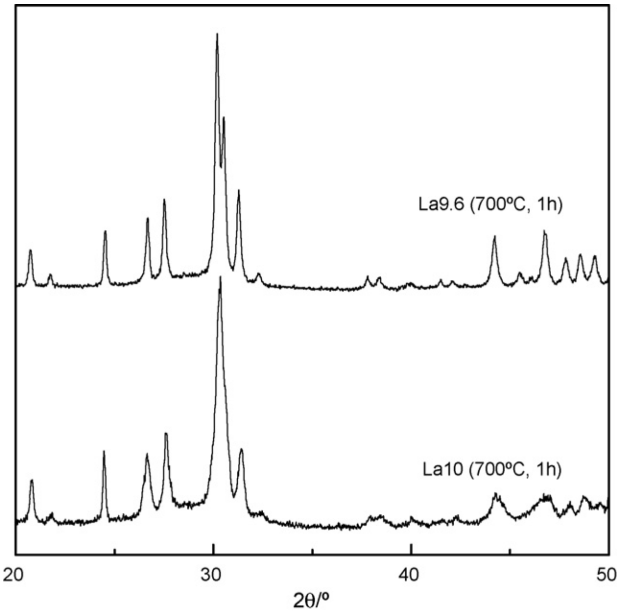

Fig. 1. XRD patterns of $La_{10}Ge_{5.5}Al_{0.5}O_{26.75}$ and $La_{9.6}Ge_{5.5}Al_{0.5}O_{26.15}$ as synthesised at 700 °C for 1 h.