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New approach to develop dense lanthanum silicate oxyapatite sintered ceramics with high conductivity

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ABSTRACT

Recently, apatite-type lanthanum silicate, $La_{9.33}(SiO_4)_6O_2$, and its analogues with cationic doping in the La/Si site have been attracting significant interests due to their high oxide ion conduction. However, the well-known synthesis method is solid-state reaction, which suffers from problems such as the high sintering temperatures for dense pellets and the impurity phases in the final ceramics. In this paper apatite-type lanthanum silicates were prepared by precipitate method combining with an azeotropic-distillation process. The influences of powder calcination temperature on the relative density were investigated and the optimal calcination temperature was proved to be 1100 °C. The main phase of the powder calcined at 1100 °C was lanthanum silicate $La_{9.33}(SiO_4)_6O_2$ with trace impurities La_2O_3 and La_2SiO_5. However, dense pellet (96.63%) with pure lanthanum silicate phase was obtained at relatively low temperature (1550 °C). Electrical measurements have shown that conductivity behaviors of the sintered pellets were also calcination-temperature dependent. The highest overall conductivity values, $\sigma_{500\,°C} = 1.58 \times 10^{-3}\,S\,cm^{-1}$ and $\sigma_{800\,°C} = 2.21 \times 10^{-2}\,S\,cm^{-1}$, were obtained for pellet prepared from powder calcined at 1100 °C, which was much higher than that synthesized by other methods. The samples presented activation energies of 0.66 ± 0.01 eV. The results in the present study demonstrate that the precipitate-azeotropic-distillation approach is an alternative method to synthesize lanthanum silicate powders.

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1. Introduction

Over the past few years there has been a considerable interest in solid oxide fuel cells (SOFCs) due to their high efficiency and environmental benefits [1,2]. One of the key components of SOFC devices is solid electrolyte and the traditional solid electrolyte is yttria-stabilized zirconia (YSZ) [3]. Although YSZ is considered to be the most reliable solid electrolyte so far, its high working temperature (~1000 °C) may cause problems such as materials interconnection and lifetime. Hence, many studies have been made on other solid electrolytes as alternatives to zirconia, e.g. Bi_2O_3- [4] and CeO_2-based [5] materials.

Rare earth(Ln)-based apatites, with the general formula $Ln_{10-x}B_6O_{27-x/2}$ (B = Si, Ge), are another promising solid electrolyte for SOFC applications [4]. Although the electrical conductivity of pure lanthanum silicate oxyapatite is not high, it seems to have an advantage during a lower temperature operation [6]. Therefore, enormous amounts of efforts were found to devote to synthesis various stoichiometric compounds, including cationic doping in the Ln site or in the B site, to enhance the electrical properties [7–18].

Traditional preparation method for oxyapatite synthesis is solid-state reaction, which requires ball-mill and extensive heat treatment at ≥1600 °C [7–18]. Ball-mill operation has the drawbacks of contamination and poor chemical homogeneity while high temperature presents some disadvantages such as a poor control of the morphology and particle size, which leads to a decrease in the reactivity of the powders and deteriorate the electrical conductivity. During recent years, several wet-chemical approaches have been developed and used for oxyapatite synthesis. For instance, Masubuchi et al. [19] prepared apatite-type $La_{9.33}(SiO_4)_6O_2$ by alcoxide-hydrolysis while Jiang et al. [20] synthesized lanthanum silicate oxyapatite, $La_{10}Si_6O_{27}$, by a water-based gel-casting route. Chesnaud et al. [21] adopted freeze-drying technique combining with spark plasma sintering process to significantly reduce sintering temperatures and operating time. Tao et al. [22] and other groups [23–25] used sol–gel method to prepare apatite-type lanthanum silicates at relatively low temperatures. Comparing with the conventional solid-state method, it is easy for wet-chemical approaches to obtain a homogenous mixture of the oxide precursors and decrease the formation temperature and further improve sinterability of oxyapatites.

In the present work, we introduce a carbonate-precipitation combining with an azeotropic-distillation process for the facile synthesis of $La_{9.33}(SiO_4)_6O_2$ dense ceramics. This method is based on the fact that lanthanum element forms carbonate precipitate more readily on nanoscale nuclei of silica at high pH value, which

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guarantees relative homogeneity of La^{3+} and Si^{4+} in the precursor. Besides homogeneity, this method allows additional removal of detrimental impurities and unwanted reaction products. On the other hand, introducing azeotropic-distillation process can effectively eliminate water molecules on the surface of particles and reduce hard agglomeration between particles. Thus, well-dispersed nanopowder precursors and highly dense sintered pellets (>95%) were obtained. As a result, the ionic conductivities of the apatite electrolyte prepared by this method are much higher than that prepared by conventional solid-state reaction method and wet-chemical methods.

2. Experimental

2.1. Sample preparation

The silica source for the synthesis of the lanthanum silicate $La_{9.33}(SiO_4)_6O_2$ was sodium silicate ($Na_2O\cdot nSiO_2$, $n\approx 3.2$). The dilute sodium silicate solution was filtered and then penetrated through strongly acidic cationic-exchange resin to remove sodium ion. The silica content of the effluence was analyzed by chemical method. The resulting transparent solution was immediately mixed with the solution of high purity (99.9%) $La(NO_3)_3\cdot 6H_2O$ according to the molar ratio of La_2O_3:SiO_2 (9.33:6). Then the mixture was dripped into the solution of ammonium carbonate ($(NH_4)_2CO_3$) at room temperature under vigorous stirring. After aging for 2 h, the resultant colloid was filtered and washed repeatedly with deionized water to remove the remaining ammonium nitrate and other impurities to produce a gel. A small part of the as-prepared gel was dried in air and used for analyzing its phase composition. Other wet gel was stirred with *n*-butanol and distilled to remove water as azeotrope. The dehydrated powder was further dried in a vacuum oven at 60 °C for more than 12 h. The obtained powders were calcined at different temperatures for 2 h to examine the phase formation of apatite-type lanthanum silicates.

The calcined powders were uniaxially pressed (10 MPa) into pellets, subsequently cold isostatically pressed at 180 MPa pressure, and then sintered to1550 °C at a rate of 5 °C/min and held for 2 h before the samples were cooled to room temperature. The apparent densities of sintered pellets were determined using Archimedes principle; thus, the relative density was derived using the formula:

$$Relative\ density\ = \frac{Apparent\ density}{Theoretical\ density}. \tag{1}$$

2.2. Property measurements

Thermal decomposition of the precursor was monitored by Thermogravimetric and Differential Scanning Calorimeter (TG-DSC) with instrument NETZSCH STA 409 PC/PG in air atmosphere. The powder X-ray diffraction (XRD) intensities were recorded with X-ray diffractometer (PANalytical X'Pert PRO, Netherlands). The crystalline phases were analyzed with PANalytical X'Pert High Score Plus and identified using the International Centre for Diffraction Data (ICDD) Powder Diffraction Files (PDF). The impurity elements of the powders were determined by wavelength dispersive X-ray fluorescence (WDXRF) spectrometry (Bruker AXS, S4 PIONEER).

The size distribution and shape of the precursor and the azeotropic-distillation powder were observed using transmission electron microscopy (TEM, Tecnai G^2 20, FEI Company, Netherlands). Some micro-structural aspects of sintered pellets were revealed by scanning electron microscopy (SEM, JSM-6700F). The surface of the pellets was treated before observation by polishing with SiC paper and a thermal etching at 1500 °C. INCA X-ray microanalysis system (OXFORD) was used to detect energy dispersive spectroscopy (EDS) for elemental analysis in micro-regions of sintered pellets.

2.3. Electrical measurements

Electrical conductivities of the sintered pellets were measured by electrochemical impedance spectroscopy using an impedance analyzer (PARSTAT 2273). Before measurements, both disc sides were coated with Pt paste and fired at 1000 °C for 1 h to ensure a good bond between the sample surfaces and the platinum electrodes. The measurements were conducted in air in the temperature range from 250 to 800 °C and in the frequency range from 0.1 Hz to 1 MHz with an increment of 50 °C. Curve fitting and resistance calculation were done by ZSimpWin software. The conductivities were calculated using the expression of $\sigma = l/SR$, where l is the sample thickness and S is the electrode area of the sample surface. Activation energies (E_a) were calculated by fitting the conductivity data to the Arrhenius relation for thermally activated conduction, which is given as:

$$\sigma T = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

where σ, σ_0, E_a, k, T are the conductivity, pre-exponential factor, activation energy, Boltzmann constant and absolute temperature, respectively.

3. Results and discussion

3.1. Analysis of XRD and TG-DSC of precursor

The phase of direct drying precursor and powders calcined at 500 °C and 800 °C was investigated by XRD and the results were shown in Fig. 1. The crystalline phase of the precursor was identified as $La_2(CO_3)_3\cdot 8H_2O$ (PDF No 01-073-0439) from a comparison of the registered patterns. However, the pattern did not present the diffraction peak of SiO_2. The reason may be attributed to the amorphous nature of silica. On the other hand, the great bulk of silica particles were enwrapped by $La_2(CO_3)_3\cdot 8H_2O$ precipitate, as observed in Fig. 4a.

In order to determine the high-temperature properties of the precursor, for example, the decomposition temperature of the components, phase formation and transition temperatures, the drying precursor was investigated by TG-DSC, as shown in Fig. 2. The TG curve illustrates four distinct stages of weight loss with ~46% total weight loss. The first abrupt weight loss between 30 and 280 °C was associated with an endothermic peak at ~104 °C in the DSC curve. This was ascribed to the loss of water molecules of $La_2(CO_3)_3\cdot 8H_2O$ and the value of weight loss 23.6% was in good agreement with the calculated value of 23.9% for the removal of 8 water molecules. The second and the third weight loss (total 14.3%) between 280 and

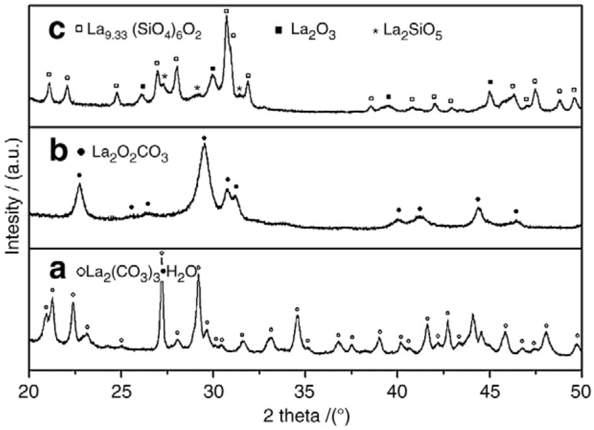

Fig. 1. XRD patterns of direct drying precursor (a), powder calcined at 500 °C (b) and 800 °C (c).

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