

The effect of dual substitution of Na and Al on ionic conductivity of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics

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ABSTRACT

The Na and Al dual substitution $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ samples were synthesized by the conventional solid-state reaction method. The oxygen ion conductivity and migration in the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.02, 0.04, 0.06$ and 0.08) samples were investigated. The grain conductivity and relaxation activation energy of the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ samples show the trend of declining-rising-declining with the increase of Al-doped content. The highest grain conductivity can arrive at 0.0016 S/cm for the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.06$) sample at 673 K and the corresponding activation energy is about 0.80 eV , which are the lowest results of oxygen ion diffusion in the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.02, 0.04, 0.06$ and 0.08) samples. The mobile oxygen vacancy content decreases with increasing Al-doping content in the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ compounds. The sudden change of grain conductivity in NBT-NaAl6 sample may be from the lower activation energy and better oxygen vacancy mobility. These results are helpful to improve the electrical performance by doping methods.

Introduction

Oxide ion conductors are the basis of the solid oxide fuel cell (SOFC), oxygen separation membranes, oxygen pump and sensors, chemical looping devices *ect* [1–6]. Conventional solid oxide fuel cells with yttria-stabilized zirconia (YSZ) as electrolyte require very high operation temperature. The higher operation temperature of solid oxide fuel cells causes significant problems such as the reaction among the different constituent elements, thermal expansion coefficient mismatch of different composition materials and shortening the electrode materials service life. So, it is necessary for improving the performance and reducing the capitalized cost of SOFCs to reduce the operation temperature. It is one of the effective methods of reducing operation temperature to explore the novel electrolyte materials with higher conductivities in the lower temperature, e.g. in the range from 673 K to 873 K .

Some doped or co-doped ceria based solid electrolytes own higher oxide ionic conductivity at the middle temperature zone and have been considered as promising candidate electrolyte materials of middle-temperature SOFCs [7]. However, the application of the CeO_2 -based electrolyte materials was limited for the very high sintering temperature ($> 1673 \text{ K}$), lower mechanical behavior and higher electronic conduction in reducing atmosphere [8]. Recently, Li et al. found a

higher ionic conductivity for the Mg-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) materials. The improvement of NBT materials can be observed after doping with Mg^{2+} , which substitutes the tetravalent titanium ions on the B-sites of the perovskite NBT (Mg_{Ti}'') and introduces more oxygen vacancy content in the NBT compound [9]. Yang et al. reported that the bulk conductivity of the $\text{Na}_{0.5}\text{Bi}_{0.49}\text{TiO}_3$ (NB49T) compounds doped by the divalent cations (Ca^{2+} , Sr^{2+} and Ba^{2+}) can be obviously improved [10]. In addition, Na^+ ions were introduced into the NBT compound to form the solid solutions ($\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$). The grain conductivity of the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_{2.96}$ compound can reach $1.6 \times 10^{-3} \text{ S/cm}$ at 673 K , five times higher than that of the undoped NBT compound, indicating that Na^+ ion dopant is an effective way to enhance the oxygen ion conductivities of NBT compound [11]. However, there are few jobs on the electrical performance of A sites and B sites co-doped NBT compound. In this paper, Na^+ and Al^{3+} dual substitution NBT ceramics were prepared. The AC impedance spectroscopy was used to study the oxygen ionic conductivity of Na^+ and Al^{3+} ions dual substitution NBT ceramics. The dielectric relaxation spectroscopy was employed to investigate on the oxide ion migration mechanism Na^+ and Al^{3+} ions dual substitution NBT ceramics [12].

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Experimental procedure

Sample preparations

Na^+ and Al^{3+} co-doped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ samples were synthesized via conventional solid-state reaction method using commercially obtained Analytical reagent-grade powders Na_2CO_3 , Bi_2O_3 , TiO_2 and Al_2O_3 with purities > 99% as starting materials. Prior to weighting, the starting materials except for TiO_2 (dried at 1073 K for 8 h) are dried for 563 K for 8 h. The detailed synthesis process can be found in the ref.10. The obtained powders were pressed into the bar or pellet sample and then annealed at 1323 K for 6 h to receive the bar samples carried out the electrical performance measurements.

Structure and electrical measurements

The structures of the desired compounds were checked by X-ray diffraction (XRD, Bragg-Brentano X'Pert MPD PRO diffractometer) technique. The XRD patterns were recorded at room temperature in the 2θ range from 10° to 90° using $\text{Cu-K}\alpha$ radiation. The sintered samples were coated with silver paste on both sample surfaces as electrode for electrical test. The silver pastes were cured at 973 K for about 1 h. The dielectric and impedance parameters were measured by an Impedance Analyzer (IM 3536, Japan) instrument (10 Hz to 8 MHz).

Experimental results

Structural characteristic

Fig. 1 gives the room temperature XRD patterns of $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.02, 0.04, 0.06$ and 0.08) compounds. From the RT-XRD figures, it can be seen that there are no other peaks with the Na^+ and Al^{3+} ions introduced into the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ compound, indicates that $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.02, 0.04, 0.06$ and 0.08) compounds are the single perovskite structure.

Conductivity of $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ compounds

The impedance spectrum of $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.06$, NBT-Na4Al6) sample at 533 K were shown in Fig. 2. From this figure, three different semicircles could be obtained and the effects of grain, grain boundary and electrode reaction resistance could be separated, indicating that the impedance spectrum can be fitted by an

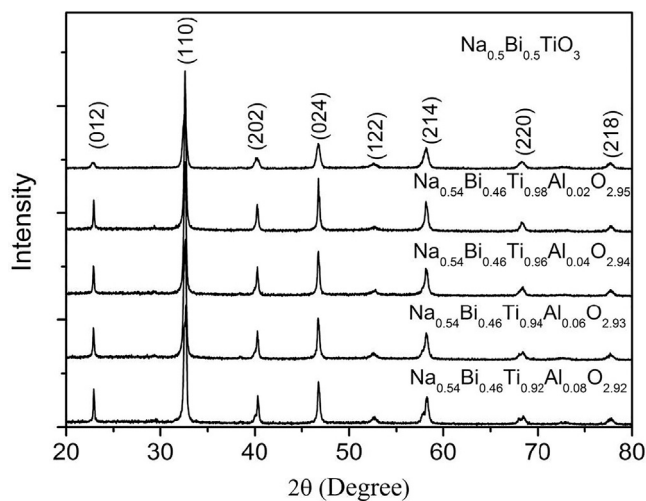


Fig. 1. The observed X-ray diffraction patterns at room temperature for the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ and $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.02, 0.04, 0.06$ and 0.08) compounds.

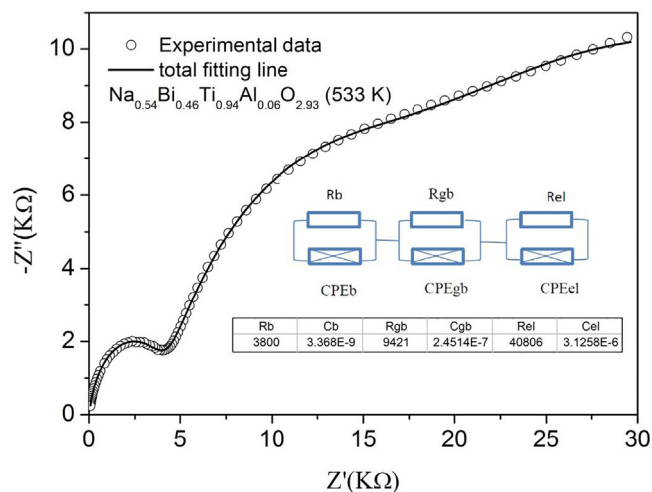


Fig. 2. The AC impedance spectra and the fitting lines of the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.06$) sample at 533 K in air. An equivalent circuit consisting of the three R-CPE elements in series is shown.

equivalent circuit consisting of three different R-CPE elements in series, corresponding to grain, grain boundary and electrode effects [11], seen in the inset. From the inset table in Fig. 2, the fitting values of C_b and C_{gb} are 3.369×10^{-9} F and 2.451×10^{-7} F, respectively, which are the representative values for relaxation processes of grain and grain boundary in oxygen ion conductors [11].

The grain conductivity can be thus calculated as $\sigma_b = L/(SR_b)$, where L and S are the length of the measuring sample and electrode surface area. The grain conductivities of the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{TiO}_3$ samples doped with different Al-doped content measured at 553 K, 593 K, 633 K and 673 K are given in Fig. 3. From this figure, the grain conductivities of $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ samples change non-monotonically with the different Al-doped content. With Al-doped content increasing ($x < 4$ mol%), grain conductivities of $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ samples decrease. And then grain conductivities increase with increasing Al-doped content from 4 mol% to 6 mol% and the highest grain conductivity arrives at 0.0016 S/cm for NBT-Na4Al6 sample at 673 K. Subsequently, the conductivities of the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ samples decrease with the increment of Al-doped content again. It is not difficult to find that the grain conductivity of the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.08$, NBT-Na4Al8) is lower than those of the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.02, 0.04$ and 0.06)

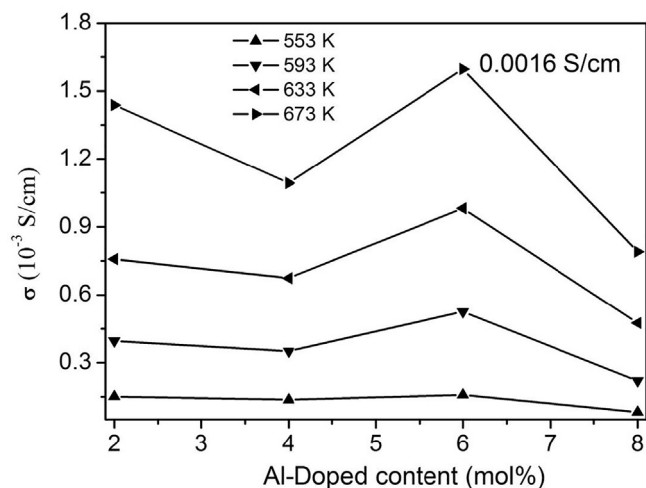


Fig. 3. The grain conductivities of the $\text{Na}_{0.54}\text{Bi}_{0.46}\text{Ti}_{1-x}\text{Al}_x\text{O}_{2.96-x/2}$ ($x = 0.02, 0.04, 0.06$ and 0.08) compounds measured at 553 K, 593 K, 633 K and 673 K.

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