Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Li ion conduction of perovskite $Li_{0.375}Sr_{0.4375}Ti_{0.25}Ta_{0.75}O_3$ and related compounds

Yazhou Kong[a,b], Ying Li[a,b,*], Jiawei Li[a,b,d], Chuanbo Hu[a,b], Xiaohua Wang[c], Jiayao Lu[a,b]

[a] School of Metallurgy, Northeastern University, Shenyang 110819, China
[b] Liaoning Key Laboratory for Metallurgical Sensor and Technology, Shenyang 110819, China
[c] College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun 113001, China
[d] Jiangsu Lithitech Co. Ltd, Changzhou 213000, China

ARTICLE INFO

Keywords:
Conductivity
Ceramics
Perovskite
Solid electrolyte
Isostructure

ABSTRACT

In this work, perovskite-structured $Li_{0.375}Sr_{0.4375}M_{0.25}N_{0.75}O_3$ (M = Ti, Sn, N = Nb, Ta) solid electrolytes were synthesized by conventional solid state reaction method. Phase compositions, fractured morphologies and conductivities of these compounds were investigated by X-ray diffraction, scanning electron microscope and AC-impedance spectroscopy, respectively. X-ray diffraction analysis confirms that all of $Li_{0.375}Sr_{0.4375}M_{0.25}N_{0.75}O_3$ (M = Ti, Sn, N = Nb, Ta) ceramics present perovskite structure. Pure $Li_{0.375}Sr_{0.4375}Ti_{0.25}Ta_{0.75}O_3$ and $Li_{0.375}Sr_{0.4375}Sn_{0.25}Ta_{0.75}O_3$ perovskite ceramics were obtained. But impurities were detected in $Li_{0.375}Sr_{0.4375}Ti_{0.25}Nb_{0.75}O_3$ and $Li_{0.375}Sr_{0.4375}Sn_{0.25}Nb_{0.75}O_3$. Among all investigated compounds, $Li_{0.375}Sr_{0.4375}Ti_{0.25}Ta_{0.75}O_3$ shows the highest total ionic conductivity of 2.60×10^{-4} S cm^{-1} at room temperature and the lowest activation energy of 0.347 eV. Conductivities of $Li_{0.375}Sr_{0.4375}Sn_{0.25}Ta_{0.75}O_3$ and $Li_{0.375}Sr_{0.4375}Sn_{0.25}Nb_{0.75}O_3$ were 4.4×10^{-5} S cm^{-1} and 1.82×10^{-6} S cm^{-1}, respectively. Their conductivities were much lower than $Li_{0.375}Sr_{0.4375}Ti_{0.25}Ta_{0.75}O_3$ and $Li_{0.375}Sr_{0.4375}Ti_{0.25}Nb_{0.75}O_3$.

1. Introduction

Research towards novel Li ions conducting ceramics is attractive due to the interest for solid state batteries based on solid electrolyte [1]. A variety of oxides have been considered to be used as lithium ion conducting materials. Based on structure of oxides, these lithium ion conducting materials can be classified into several groups, including (a) simple oxide salts [2]; (b) LISICON type [3,4] $Li_{2+2x}Zn_{1-x}GeO_4$; (c) NASICON [5,6] type compounds $Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$ and $Li_{1.3}Ti_{1.7}Ge_{0.3}(PO_4)_3$; (d) garnet-type $Li_7La_3Zr_2O_{12}$ [7] and (f) perovskite-structured $La_{2/3-x}Li_{3x}TiO_3$ [8]. Among these solid state lithium ion conducting materials, perovskite (ABO_3) type $Li_{0.5}La_{0.5}TiO_3$ (LLTO) is one of the most promising solid electrolytes. LLTO exhibits high bulk conductivity of 10^{-3} S cm^{-1}, which is attractive for the application in all solid state Li ion batteries [9]. However, there are two drawbacks for LLTO ceramics, (a) low grain boundary conductivity (10^{-5} S cm^{-1}) at room temperature and (b) Ti^{4+} in LLTO can be reduced to Ti^{3+} when it is in contact with metallic lithium [10–13]. A lot of works have been done aiming at improving performance of perovskite type solid electrolytes. Thangadurai et al. [14] studied crystalline structure and ionic conductivity of a series of novel perovskite Li ion conductors with the formula of $LiSr_{1.65}B_{1.3}B'_{1.7}O_9$ (B = Ti, Zr; B′ = Nb, Ta). These compounds present perovskite structure and high Li ion conductivity. Researchers [15–18] further optimized composition of $LiSr_{1.65}B_{1.3}B'_{1.7}O_9$ (B = Ti, Zr; B′ = Nb, Ta). They found that $Li_{0.375}Sr_{0.4375}M_{0.25}N_{0.75}O_3$ (M = Zr, Hf; N = Nb, Ta) exhibits the highest Li ion conductivity among corresponding material system. Furthermore, sintering additives and powder-bed sintering method are beneficial to improve conductivity of solid electrolyte [19–21].

Sn^{4+} and Ti^{4+} have similar chemical and physical properties with Zr^{4+} and Hf^{4+}. So, $Li_{0.375}Sr_{0.4375}M_{0.25}N_{0.75}O_3$ (M = Ti, Sn; N = Nb, Ta) may have high conductivity as well as $Li_{0.375}Sr_{0.4375}M_{0.25}N_{0.75}O_3$ (M = Zr, Hf; N = Nb, Ta). But as far as we know, $Li_{0.375}Sr_{0.4375}M_{0.25}N_{0.75}O_3$ (M = Ti, Sn, N = Nb, Ta) have never been reported. In this work, the novel perovskite oxides $Li_{0.375}Sr_{0.4375}M_{0.25}N_{0.75}O_3$ (M = Ti, Sn, N = Nb, Ta) were synthesized and characterized. Furthermore, structure and conductivity of derivative $Li_{0.5}Sr_{0.25}M_{0.5}W_{0.5}O_3$ (M = Ti, Sn) were also studied (shown in Supplementary materials).

2. Experimental

$Li_{0.375}Sr_{0.4375}M_{0.25}N_{0.75}O_3$ (M = Ti, Sn, N = Nb, Ta) ceramic samples were synthesized by solid state reaction method. Stoichiometric

* Correspondence to: No. 3-11, Wenhua Road, Heping District, Shenyang 110819, China.
E-mail addresses: Li_ying2007@163.com, liying@smm.neu.edu.cn (Y. Li).

https://doi.org/10.1016/j.ceramint.2017.11.186
Received 31 October 2017; Received in revised form 7 November 2017; Accepted 25 November 2017
0272-8842/ © 2017 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

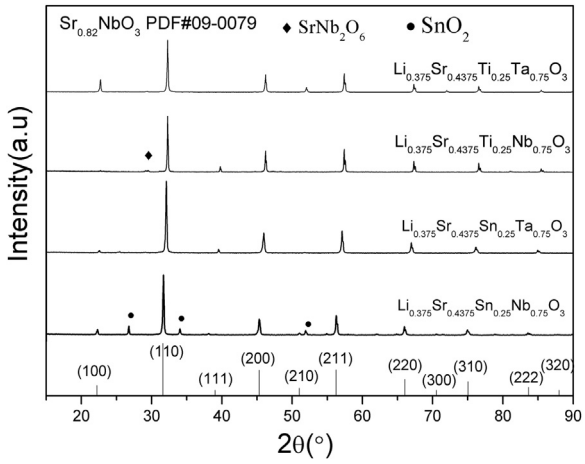

Fig. 1. XRD patterns of ceramics.

Table 1
Compositions and lattice parameters of ceramics.

Compounds	Compositions	Lattice Parameter/ Å
LSTT	$Li_{0.375}Sr_{0.4375}Ti_{0.25}Ta_{0.75}O_3$	3.979
LSST	$Li_{0.375}Sr_{0.4375}Sn_{0.25}Ta_{0.75}O_3$	3.986
LSTN	$Li_{0.375}Sr_{0.4375}Ti_{0.25}Nb_{0.75}O_3$	3.979
LSSN	$Li_{0.375}Sr_{0.4375}Sn_{0.25}Nb_{0.75}O_3$	4.003

amounts of Li_2CO_3, $SrCO_3$, TiO_2, SnO_2, Nb_2O_5, and Ta_2O_5 were used as starting material. 20 wt% excess Li_2CO_3 was added into starting materials due to the evaporation of lithium during high temperature sintering processing. These raw materials were mixed thoroughly by ball-milling with ethanol as solvent. The ground powders were then transferred into a glass dish to evaporate solvent. Then the powders were transferred into an alumina crucible and heated to 1100 ˚C for 15 h in a furnace. The resultant powders were pressed into pellets with the diameter of 15 mm by using isostatic pressing at 200 MPa for 9 min. These pellets were sintered in the furnace in a covered zirconia crucible (1450 ˚C for Sn-containing compounds and 1350 ˚C for Ti-containing compounds, respectively). Each pellet was covered by corresponding mother powder during sintering.

Table 2
Densities, total conductivities and activation energies of ceramic pellets.

Samples	Density/g cm^{-3}	Conductivity/S cm^{-1}	Activation energy/eV
LSTT	3.92	2.60×10^{-4}	0.347
LSST	5.32	0.46×10^{-4}	0.377
LSTN	3.51	0.44×10^{-4}	0.405
LSSN	4.07	1.82×10^{-6}	0.420

X-ray diffraction patterns were recorded with panalytical X' Pert PRO with a Cu Kα radiation in a range of 2θ from 5˚ to 90˚. Ionic conductivities of ceramic pellets were determined via impedance spectra using a Solartron 1260 impedance analyzer. To carry on the impedance measurements, Au ink was painted on both surfaces of ceramic pellets as electrode. The measurements were performed in a range of frequencies from 10 MHz to 1 Hz and in a temperature range from 15 ˚C to 120 ˚C with an applied voltage of 500 mV. The fracture microstructure of the ceramic pellets was recorded using scanning electron microscope (SEM) with JEOL-7600F.

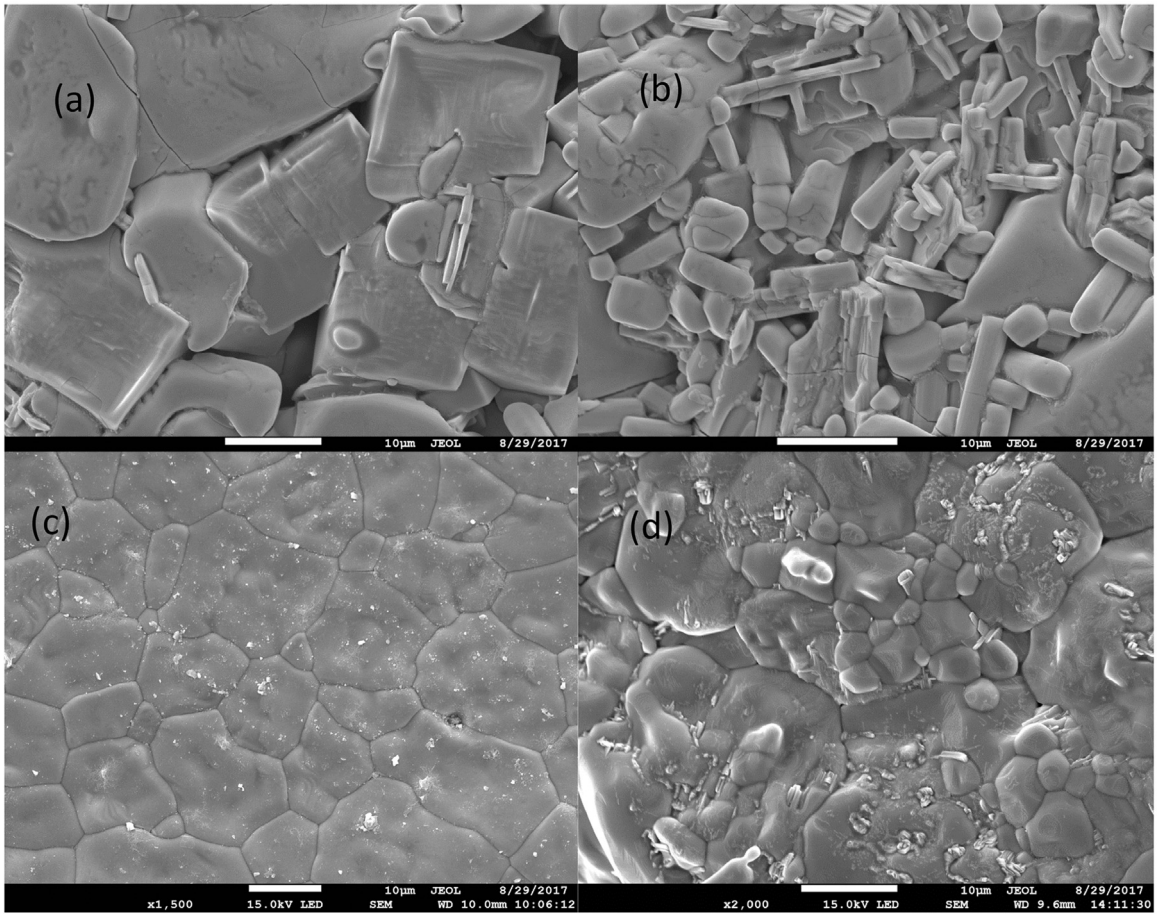

Fig. 2. SEM images of LSSN (a), LSTT (b), LSST (c) and LSTN (d).

Download English Version:

https://daneshyari.com/en/article/7888325

Download Persian Version:

https://daneshyari.com/article/7888325

Daneshyari.com