Solid State Ionics 181 (2010) 1415–1419

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Synthesis, ionic conductivity, and chemical compatibility of garnet-like lithium ionic conductor $Li_5La_3Bi_2O_{12}$

Y.X. Gao [a], X.P. Wang [a], W.G. Wang [b], Z. Zhuang [a], D.M. Zhang [a], Q.F. Fang [a,*]

[a] Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[b] College of Physics and Electronic Information, Yan'an University, Yan'an 716000, People's Republic of China

ARTICLE INFO

Article history:
Received 8 January 2010
Received in revised form 26 June 2010
Accepted 20 August 2010

Keywords:
Lithium ionic conductor
$Li_5La_3Bi_2O_{12}$
Pechini method
Ionic conductivity

ABSTRACT

Garnet-like $Li_5La_3Bi_2O_{12}$ powders with particle size of 80–100 nm were prepared by the Pechini method using lithium carbonate, bismuth nitrate, and lanthanum nitrate as precursors, and high density $Li_5La_3Bi_2O_{12}$ ceramics were synthesized at 1023 K from these powders. The lowest temperature to synthesize the pure garnet-like $Li_5La_3Bi_2O_{12}$ phase is only 923 K by the Pechini method, 125 K lower than that in the solid state reaction method, and the reaction time in the Pechini method (~5 h) is much shorter than that in the solid state reaction route (~48 h). The total (bulk plus grain boundary) conductivity of polycrystalline $Li_5La_3Bi_2O_{12}$ ceramics prepared by the Pechini method was as high as 2.4×10^{-5} S/cm at room temperature with an activation energy of 0.40 eV. The $Li_5La_3Bi_2O_{12}$ compounds were chemically stable against the widely used cathode materials $LiCoO_2$ up to 873 K but not chemically stable against the $LiMn_2O_4$ if the temperature is higher than 673 K.

1. Introduction

Metal oxide materials showing high lithium ionic conduction are particularly attractive in recent years owing to their potential applications as solid electrolytes in lithium ionic secondary battery and electrochemical devices [1]. So far, fast lithium ionic conduction has been reported in a wide range of materials, such as $Li_{14}ZnGe_4O_{16}$ (LISCION) [2,3], lithium nitride Li_3N [4], Li-β-alumina [5,6], NASICON-type $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ [7,8], and perovskite-type $(La,Li)TiO_3$ (LLT) [9–12]. Among the above mentioned lithium electrolytes, perovskite-type LLT had been recognized as one of the best conductors exhibiting a bulk lithium ionic conductivity over 1×10^{-3} S/cm with an activation energy of 0.4 eV and a total (bulk plus grain boundary) conductivity of 7×10^{-5} S/cm at room temperature [13]. Furthermore, total lithium ionic conductivity at room temperature as high as 10^{-3} S/cm has been realized in several systems, for example NASICON-type $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ [7,8] and $Li_7P_3S_{11}$ [14]. However, the low electrochemical stability limits the actual application of such highly conductive phases in rechargeable lithium batteries.

Garnet-like metal oxides $Li_5La_3M_2O_{12}$ (M = Nb, Ta, Bi) were found to be a novel class of fast lithium ionic conductors [15–21] and exhibit high lithium ionic conductivity and chemical inertness versus Li, making them promising for application as electrolyte in all solid state lithium secondary batteries. Among these garnet-like lithium electrolytes, the bismuth containing compound was noted to have the highest bulk ionic conductivity of 4.0×10^{-5} S/cm at room temperature with a low activation energy of 0.49 eV (from 22 °C to 100 °C), which was attributed to the largest cell parameter compared with the Nb and Ta containing compounds [20].

Generally, there are two ways to synthesize the metal oxide lithium electrolytes: one is the conventional solid state reaction from mixtures of oxide, carbonate, hydroxide, etc; the other is the sol–gel method based on hydrolysis and condensation of alkoxide and nitrate. In the solid state reaction routes, relatively high reaction temperature and long reaction time are necessary. Taking $Li_5La_3Bi_2O_{12}$ compound [20] as an example, the reported lowest synthesis temperature is about 1048 K and the reaction time at such high temperature is as long as 48 h. In such astringent synthesis conditions it is difficult to control the chemical stoichiometry of $Li_5La_3Bi_2O_{12}$ compound owing to the volatile loss of lithium and bismuth components.

In the sol–gel synthesis route however, the synthesis temperature and reaction time are much lower and shorter than in the solid state reaction method, respectively, since the starting materials can be mixed at the atomic or molecular level. Moreover, uniform particle size distribution and small particle size at the nanometer level will obviously enhance the sintering activity of the powders and therefore increase the bulk density of the ceramics. Owing to such evident advantages, the sol–gel method has been widely used to prepare lithium ionic electrolytes [21–24]. So far however, the $Li_5La_3Bi_2O_{12}$ series are unexceptionally synthesized by the conventional solid state reaction method.

In the present investigation, the nanocrystalline $Li_5La_3Bi_2O_{12}$ powders were synthesized by the Pechini method using the metal inorganic salts as chemical precursors, deionized water as solvent,

---

* Corresponding author. Tel.: +86 551 5591459; fax: +86 551 5591434.
E-mail address: qffang@issp.ac.cn (Q.F. Fang).

0167-2738/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2010.08.012

citric acid as chelating agent, and polyethylene glycol as surface active agent, respectively. The electrical property of the bulk $Li_5La_3Bi_2O_{12}$ ceramics and the chemical compatibility between nanocrystalline $Li_5La_3Bi_2O_{12}$ powders and the widely used cathode materials ($LiCoO_2$ and $LiMn_2O_4$) were studied.

2. Experimental

2.1. Preparation of $Li_5La_3Bi_2O_{12}$

The $Li_5La_3Bi_2O_{12}$ was prepared in open air with analytical reagents of lithium carbonate (Li_2CO_3, 98%), bismuth nitrate ($Bi(NO_3)_3$•$5H_2O$, 99%) and lanthanum nitrate ($La(NO_3)_3$•$6H_2O$, 99%) as raw materials. The amount of the selected chemical precursors was weighted in molar ratio of the components of $Li_5La_3Bi_2O_{12}$.

In the synthesis process of $Li_5La_3Bi_2O_{12}$ precursor, Li_2CO_3 was firstly dissolved in nitric acid to prepare lithium nitrate and then the deionized water was introduced to prepare transparent solution under vigorous stirring. Then the corresponding amount of La $(NO_3)_3$•$6H_2O$ was poured into the above solution and citric acid (designated as CA) was added at a molar ratio of CA: cationic ion (denoted as CI, including Li^+, La^{3+} as well as the subsequently added Bi^{5+}) = 1:1 to avoid precipitation and to chelate cationic ions [25]. After that, the corresponding molar mass of $Bi(NO_3)_3$•$5H_2O$ was added into the above mixed solution and an appropriated amount of polyethylene glycol (designated as PEG) was added as surface active agent. The pH value of the solution was maintained at a constant value of 0.5 by dripping nitric acid in time. The solution was stirred vigorously at 333 K until a transparent gel was formed. The final yellow gel was heated at 373 K for 12 h and then calcined between 873 K and 973 K for 5 h to obtain pure phase $Li_5La_3Bi_2O_{12}$ powders with different particle size.

To prepare bulk ceramic samples for electrical conductivity measurements, the $Li_5La_3Bi_2O_{12}$ powders calcined at 923 K was sufficiently ground in an agate mortar and then pressed into pellets at an isostatic pressure of 300 MPa. Dense $Li_5La_3Bi_2O_{12}$ pellets (about 1.2 mm in thickness and 8.2 mm in diameter) were obtained by sintering the pressed pellets at 1023 K in air for 5 h.

2.2. Characterization of $Li_5La_3Bi_2O_{12}$

The decomposition behavior of gels dried at 373 K for 12 h was monitored on a thermo-gravimetric analyzer (Pyris 1 TGA, Perkin-Elmer) in air with a heating rate of 10 K/min. The powder X-ray diffraction (XRD) patterns were recorded on a θ/θ Bragg–Brentano X'Pert MPD PRO diffractometer (Cu Kα1 + 2 radiations) at room temperature in a scanning range from 10° to 80° with a step of 0.033°. Structural refinement was done using the Fullprof suite of Rietveld software, in which the pseudo-Voigt function was used as the profile function. The surface morphology of powders calcined at different temperatures and the bulk ceramic was characterized by field-emission scanning electron microscope (FESEM, Sirion 200, FEI).

Impedance spectra of the bulk $Li_5La_3Bi_2O_{12}$ electrolyte at different temperatures were isothermally collected in air on a computer-controlled frequency response analyzer (Hioki 3531 Z-Hitester) in the range of 42 Hz to 5 MHz. The amplitude of the applied voltage is 0.5 V. Silver electrodes were closely affixed to the both sides of wafer-shaped sample by firing the silver paste at 600 °C for 1 h. Prior to each measurement, the sample was stabilized at a given temperature for at least 30 min to ensure thermal equilibrium.

2.3. Chemical compatibility between $Li_5La_3Bi_2O_{12}$ and lithium battery cathode materials

Chemical compatibility of $Li_5La_3Bi_2O_{12}$ with the commercially used lithium battery cathode materials $LiCoO_2$ and $LiMn_2O_4$ was researched by examining the phase composition after the 1:1 wt.% mixed powders were heated between 573 K and 873 K for 24 h in air. In this investigation, the $LiCoO_2$ and $LiMn_2O_4$ powders were also prepared by the sol–gel method, as described in Refs. [26,27]. Prior to heating treatment, the mixture of the cathode powders and $Li_5La_3Bi_2O_{12}$ powders were ball-milled with zirconia balls in ethanol for 12 h in order to completely mix the powders.

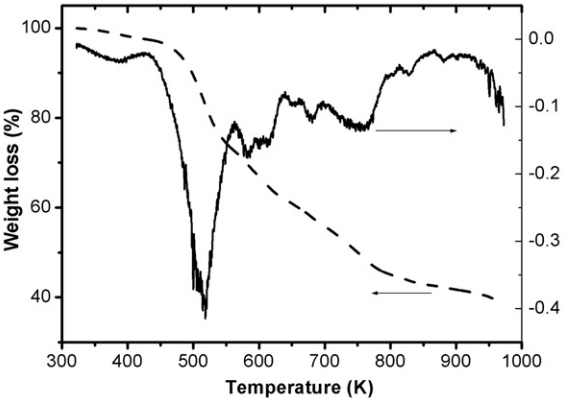

Fig. 1. TGA curves and its derivative of the $Li_5La_3Bi_2O_{12}$ gels obtained in air with a heating rate of 10 K/min.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the TGA curve and the corresponding derivative curve of the dry gel fired in air with a heating rate of 10 K/min in the temperature range of 323–973 K. There are several weight loss steps, as evidenced more clearly by the peaks in the derivative curve. In the relatively low temperature range of 320–420 K there is a small weight loss (~2%) that can be attributed to the evaporation of remaining water. In the temperature range of 420–780 K, the largest step located around 500 K and several small steps at higher temperature appear, representing a total weight loss of 49%, which can be assigned to the volatile loss of the organic solvent and the decomposition of the polymer. The last step with 8% weight loss in the temperature range of 780–920 K may originate from the elimination of the residual carbon, as observed in other reports [28]. This indicates that the gel must be calcined at above 920 K to completely remove the impurity components.

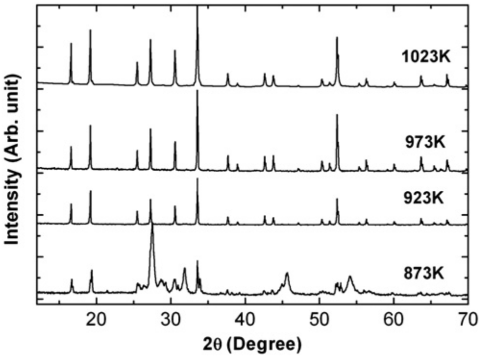

Fig. 2. Powder XRD patterns of $Li_5La_3Bi_2O_{12}$ precursors calcined at 873 K, 923 K and 973 K, respectively and the pattern of $Li_5La_3Bi_2O_{12}$ nanocrystalline powders sintered at 1023 K.