High oxide ion conducting solid electrolytes of bismuth and niobium co-substituted La$_2$Mo$_2$O$_9$

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ABSTRACT

Bismuth and niobium co-substitutions on lanthanum molybdate with the nominal formula La$_{2-x}$Bi$_x$Mo$_{2-x}$Nb$_x$O$_{9-\delta}$ ($x = 0$–0.24) (LBMN) are synthesized via solid state reaction. Their structures and properties are studied by powder X-ray diffraction (XRD), thermal analysis, electron diffraction, and impedance spectroscopy. XRD experiments and thermal analysis demonstrate the stabilization of the high temperature cubic phase when $x \geq 0.04$. Studies of the polar area in electron diffraction confirm the inhomogeneous nature of the composition. A modified Debye relaxation approach is employed to learn the ion dynamics, and it shows non-monotonic functions in relaxation parameters τ_0 and the activation energy E_a, which is in agreement with the volume variation of the basic [O1La3Mo] tetrahedral as a new structural description. As a result, the LBMN system exhibits good performance in electrical conductivities at high temperature, and shows a decrease of the average thermal expansion coefficients (TECs) along the dopant content.

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Introduction

Oxide-ion conductors are used extensively for the electrochemical applications, such as oxygen separation, oxygen sensors, and the fuel cell component as electrolytes [1–3]. As a new generation of power system, solid oxide fuel cells (SOFCs) have gained considerable attention due to their high efficiency of energy conversion and environmental compatibility. Hydrocarbon fuels can be used directly without external reforming. Conventional SOFCs with stabilized ZrO$_2$ electrolytes require high operating temperatures accompanying with high manufacturing cost and low reliability. La$_2$Mo$_2$O$_9$ (LMO), with higher oxide-ion conductivity than conventional yttrium stabilized zirconias (YSZ), is considered to be one potential electrolyte material in SOFCs [4–6], although the stability of

LMO in reduced environments is still need solved. Significant amounts of work have been carried on the so-called LAMOX family derived from the parent compound La$_2$Mo$_2$O$_9$ as new fast oxide-ion conductors.

Lone pair substitution (LPS) conception was introduced to learn the structure of LMO compared with β-SnWO$_4$. The substitution of cations Sn^{2+} with lone-pair by La^{3+} without lone-pair electrons will bring extra vacancies at the anionic sublattice [5,6]. O sites in La$_2$Mo$_2$O$_9$ are denoted as full occupied O1 and partial occupied O2 and O3. The oxygen-ion diffusion is enhanced by these high concentrations of intrinsic oxygen vacancies in the crystal lattice. As known, La$_2$Mo$_2$O$_9$ ceramic experiences a phase transition from cubic β-LMO at high temperature to monoclinic α-LMO at low temperature with a sharp decrease in ionic conductivity. Meanwhile, the oxygen transport mechanism changes from a

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thermally activated Vogel-Tamman-Fulcher (VTF) type to thermally assisted Arrhenius type [7—9]. To avoid the ionic conductivity decrease, induced by the phase transition, various types of substitutions on La site (K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Pr^{3+}, Y^{3+}, Dy^{3+}, Sm^{3+}, Eu^{3+}, Nd^{3+}, Gd^{3+}, Bi^{3+}) [9—23] or Mo site (W^{6+}, Cr^{6+}, V^{6+}, Nb^{5+}, P^{5+}, S^{6+}) [24—31] have been devoted to the stabilization of high conductive β-phase. Some wet chemical routes have also been employed to study the LAMOX family, as the microstructure and the electrical properties of ceramics are closely related to the methods, i.e. the molten salt solvent method [32,33], freezing drying method [34], gel combustion method [35] and microwave assisted method [36,37]. In most of these cases, the substitutions can suppress the $\beta \rightarrow \alpha$ transition and retain the β phase to the room temperature. However, the parent β-LMO ceramic always exhibits higher conductivity at high temperature range compared with the β-LAMOX series.

Previous reports have demonstrated that the partial substitutions La^{3+} by lone-pair cations Bi^{3+} or Pb^{2+} can effectively suppress this phase transition, and their structural refinements were provided [9,10]. Through the studies of ionic displacements as well as the temperature factors, the increase of the conductivity at the high temperature range, for the VTF region, can be attributed to the new framework-assisted migration from O1 ions toward their intrinsically embedded vacancies at neighboring O2 and O3 sites [9]. The VTF behavior of conductivity can be regarded as a change from the static disorder to dynamic oxygen disorder in the LAMOX materials. However, it is curious about the way of the existence of the lone-pair electron, introduced by Bi^{3+}, when there is a single isovalent substitution. According to the LPS conception, it will remind us the oxygen depletion in this system. At the same time, in recent studies, Bi^{3+} can adopt highly asymmetric anion with the lone pair directing to vacancies, probed by Mohn et al., in learning the anionic conductor Bi_2O_3 [38,39]. Based on these, the lower value Nb^{5+} substituting on Mo^{6+} site is employed to balance the misfit of the oxygen site. A systematical investigation of the influence of bismuth and niobium double substitutions on the structural and electrical properties of the fast oxide-ion conductor LMO is presented. Interesting changes are expected in crystallographic and transport properties of this system. In search of a well-balanced point in this LAMOX family, we have extensively studied the pseudoternary system $La_2Mo_2O_9$-"$Bi_2Mo_2O_9$"-"$La_2Nb_2O_9$" (shown in Figure S1. The quotation marks are used because they do not exist in pure form). In the current paper, focused research will carry on the characterization of the $La_{2-x}Bi_xMo_{2-y}Nb_yO_{9-\delta}$ ($x = y$) series. A modified Debye relaxation model is employed to learn the diffuse anomalies in the ceramics. The effects of the substitution with the suppressed phase transition are investigated in detail on the ionic conduction and oxygen-ion diffusion of LMO.

Experimental

$La_{2-x}Bi_xMo_{2-x}Nb_xO_{9-\delta}$ ceramics ($x = 0$, 0.04, 0.08, 0.12, 0.16, 0.20 and 0.24, respectively) were synthesized by the conventional solid state reaction method with mixing appropriate amount of high purity La_2O_3, Bi_2O_3, Nb_2O_5 and MoO_3 raw powders. Prior to use, La_2O_3 was calcinated at 950 °C for 12 h in air to remove carbon dioxide and adsorbed water. The powders were mixed and then ball milled for 6 h with ethyl alcohol. After that, they were calcinated at 550 °C for 12 h in air, and ball milled again for 6 h. The obtained powders were compacted into pellets by cold isostatic pressing. In case of bismuth volatility, we dealt with the pellets by burying sintering process in air at 1050 °C-1100 °C for 12 h.

Thermal analyses were performed on a dilatometer (DIL 402C, Netzsch, Selb, Germany) from room temperature (RT) to 900 °C under air flow at a heating rate of 5 °C min^{-1}. Phase structures of powders and the sintered pellets were learned by XRD (XRD-7000, Shimadzu, Kyoto, Japan) with Cu radiation. Long-run diffractograms were collected in the Bragg angle (2θ) range from 10° to 130° for the structure determination. The full-pattern matching and structural refinements were carried by the Rietveld program FullProf [40]. The crystal structure was drawn using the Vesta software [41]. Archimedes method was employed to measure the specimen density. The theoretical density was calculated from the lattice parameter derived from the XRD diffraction pattern. The elaboration parameters and characteristics of the ceramics prepared are listed in Table 1. Transmission electron microscopy (TEM; Tecnai F30, FEI, Hillsboro, OR, USA) were used to get the lattice images with Inca energy-dispersive spectrometer (EDS) operated at the accelerating voltage of 300 kV. TEM specimens were prepared through grinding, cutting, dimpling and ion milling procedures from the as-sintered pellets. To minimize the residual stresses, the dimpled pellets were annealed at 500 °C for 2 h before Ar-ion milling. High temperature XRD (2θ, 10°-80°) was also conducted to investigate the phase transition ranging from RT to 900 °C. A stabilization time of 30 min was applied between each measurement.

Table 1 — Composition, synthesis temperature, density, crystal symmetry of the room temperature phase, thermal expansion coefficient and electrical conductivity for the $La_{2-x}Bi_xMo_{2-x}Nb_xO_{9-\delta}$ system.

x	T_{sint} (°C)	D_{obs}/D_{th} = density (%)	Symmetry	T_{tran} (°C)	$TEC_{580-800 \, °C}$ ($\times 10^{-6} \, K^{-1}$)	$\sigma_{800 \, °C}$ ($S \times cm^{-1}$)
0	1100	5.460/5.561 = 98.18	Monoclinic	580	20.3	0.08
0.04	1100	5.495/5.590 = 98.30	Cubic	497	17.8	0.035
0.08	1100	5.487/5.599 = 97.99	Cubic	500	17.64	0.042
0.12	1100	5.488/5.609 = 97.86	Cubic	502	17.96	0.123
0.16	1100	5.500/5.621 = 97.85	Cubic	507	17.19	0.071
0.20	1100	5.487/5.630 = 97.47	Cubic	510	16.82	0.111
0.24	1050	5.487/5.641 = 97.28	Cubic	513	16.51	0.93