

Effect on ionic conductivity of $\text{Na}_{3+x}\text{Zr}_{2-x}\text{M}_x\text{Si}_2\text{PO}_{12}$ (M=Y, La) by doping rare-earth elements

Qingkai Zhang¹, Feng Liang^{1,2*}, Tao Qu^{1,2}, Yaochun Yao¹, Wenhui Ma¹, Bing Yang¹ and Yongnian Dai¹

¹ Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China

² State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China

E-mail: liangfeng@kmust.edu.cn.

Abstract. NASICON structure solid electrolyte with the composition of $\text{Na}_{3+x}\text{Zr}_{2-x}\text{M}_x\text{Si}_2\text{PO}_{12}$ (M=La, Y) were prepared by solid-state method. The effects of La and Y doping on the density and ionic conductivity of NASICON solid electrolyte were investigated. The results show that the doping of La and Y can improve the ionic conductivity of NASICON structure solid electrolyte because of the higher carrier concentration, migration efficiency, and higher density. The $\text{Na}_{3.3}\text{Zr}_{1.7}\text{La}_{0.3}\text{Si}_2\text{PO}_{12}$ has the highest ionic conductivity of 6.7×10^{-3} S/cm at 25 °C.

1. Introduction

Safety accidents occur frequently for traditional battery based on liquid electrolytes. Therefore, researchers pay more attention to new battery systems by using solid-state electrolytes to replace liquid electrolytes, because these new batteries can completely solve the potential safety problems of batteries ^[1]. Sodium based solid-state electrolytes have attracted much attention because of their excellent performances and low cost compared with lithium-based solid-state electrolytes. NASICON-type $\text{Na}_{1+n}\text{Zr}_2\text{Si}_n\text{P}_{3-n}\text{O}_{12}$ ($0 \leq n \leq 3$) is a well-known family of sodium based solid-state electrolytes with excellent ionic conductivity, good chemical and thermal stability, since they were discovered by Hong ^[2] and Goodenough ^[3] in 1976. A three-dimensional network of ZrO_6 octahedral shares corners with PO_4/SiO_4 tetrahedral. The sodium ions are located in the interstitial sites in this framework. Within this series of compositions, the highest total ionic conductivity of 6.7×10^{-4} S/cm is obtained for $n=2$ ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) ^[2].

In particular, all-solid-state sodium-ion batteries with ceramic NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) structure electrolytes demonstrated to be a safe, inexpensive, and reliable alternative to other batteries ^[4-7]. Furthermore, sodium-air and sodium-sulfur batteries with a NASICON electrolyte have also shown promise as high energy density storage devices ^[8-11]. The high ionic conductivity of NASICON is required for application in solid-state battery. However, its Na^+ conductivity at room temperature is orders of magnitude lower than that of organic electrolyte counterparts ^[12]. Therefore, increasing the ionic conductivity of NASICON could both improve the power density of sodium based batteries and open up the possibility of application of room temperature sodium based batteries. The rare-earth element doping of NASICON with zirconium sites can increase the density of solid-state electrolyte ^[13]. In this study, La-doped, Y-doped, and undoped NASICON samples with high ionic conductivity



were prepared by the solid-state method. The reason of increase ionic conductivity by doping was explained by comparing the microstructure of these samples.

2. Experiment

NASICON samples of nominal composition $\text{Na}_{3.3}\text{Zr}_{1.7}\text{La}_{0.3}\text{Si}_2\text{PO}_{12}$ (La-doped), $\text{Na}_{3.2}\text{Zr}_{1.8}\text{Y}_{0.2}\text{Si}_2\text{PO}_{12}$ (Y-doped), and $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ were synthesized by conventional solid-state method^[10]. Stoichiometric amounts of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, ZrO_2 , SiO_2 , Y_2O_3 , La_2O_3 , and Na_2CO_3 were ball-milled with zirconia balls in a zirconia vessel for 30 min at 300 rpm using high-energy mechanical milling (HEMM). The mixed powder was calcined at 1100 °C for 12 h. The obtained powders were ball-milled using HEMM again for 18 h with zirconia balls using ethanol as dispersant. The resultant powder was shaped into disk by uniaxial pressing, which was followed by cold isostatic pressing at 200 MPa. Sintering was performed in air at 1225 °C for 15 h in an alumina crucible, during which the disk was embedded in the calcined powder to suppress Na volatilization. The heating rate for calcining and sintering was 3 °C/min.

The phase analysis was operated by a MiniFlex 600 diffractometer with Cu-K α radiation in the 2 θ range from 10° to 70° at a scanning step rate of 0.02 °/s as X-ray diffraction (XRD) analysis. The microstructure of the samples were observed by scanning electron microscopy (SEM) (VEGA-3SBH, Czech Republic). Density of the sintered pellets was measured by the Archimedes method. Ionic conductivity of Na^+ was measured by impedance spectroscopy at 25 °C using a 1260A impedance analyzer (Solartron, UK) with a modulation voltage of 100 mV in a frequency range of 20 to 8 MHz at 25 °C. The bulk and grain boundary conductivity of samples were calculated by using Zview software.

3. Results and Discussion

Figure 1 shows the XRD patterns of all samples. The peaks of undoped NASICON coincide with standard card (PDF84-1200). Monoclinic ZrO_2 was a common impurity for all samples because of the sodium and phosphorus volatilization at high temperature, which is generally observed in all types of NASICON^[14]. The XRD patterns of the doped samples shift slightly to a small angle with larger lattice parameter suggest successful doping of Y and La into the crystal lattice^[15, 16]. And the containing secondary phase of $\text{Na}_3\text{La}(\text{PO}_4)_2$ is the other indication that the zirconium site was successfully doped^[17].

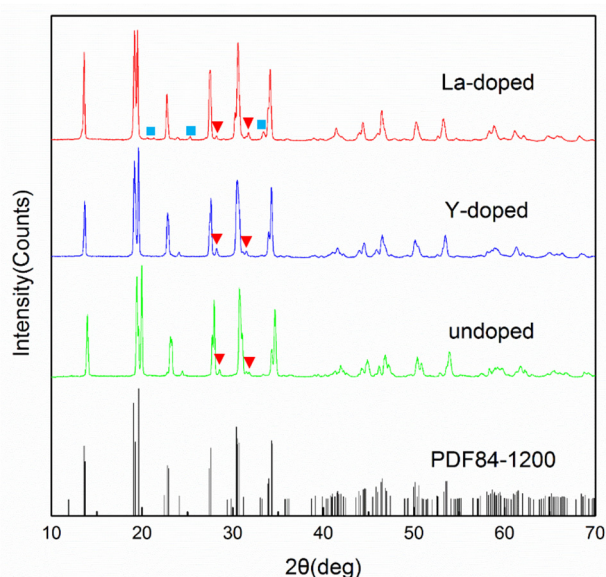


Figure 1. XRD patterns of La-doped, Y-doped, and undoped NASICON. Triangles and rectangles represent ZrO_2 and $\text{Na}_3\text{La}(\text{PO}_4)_2$ impurities, respectively.

As shown in Figure 2, the SEM images indicate the microstructure of three NASICON samples. In general, the particle size is in the micrometer range and the grains are well connected. All of NASICON samples were defined by cubic grains with the particle size of 2-4 μm , La-doped

NASICON has greater necking between particles, smaller average particle size, and much more rounded grains than others. SEM images show that the density of sample improved by doping La and Y. It was verified by density measurement results. The density of undoped, Y-doped, and La-doped NASICON is 3.18 g/cm^3 , 3.20 g/cm^3 , and 3.22 g/cm^3 , respectively. Doping rare earth elements can reduce the sintering temperature and holding time, which is beneficial to elimination of pores and growth of grains, and increase the density of materials [18].

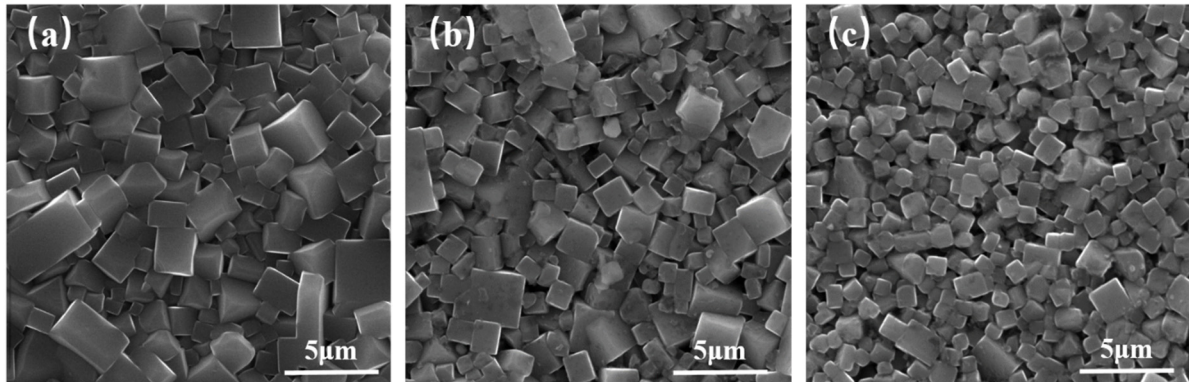


Figure 2. SEM images of NASICON: (a) undoped; (b) Y-doped; (c) La-doped.

The AC impedance results for all samples are shown in Figure 3. The bulk impedances of undoped, Y-doped, and La-doped NASICON are 58.72Ω , 25.07Ω , and 18.55Ω , the grain boundary impedances of undoped, Y-doped, and La-doped NASICON are 28.42Ω , 27.82Ω , and 15.74Ω . The decrease of the bulk and grain boundary impedances due to the uniformity of grains by doping La and Y. The ionic conductivity of undoped, Y-doped, and La-doped NASICON are $2.6 \times 10^{-3} \text{ S/cm}$, $4.3 \times 10^{-3} \text{ S/cm}$, and $6.7 \times 10^{-3} \text{ S/cm}$ at 25°C . This is because doping Y^{3+} ($0.90 \text{ \AA}$) and La^{3+} ($1.06 \text{ \AA}$) with larger ionic radii than Zr^{4+} ($0.79 \text{ \AA}$) increases carrier concentration, improves the sodium ion channel, and reduces bulk impedance and grain boundary impedance.

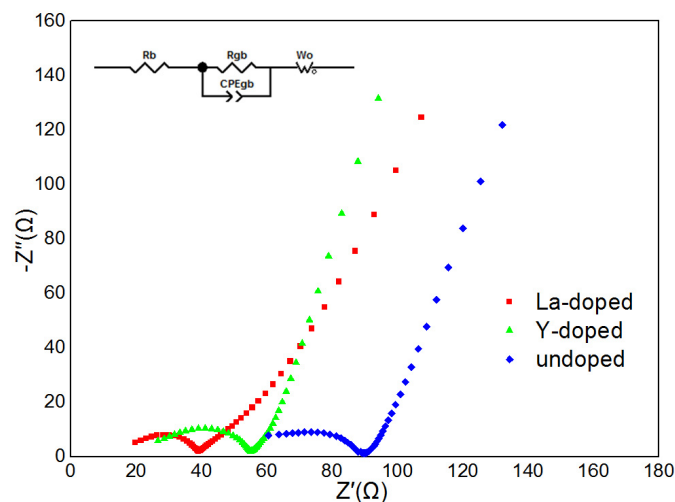


Figure 3. EIS plots of undoped, Y-doped, and La-doped NASICON at 25°C .

The reasons for increasing the ionic conductivity of NASICON by doping are as follows: (1) improving the concentration of charge carriers via aliovalent substitution; (2) tailoring the size of the ionic transport channel through substituting the skeleton ions with proper ions; (3) increasing the density of ceramics and obtaining uniform grains to reduce the grain boundary resistance via aliovalent substitution.

4. Conclusion

La-doped, Y-doped, and undoped NASICON samples were prepared by the solid state method at the temperature of 1225 °C. It was found that the ionic conductivity of NASICON-type solid electrolyte doped by rare earth elements was higher than that of the undoped one. La-doped NASICON exhibits the highest ionic conductivity of 6.7×10^{-3} S/cm at 25 °C. The doping of rare earth elements can increase the density of NASICON, increase carrier concentration, improve the sodium ion channel, thereby increasing the ionic conductivity of these materials.

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