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Journal of Alloys and Compounds 456 (2008) 234–238

Journal of ALLOYS AND COMPOUNDS

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Synthesis and characterization of nanocrystalline $La_2Mo_2O_9$ oxide-ion conductor by a novel polyaspartate precursor method

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Received 28 December 2006; received in revised form 31 January 2007; accepted 1 February 2007
Available online 6 February 2007

Abstract

A nanocrystalline $La_2Mo_2O_9$ oxide-ion conductor was synthesized by a novel poylaspartate precursor method at very low temperature of 430 °C. The obtained product was characterized by XRD, TEM, dilatometer, SEM and AC impedance spectroscopy. Due to nanocrystalline nature, $La_2Mo_2O_9$ could be sintered to a density more than 97% of theoretical density even at relatively low temperature of 800 °C. The sintered $La_2Mo_2O_9$ sample exhibited a conductivity of 0.16 S/cm in air at 750 °C. In addition, the ionic transport number of $La_2Mo_2O_9$ was determined by modified electromotive force method in the temperature range of 600–800 °C and it remains higher than 99% ($t_o > 0.99$) in air.

Keywords: $La_2Mo_2O_9$; Nanocrystalline powder; Polyaspartate precursor; Sintering; Ionic conductivity

1. Introduction

Oxide-ion conductors with high conductivity of oxygen ions have been attracting considerable interests because of their potential applications in solid oxide fuel cells (SOFC), oxygen pumps, oxygen sensors and oxygen-permeable membrane catalysts [1–3]. The main oxide-ion conductors known to date belong to four distinct structure groups, i.e., fluorite type, deficient perovskites, Aurivillius type phases and pyrochlores [4–7]. Among the all oxide-ion conductors, the most widely studied and commonly used is yttria stabilized zirconia (YSZ), which had been successfully applied in SOFC and oxygen sensors [1–3]. However, one of the main limiting factors associated with their use is their relatively low oxide-ion conductivity at below 1000 °C. Therefore, much of the research carried out in this field has been focused on the search for materials with high conductivity at lower temperatures.

Recently, Lacorre et al. [8,9] reported a new kind of oxide-ion conductor, lanthanum molybdate ($La_2Mo_2O_9$) with a cubic structure, which exhibited good oxygen ionic conductivity as high as 0.06 S/cm at 800 °C and this is higher than the YSZ at intermediate temperature. But in most of these studies, $La_2Mo_2O_9$ has been synthesized using solid-state reactions [8–14] that involve, the mechanical mixing of the component oxides followed by high temperature heating and extended grinding. These synthetic conditions require long-range diffusion of the reactants, which may result in inhomogeneity, abnormal grain growth, poor control of stoichiometry and low sinterability. In order to overcome the above drawbacks, some wet chemical methods have been proposed for the preparation of $La_2Mo_2O_9$ powder [15–20]. These methods have some advantages such as good control of stoichiometry, relatively shorter processing time and production of submicron-sized particles with narrow size distribution. However, these methods require high sintering temperature (≥1000 °C) to achieve the desired density. Such high sintering temperatures leave very little margin for the microstructural control of the resultant ceramics. Nanocrystalline powders provide faster densification kinetics, lower sintering temperatures, better mechanical properties of the electrolytes and generally improve the electrical properties [21]. In this respect, it is important to develop powders of high quality with particle size in the nanometric range. The synthesis of nanocrystalline $La_2Mo_2O_9$ by different precursor methods such as citrate, precipitation, acetylacetonate and freeze–dried methods are reported very recently [22,23], but these synthetic procedures are tedious and time-consuming, which involves

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doi:10.1016/j.jallcom.2007.02.007

many complicated pretreatment processes. To overcome these drawbacks, we have reported very recently the synthesis of nanocrystalline $La_2Mo_2O_9$ by polymer pyrolysis method [24].

In this paper, we report at the very first, the synthesis of $La_2Mo_2O_9$ nanoparticles in a very pure state by a novel combustion method using aspartic acid as the polymerizable combustion fuel at very low temperature of 430 °C. The obtained product was characterized by XRD and TEM analysis. In addition sinterability, conductivity and ionic transport number were also studied.

2. Experimental

The nanocrystalline $La_2Mo_2O_9$ was synthesized by using aspartic acid as a polymerizable combustion fuel. The flow chart for the synthesis of $La_2Mo_2O_9$ is shown in Fig. 1. A stoichiometric amount of lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$), were taken along with aspartic acid and made into a homogeneous solution with triple distilled water. The stoichiometry amount of the redox mixture used for the combustion reaction was calculated based on the total oxidizing (O) and reducing (F) valencies of the components which serve as the numerical coefficient for the stoichiometric balance to equivalent ratio (ϕ_e) was maintained at unity (O/F), so that the heat released by the combustion is maximum [25]. The resultant homogeneous solution was evaporated to dryness by heating at 100 °C on a hot plate with continuous stirring. As the water evaporated, the solution became viscous brown colour gel. The temperature of the hot plate was then kept at 200 °C undergoes a thermal polymerization to form well-distributed polyaspartate of La–Mo precursor powder. Based on the results of thermal analysis (Perkin Elmer TG/DTA, Model: Pyris Diamond), the precursor powder was heated to 430 °C for 4 h to get the nanocrystalline $La_2Mo_2O_9$ powder. The room temperature X-ray powder diffraction (XRD) data were collected on a diffractometer (Model: Philips X'Pert MPD®) with Cu Kα radiation. Data were recorded in the 2θ-range of 20–70° with 0.02° step. The particle size and morphology of the synthesized $La_2Mo_2O_9$ powder was observed by JEOL-Transmission electron microscopy (Model: 1200 EX).

The synthesized nanocrystalline $La_2Mo_2O_9$ powder was pressed at 150 MPa into a pellet with 10 mm diameter and 1.5–2 mm thickness using a die. The green density of pellet is ~62% of theoretical density. Non-isothermal sintering behaviour of the green pellet was measured on a dilatometer (Model: Netzsch, DIL 402C) from room temperature to 900 °C at a heating rate of 5 °C/min and a cooling rate of 5 °C/min. Isothermal sintering was performed on the green pellet using a heating rate of 5 °C/min and a holding time of 5 h at various temperatures (600–900 °C). The density of the sintered pellets were also determined by the Archimedes' method using distilled water as the immersion medium. The microstructure of the sintered pellet was monitored by JEOL-Scanning electron microscopy (Model: JSM-840A).

The synthesized nanocrystalline $La_2Mo_2O_9$ powder was pressed into 10 mm diameter and 1.5–2 mm thick pellet at 150 MPa to perform the electrical characterization. The resultant pellet was sintered in air at 800 °C for 5 h. Pt-paste electrodes were painted on each side of the pellet and then fired at 800 °C for 15 min to ensure maximum conductivity and adherence. The sample was characterized by AC impedance spectroscopy (Solartron 1260) in atmospheric air, using four Pt wires [26]. The measuring frequency range was 0.1 Hz to 1 MHz with an applied voltage of 25 mV in the temperature range of 800–550 °C and 200 mV in the temperature range of 550–300 °C. Analysis of the impedance spectra was made by equivalent circuits using the ZView program [27]. The oxygen-ion transference number was determined by the modified electromotive force (EMF) and faradaic efficiency (FE) methods, taking electrode polarization into account [28,29]. This measurement was carried out under zero oxygen chemical potential gradient in air at 600–800 °C.

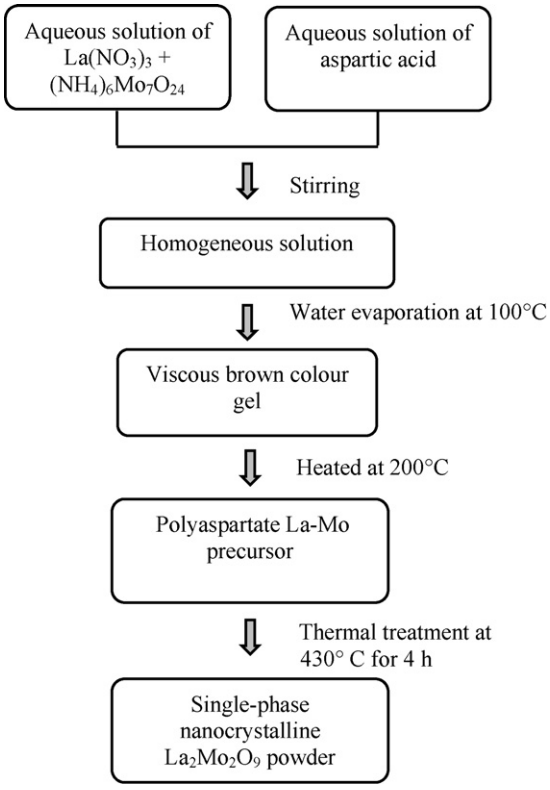

Fig. 1. Flow chart for the synthesis of nanocrystalline $La_2Mo_2O_9$ powder.

3. Results and discussion

Polyaspartic acid is a long chain linkage of aspartic acid (amino acid). Hence it has the dual nature. It can act as an excellent fuel as well as good dispersing agent [30]. Aspartic acid easily undergoes thermal polymerization [31], to form well-distributed polyaspartates of La–Mo precursor. In the polyaspartate precursor, the metallic La and Mo ions are dispersed homogeneously throughout the polymer matrix. Such a structure effectively controls the particle size to get the nanocrystalline particles. Moreover, this uniform immobilization of metallic ions in the polymer chain favours the formation of uniformly distributed solid solution of metallic oxide and also avoids the agglomeration of nanoparticles during the combustion process.

The TG/DTA curve for the La–Mo precursor sample is shown in the Fig. 2. The weight loss of the precursor occurs in three

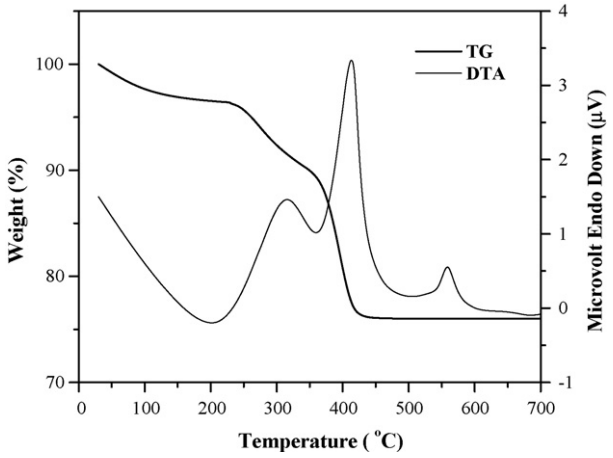

Fig. 2. TG/DTA curves for La–Mo precursor sample.