Preparation and Ionic Conductivity of Al-Doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$

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Al-doped $\text{Mg}_{0.5(1-x)}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ has been prepared by a sol-gel method and the conductivity has been evaluated by an ac impedance method to determine the optimum lattice volume for Mg-ion conduction. Instead of using Ti in the samples, 10–15 mol% Al was used, resulting in lattice contraction in the c-axis direction. The samples, sintered at 500–800°C for 12 h by a reaction sintering method, had a relative density of 70–80% and their grain size was 2–3 μm . The ionic conductivity calculated from the grain and grain boundary resistance at 600°C was 7.1×10^{-5} and 1.3×10^{-5} S/cm, respectively. The activation energy of the grain conductivity was 128 kJ/mol in the temperature range of 300 to 600°C. By comparing ionic conductivity of various-doped titanium phosphates, optimum lattice volume was estimated to be 1.304 nm³.
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1. Introduction

The NASICON-type crystal structure ($\text{A}_x\text{M}_2(\text{XO}_4)_3$; A = alkali and alkaline-earth metal, M = transition metal, X = metalloid) as shown in Fig. 1 exhibits A-ion nonstoichiometry and conductivity. The structure has a three-dimensional network frame comprising of MO_6 octahedra and XO_4 tetrahedra, with A-ions located in the large interstitial sites. NASICON-type materials have been given a great deal of attention in recent years due to their potential as multivalent ionic conductors. Nomura *et al.* investigated the phase transition and electrical conductivity of zirconium phosphates, $\text{A}^{\text{II}}\text{Zr}_4(\text{PO}_4)_6$ (A = Mg, Ca, Ba, Mn, Co, Ni, Zn, Cd and Pb).^{1,2)} Imanaka *et al.* studied Al, rare earth (Sc, Eu, Gd, Er, Tm, Yb and Lu) and tetravalent (Ti, Hf and Ge) cation conduction in phosphates and tungstates.^{3–5)} In our previous study, the crystal structure and ionic conductivity of trivalent (Fe^{3+} , Mn^{3+} , Co^{3+})- and pentavalent (Nb^{5+})-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ were studied.^{6,7)} Based on the findings in these reports, it is reasonable to assume the existence of an optimum lattice volume with high cation conductivity; large lattice expansion in Nb-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ leads to lower ionic conductivity and higher activation energy than in trivalent-doped and undoped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ while smaller cation doping (such as Co^{3+}) improves ionic conductivity. To further clarify the relationship between the dopants and ionic conductivity, we investigated the doping of $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ with Al, which has a smaller ionic radii (0.054 nm) than Co^{3+} (0.061 nm),⁸⁾ and its crystal structure and electrical conductivity were evaluated.

2. Experimental

Al- and Fe-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ were prepared by the sol-gel method. Two solutions were prepared; in one solution, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, titanium tetra-butoxide tetramer $\text{C}_4\text{H}_9\text{O}[\text{Ti}(\text{OC}_4\text{H}_9)_2\text{O}]_4\text{C}_4\text{H}_9$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in ethanol, and in the other, $\text{NH}_4\text{H}_2\text{PO}_4$ was dissolved in distilled water with a concentration of 0.1 mol/l separately. These solutions were mixed

Fig. 1 NASICON-type crystal structure.

into the stoichiometric ratios of the target samples. The obtained gels were dried at 90°C for periods of 12 h or longer and heated at 300°C for 12 h. The precursors were pressed into pellets, and then crystallized and sintered at 600–800°C for 12 h. Analysis was performed by X-ray diffractometry (XRD) to identify the phases present. The microstructure was observed by a scanning electron microscope (SEM). To evaluate the electrical conductivity, Pt electrodes were applied on both sides of the sintered samples, and ac impedance measurements were taken in the frequency range of 0.01 to 10⁷ Hz. In order to determine the exact ionic conductivity in the ac impedance measurements, direct-current measurement was also performed.

3. Results and Discussion

Firstly, Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ was prepared with Al substituted for Ti sites. In undoped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$, Mg ions occupy 50% of all the interstitial sites, whereas in the Al-doped phosphates, the Mg concentration increases with increasing Al content, and thus holds the charge neutrality. The XRD profiles of Al, Fe-doped and undoped $\text{Mg}_{0.5}$ -

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Fig. 2 XRD profiles of Al-, Fe-doped and undoped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ powder.

$\text{Ti}_2(\text{PO}_4)_3$ are shown in Fig. 2. As the content of the dopants increases, peaks close to the basal planes, such as (024) and (116), shift toward higher angles, indicating lattice contraction in the c -axis direction. Figure 3 shows the lattice constant as a function of dopant content for Al-doped samples and other cation-doped samples.⁷⁾ The trivalent-doped samples clearly experience lattice contraction in the direction of c -axis, and the Al-doped samples have the smallest lattice constant. In addition, the lattice constant of the 15 mol% Al-doped sample is almost same as that of the sample doped with 10 mol% Al, indicating the solubility limit is around 10 mol% Al, even though no secondary phase can be seen for the 15 mol% Al-doped sample in Fig. 2. To see the effect of the dopant on microstructure and ionic conductivity, 10 mol% Al-, Fe-doped and undoped samples were investigated.

To evaluate the ionic conductivity precisely, a well sintered body is required. For that purpose, the reaction sintering in this study was carried out at lower temperatures than those reported in previous studies. The densification conditions, relative density and grain size of the undoped and doped phosphates are summarized in Table 1, and the SEM images of the samples after reaction sintering at relatively lower temperatures are shown in Fig. 4. Due to its poor sinterability, $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ itself required high sintering temperatures of around 1150–1200°C; however, such high temperatures resulted in partial decomposition. On the other hand, during the reaction sintering of the precursors at low temperatures,

Fig. 3 Lattice constant of doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ as a function of dopant content.

Table 1 Sintering conditions, relative density and grain size of undoped and doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$.

Compound	Condition	R. D.	Grain size	Phase
$\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$	1200°C, 10 h	76%	5–10 μm	Dual
	700°C, 12 h	80%	2–3 μm	Single
(Reaction sintering)				
$\text{Mg}_{0.6}\text{Fe}_{0.2}\text{Ti}_{1.8}(\text{PO}_4)_3$	1150°C, 2 h	74%	5–10 μm	Dual
	750°C, 12 h	93%	2–3 μm	Single
(Reaction sintering)				
$\text{Mg}_{0.6}\text{Al}_{0.2}\text{Ti}_{1.8}(\text{PO}_4)_3$	800°C, 12 h	54%	2–3 μm	Single
	600 → 700°C, 12 h	72%	2–3 μm	Single
(Reaction sintering)				

the precursors become dehydrated, the ammonium and acetate salts were removed, and the result was a single-phase sample with high relative density. Undoped and 10 mol% Fe-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ sintered at 700 and 750°C had a higher relative density (80%, 93%) than samples sintered at 1150–1200°C, respectively. In the case of 10 mol% Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$, two-step sintering, involving pre-sintering at 600°C for 12 h followed by sintering at 700°C for 12 h, had better relative density (72%) than samples sintered at 800°C. Grain growth was observed in all the reaction-sintered samples.

By using the ac impedance technique, the electrical conductivity of the samples was measured. Two or three semicircles can be observed in the Nyquist plots of 10 mol% Al-, Fe-doped and undoped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ densified by reaction sintering shown in Fig. 5. By fitting an equivalent circuit, the magnitude of capacitances of 10^{-12} , 10^{-8} and 10^{-7} F were derived from the semicircles observed between high and low frequencies. This suggests that first and other semicircles can be attributed to grain and grain boundary responses, respectively. For the Al-doped samples, a two-probe dc measurement was also performed. The dc conductivity was found to be lower than the grain boundary

Fig. 4 SEM images of undoped, 10 mol%Fe- and Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ after reaction sintering; sintering temperature are 700, 750 and 600 to 700°C, respectively.

conductivity by approximately two orders of magnitude. This suggests that the mobile carrier is ionic, presumably Mg^{2+} . The Arrhenius plots in Fig. 6 show the grain (open markers) and grain boundary (filled markers) ionic conductivity of undoped, 10 mol%Fe- and Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ densified by reaction sintering. The dashed lines represent the grain conductivity of undoped and 10 mol%Fe-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ sintered at 1150–1200°C. The ionic conductivity of the reaction-sintered samples was in good agreement with that for samples sintered at 1150–1200°C. For 10 mol%Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ the grain and grain boundary conductivity at 600°C were 7.1×10^{-5} and 1.3×10^{-5} S/cm, respectively. The ionic conductivity was lower than that for undoped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ by one or two orders of magnitude. The activation energy of 10 mol%Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ (128 and 144 kJ/mol) was the highest among the samples.

Fig. 5 Nyquist plots of undoped, 10 mol%Fe- and Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ measured at 500 or 600°C.

Fig. 6 Arrhenius plots of the grains (open markers) and grain boundaries (filled markers) conductivity of undoped, 10 mol%Fe- and Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ densified using the reaction sintering method. DC conductivity measured by the two-probe technique was also plotted.

The changes in the ionic conductivity and activation energy can be understood by taking the unit-cell volume into consideration. The grain conductivity and activation energy of 10 mol%M-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ at 400°C, where M denotes Fe, Mn, Co, Al and Nb, are plotted as a function of

Fig. 7 Grain conductivity and activation energy of 10 mol%M-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ at 400°C, where M donates Fe, Mn, Co, Al and Nb, as a function of the unit-cell volume.

unit-cell volume in Fig. 7.⁷⁾ While trivalent doping resulted in a reduction in the c-axis, in the case of Co- and Mn-doped samples, the unit-cell volume increases as a result of expansion in the a-axis. It should be noted that the highest grain conductivity and lowest activation energy were attained for the slightly expanded Co-doped sample. For 10 mol%-trivalent-doped titanium phosphates, a unit-cell volume of 1.304 nm^3 seems to be optimum for Mg-ion conduction. To further clarify the relationship between crystal structure and ionic conductivity, further studies are required for a better understanding of the conduction pathways themselves and their connectivity.

4. Conclusion

Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ was prepared as a single phase NASICON-type structure. The dense and single-phase sample was obtained by reaction sintering. For 10 mol%Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$, the grain and grain boundary conductivity at 600°C were 7.1×10^{-5} and $1.3 \times 10^{-5} \text{ S/cm}$, respectively. The activation energy of 10 mol%Al-doped $\text{Mg}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ (128 kJ/mol for the grain conduction) was the highest among various doped phosphates. By comparing the ionic conductivity of the phosphates, the optimum lattice volume was estimated to be 1.304 nm^3 .

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