Anisotropic trivalent ion conducting behavior in single crystals of aluminum tungstate-scandium tungstate solid solution

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An aluminum tungstate-scandium tungstate solid solution was successfully grown in a single crystal form by modified Czochralski (CZ) method. The crystal grown was transparent and a satisfactory quality was examined by a polarizing microscope measurement. The Al^{3+} ion conductivity was considerably improved by forming the solid solution and these by expanding the crystal lattice size. The lattice expansion contributes greatly to enhancing the Al^{3+} ion conducting behavior especially along *c*-axis among the three axes in the orthorhombic symmetry. By comparing the ion conducting characteristics between each axis of the single crystal and the polycrystal, the enhancement of the Al^{3+} ion conductivity is ascribed to the cooperative effects of both ion conductivity increase along *c*-axis and the conductivity enhancement in the grain boundaries. © *2002 Kluwer Academic Publishers*

1. Introduction

In recent years, trivalent ions such as aluminum, rare earths have been demonstrated to migrate in solids with the $Sc_2(WO_4)_3$ type structure and their ion conducting behavior has been extensively investigated [1–7]. The structure is composed of quasi-two dimensional layers and the trivalent ions migrate between the layers. The trivalent ion conducting properties in the $Sc_2(WO_4)_3$ type structure vary systematically with the change in both the mobile trivalent ion size and the lattice volume of the tungstate structure as reported in our previous paper [3]. In order to obtain a suitable layer for mobile ions, various kinds of solid solution have been prepared and their trivalent ion conducting characteristics have been studied in detail with intentionally expanding their lattice size by dissolving larger trivalent ions compared with the mobile ion, as a spacer in the layered structure [8, 9].

However, the above mentioned solid solutions are in a polycrystalline form and grain boundaries always appear in addition to the crystal grains and the exact trivalent ion conducting properties in the grain bulk cannot be elucidated. For the purpose of identifying the specific trivalent ion conducting behavior within the grain of $Sc_2(WO_4)_3$ type crystal, the growth of single crystals of which the lattice size can be tailored is inevitable. Especially, in order to delineate the effect of the lattice size change on the ionic conducting characteristics, the crystal should be investigated in a single crystal form to exclude the grain boundary effects. In recent years, we have succeeded in growing the single crystals of $Al_2(WO_4)_3$ ($a = 1.2493, b = 0.9045, c = 0.9092$ nm) [6, 7] by the Czochralski (CZ) method. In addition, in our previous papers [10, 11], we reported the successful growth of the $0.85Al_2(WO_4)_3$-$0.15Sc_2(WO_4)_3$ single crystal solid solution. For the purpose of realizing a high Al^{3+} ion conduction in the $Al_2(WO_4)_3$ solid, the lattice expansion of the $Al_2(WO_4)_3$ crystal lattice is essential.

In this study, the trivalent ion conducting behavior parallel to each *a*, *b*, and *c* axis were studied on the single crystal solid solution with the orthorhombic $Sc_2(WO_4)_3$ type structure and the influence of the lattice expansion on the ionic conductivity has been quantitatively investigated.

2. Experimental details

Single-crystals of $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ solid solution were grown as described in our previous papers [10, 11]. The exact Al:Sc ratio was determined by the lattice parameter change as given in Refs. [10] and [11]. Single crystals were cut perpendicular to *a*, *b*, and *c* axes, respectively. $Al_2(WO_4)_3$ polycrystals were obtained by mixing $Al(OH)_3$ (purity: 99.99% from high purity chemicals) and WO_3 (purity: 99.9% from Rare Metallic Co. Ltd.) in a stoichiometric ratio and heating at 1000°C for 12 h several times in air. The polycrystalline $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ solid solution with Al:Sc ratio of 8.3:1.7 was prepared by mixing

Al(OH)$_3$, Sc$_2$O$_3$, and WO$_3$ and heating at 1000°C for 12 h and then at 1000–1200°C for 12 h in air. The polycrystal, pulverized single crystal powder and single crystals were characterized by X-ray diffraction using Cu K$_\alpha$ radiation (M18XHF, Mac Science).

Electrical conductivity was measured by both ac and dc methods, using the respective single crystal with two Pt electrodes in the temperature range from 300 to 600°C. The ac conductivity (σ_{ac}) measurements were carried out by an ac complex impedance method with a Hewlett Packard precision LCR meter (8284 A). The polarization measurement was performed by applying a constant current of 0.1 μA between the two Pt electrodes and the voltage was monitored as a function of time both in oxygen (P_{o_2}: 10^5 Pa) and helium (P_{o_2} : 4 Pa) atmospheres. The dc conductivity (σ_{dc}) was calculated from the voltage, the applied current, the surface area and the thickness of the disc.

The single crystal was set between two ion-blocking Pt electrodes in a direction parallel to the c-axis for the dc electrolysis and a dc voltage of 10 V was applied at 900°C for 350 h in air. A voltage as high as 10 V was applied since the conductivity was considerably lower than that of the polycrystal. The dc electrolysis of the polycrystalline Al$_2$(WO$_4$)$_3$-Sc$_2$(WO$_4$)$_3$ solid solution pellet was also carried out at 3 V, 850°C for 900 h in air. Electron probe micro analysis (EPMA) (EPMA-1500, Shimadzu) was performed in order to identify the distribution of the each element in the 8.3Al$_2$(WO$_4$)$_3$-1.7Sc$_2$(WO$_4$)$_3$ solid solution single crystal.

3. Results and discussion

The temperature dependence of the electrical conductivity of single phase Al$_2$(WO$_4$)$_3$ and 8.3Al$_2$(WO$_4$)$_3$-1.7Sc$_2$(WO$_4$)$_3$ solid solution polycrystals (both have the Sc$_2$(WO$_4$)$_3$-type structure with an orthorhombic symmetry and the space group Pbcn) is shown in Fig. 1. It is seen clearly that the conductivity was enhanced 3.4 times at 600°C by mixing the larger Sc^{3+} ion
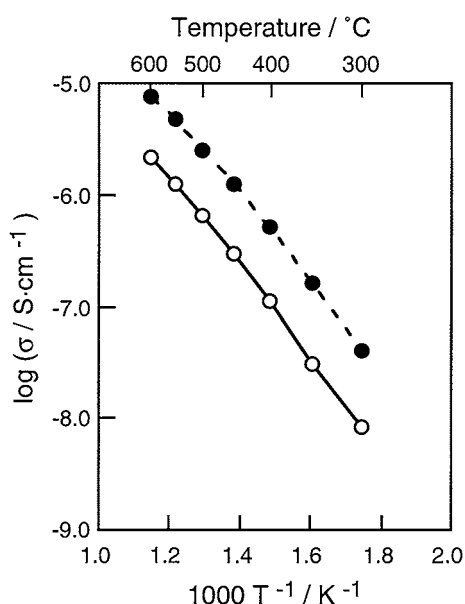

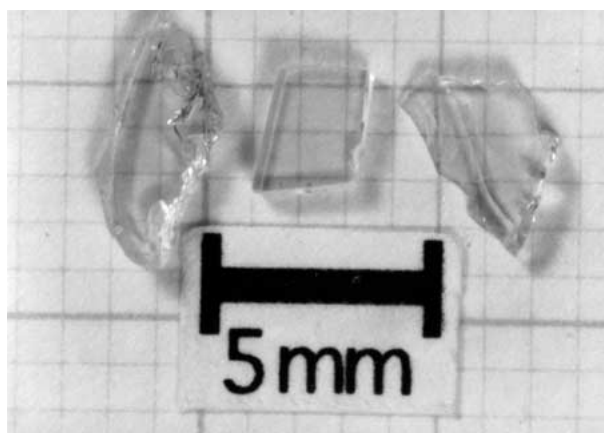*Figure 2* The photograph of the solid solution single crystals grown by the CZ method.

(0.0885 nm (6 coordinated) [12] in the single phase Al$_2$(WO$_4$)$_3$ (Al^{3+} ionic radius: 0.0675 nm (6 coordinated) [12]) to form a polycrystalline Al$_2$(WO$_4$)$_3$-Sc$_2$(WO$_4$)$_3$ solid solution phase. After dc electrolysis, deposits were clearly observed on the cathodic surface of the solid solution, and the predominant species in the deposits was found to be aluminum. This result indicates that the mobile species in the solid solution is trivalent aluminum ion. Because the activation energies of the Al$_2$(WO$_4$)$_3$ and the Al$_2$(WO$_4$)$_3$-Sc$_2$(WO$_4$)$_3$ solid solution polycrystals obtained from the log(σT)-1/T relationship are 84.2 and 71.9 kJ/mol, respectively, the Al^{3+} ion can migrate more easily in the solid solution than in the single phase Al$_2$(WO$_4$)$_3$. However, both samples are in a polycrystalline form and contain both grains and grain boundaries (from the impedance measurements, only one semi-arc was observed and it is impossible to separate contribution from grain boundary and that from bulk). Therefore, it is not possible to identify what enhances the conductivity and reduces the activation energy for Al^{3+} ion conduction.

Recently, the solid solution single crystals were successfully obtained by the CZ method with the starting mixing ratio of Al$_2$O$_3$: Sc$_2$O$_3$: WO$_3$ in 15.3 : 1.7 : 83 as shown in Fig. 2 [11] and an adequate crystallinity of the single crystals was identified by the polarization microscope observation. The peak profiles obtained for the single crystal were compared to those of Al$_2$(WO$_4$)$_3$ and Sc$_2$(WO$_4$)$_3$ polycrystals which have the same orthorhombic symmetry. The number and the peak profile for those three samples are identical, indicating that single crystal grown from the starting mixture of 15.3 : 1.7 : 83 and two end members polycrystals (Al$_2$(WO$_4$)$_3$ and Sc$_2$(WO$_4$)$_3$) are isostructural. The position of the peaks shifts to lower angle side on going from the Al$_2$(WO$_4$)$_3$ polycrystal, to the Al$_2$(WO$_4$)$_3$-Sc$_2$(WO$_4$)$_3$ single crystal grown, and to the Sc$_2$(WO$_4$)$_3$ polycrystal. The lattice parameters increase in the order from Al$_2$(WO$_4$)$_3$, Al$_2$(WO$_4$)$_3$-Sc$_2$(WO$_4$)$_3$ single crystal to Sc$_2$(WO$_4$)$_3$. The results mentioned above clearly suggest that the phase obtained for Al$_2$(WO$_4$)$_3$-Sc$_2$(WO$_4$)$_3$ single crystal is indeed the single phase of the Al$_2$(WO$_4$)$_3$-Sc$_2$(WO$_4$)$_3$ solid solution and the solid solution is identified to be 0.83Al$_2$(WO$_4$)$_3$-0.17Sc$_2$(WO$_4$)$_3$ solid solution ($a = 1.268$, $b = 0.9112$,

Figure 1 The temperature dependence of the electrical conductivity of single phase Al$_2$(WO$_4$)$_3$($\circ$) and 8.3Al$_2$(WO$_4$)$_3$-1.7Sc$_2$(WO$_4$)$_3$($\bullet$) solid solution polycrystals.
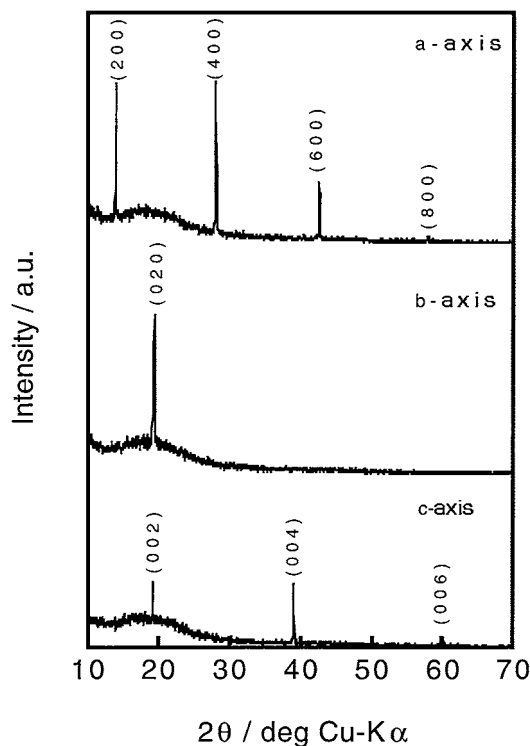
Figure 3 The X-ray diffraction pattern for the singe crystal pellet cut perpendicular to *a*, *b*, or *c* axis.

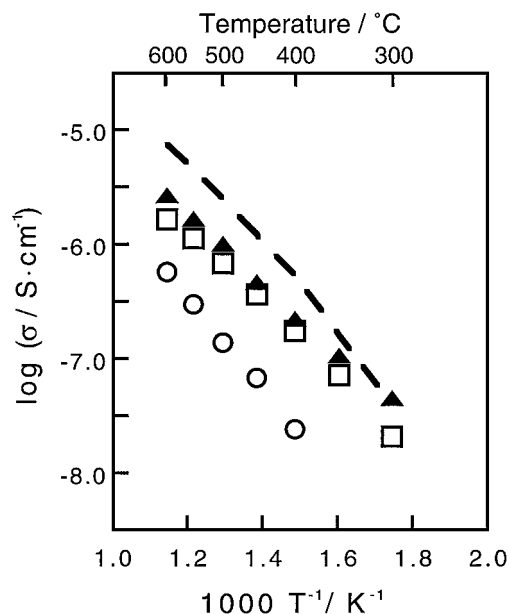*Figure 4* The temperature dependence of the electrical conductivity for the $8.3Al_2(WO_4)_3$-$1.7Sc_2(WO_4)_3$ solid solution single crystal along *a* (□), *b* (▲), and *c* (○) axis with the data for the solid solution polycrystal (– –).

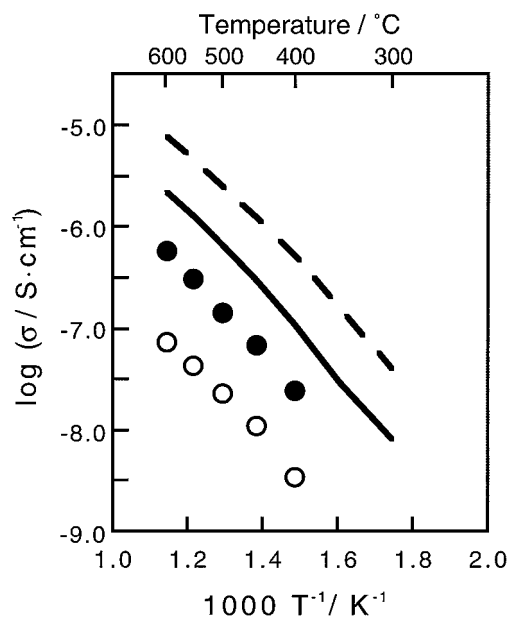*Figure 5* The temperature dependence of the electrical conductivity of the $Al_2(WO_4)_3$ single crystal (○) and the $8.3Al_2(WO_4)_3$-$1.7Sc_2(WO_4)_3$ solid solution single crystal (●) for parallel to the *c* axis with the data of polycrystalline $Al_2(WO_4)_3$ (—) and $8.3Al_2(WO_4)_3$-$1.7Sc_2(WO_4)_3$ solid solution (– –).

$c = 0.9196$ nm) in a similar manner as described in Ref. [11].

Since the solid solution is in a single crystal form which is composed of only grain bulk without any grain boundaries, it is possible to exactly elucidate the specific ion conducting characteristics in the grain itself such as along each axis. Fig. 3 presents the X-ray diffraction pattern for the single crystal pellet cut perpendicular to *a*, *b*, or *c* axes. From the figure, it can be inferred that the surface of the single crystal is cut exactly perpendicular to *a*, *b*, and *c* axis, respectively.

Fig. 4 shows the temperature dependence of the electrical conductivity of the single crystal of $0.83Al_2(WO_4)_3$-$0.17Sc_2(WO_4)_3$ solid solution along *a*, *b*, and *c* axes along with the data for the polycrystalline solid solution. The conductivity (600°C) along *b* axis shows the highest value among the three axes accompanied with the lowest activation energy of 57.4 kJ/mol, while the conductivity (600°C) along *a* axis is approximately 3/5 lower than that along *b* axis with the E_a value of 60.3 kJ/mol. In contrast, the conductivity along *c* axis at 600°C is about 1/5 lower than that along *a* and *b* axes and the E_a value of conduction along *c* axis is as high as 77.0 kJ/mol. The conductivity of the polycrystal which includes the contribution of grain boundaries in addition to that of grain, is higher than any of the conductivities along *a*, *b*, and *c* axis. The conductivity through the grain boundaries is the highest in comparison to any of the conductivities along three axes direction. The E_a value for the polycrystal is 72.6 kJ/mol and is close to the value for *c* axis (77.0 kJ/mol). The ion conduction path which holds the highest E_a value, in this case along *c* axis, determines the E_a value of the $8.3Al_2(WO_4)_3$-$1.7Sc_2(WO_4)_3$ solid solution polycrystal.

The marked difference between the conducting behaviors of single crystal $Al_2(WO_4)_3$ phase [7] and single crystal $8.3Al_2(WO_4)_3$-$1.7Sc_2(WO_4)_3$ solid solution is the conductivity along *c* axis. The conductivity of the $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ solid solution along its *c* axis is one order of magnitude higher than that of the $Al_2(WO_4)_3$ single crystal as shown in Fig. 5. (The expansion ratios for *a*, *b*, and *c*-axes are all approximately 1% and it is an isostructual expansion. However, by the expansion, $(WO_4)^{2-}$ anions rotate and as a result, the Al^{3+} ion conduction path way along *c*-axis is most enhanced among the three axes.). The conductivity data for the polycrystals of $Al_2(WO_4)_3$ and $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ are also plotted in the same
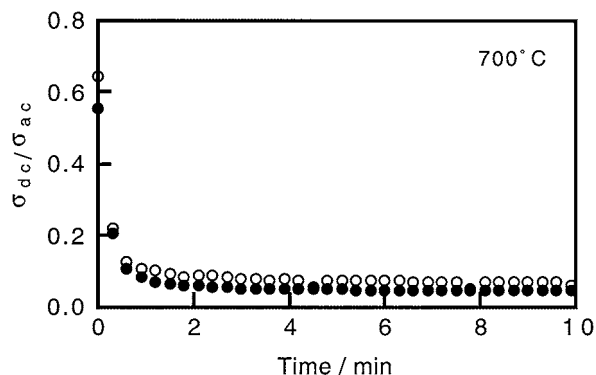
Figure 6 The time dependence of the σ_{dc}/σ_{ac} ratio in both oxygen (●) (P_{O_2} : 10^5 Pa) and helium (○) (P_{O_2} : 4 Pa) atmospheres for solid solution single crystal at 700°C. σ_{dc} and σ_{ac} denote the conductivity obtained by dc and by ac measurements, respectively.

figure. Fig. 5 clearly indicates that the conductivity enhancement along c axis direction contributes to increasing the total conductivity of the $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ solid solution polycrystal.

The time dependence of the σ_{dc}/σ_{ac} ratio along c axis for the $8.3Al_2(WO_4)_3$-$1.7Sc_2(WO_4)_3$ solid solution single crystal are presented in Fig. 6. The ratio abruptly decreased in a several minutes for both in oxygen (P_{O_2} : 10^5 Pa) and in helium (P_{O_2} : 4 Pa) atmospheres and approached to a steady state after 3 min. The appreciably high polarization behavior reaches the σ_{dc}/σ_{ac} value less than 0.05, indicating that the ion transport number is estimated to be higher than 0.95.

For the purpose of identifying the mobile species in the $8.3Al_2(WO_4)_3$-$1.7Sc_2(WO_4)_3$ solid solution, a dc electrolysis was carried out for the solid solution pellet in the direction along c axis. After the dc electrolysis, the deposits were similarly segregated on the cathodic surface of the pellet as shown in Fig. 7a. From the electron probe microanalysis (EPMA) measurements, the element detected was only Al (Fig. 7b).

Fig. 8 presents the results of the EPMA line analysis profiles of the electrolyzed single crystal from anode to cathode direction (c-axis) for the elements of Al, Sc, and W. A. Considerably higher Al segregation was observed near the cathodic surface, while some scandium element also accumulated to a certain extent owing to an appreciably higher voltage of 10 V in comparison to the decomposition voltage (ca. 3 V) of the parent $Al_2(WO_4)_3$ single crystal. The results obtained from Figs 5, 7 and 8 explicitly indicate that the expansion of the crystal lattice size in the $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ solid solution contributes greatly to realizing a macroscopic high Al^{3+} migration along c axis.

The electrical conductivity of the $Al_2(WO_4)_3$ single crystal [7] and the $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ solid solution single crystal along a and b axes are almost the same and the conductivity along a and b axes for the solid solution is below that of the polycrystalline $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ solid solution (Fig. 4). These results indicate that the conductivity in the grain boundaries of the solid solution polycrystal is higher than that along any of the three axes. Therefore, the enhancement of the trivalent Al^{3+} ion conductivity and the reduction in the activation energy for the $Al_2(WO_4)_3$-
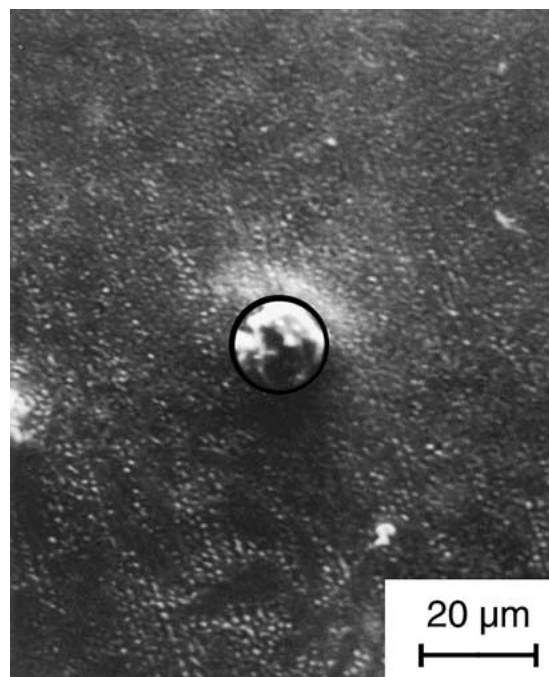
(a)
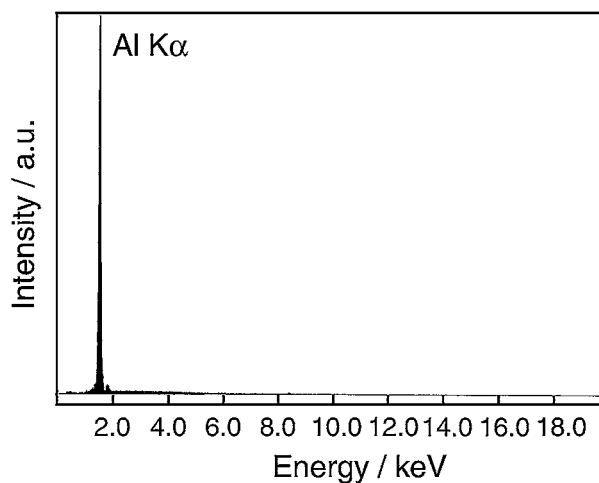
(b)

Figure 7 The SEM photograph (a) and the result of the spot analysis (b) of the deposits segregated on the cathodic surface of the pellet after the electrolysis.
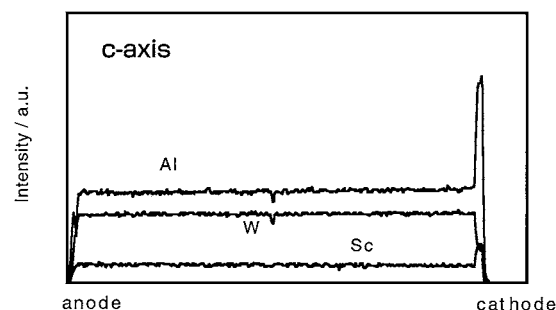

Figure 8 EPMA line analysis profiles of the electrolyzed single crystal from anode to cathode direction for the elements of Al, Sc, and W.

$Sc_2(WO_4)_3$ solid solution polycrystalline phase compared with the pure $Al_2(WO_4)_3$ polycrystalline phase (see Fig. 1), is attributed to the cooperative effect of both the increase in trivalent Al^{3+} ion conductivity along c axis in the bulk and also in the ion conductivity at the grain boundaries. By forming the solid

solution, the crystal lattice expands, while the mobile Al^{3+} ion content in the solid solution decreases. In the case for the Al^{3+} ion conduction along c axis, the lattice expansion is considerable so as to increase the Al^{3+} ion conduction and results in one order of magnitude improvement. In contrast, for the Al^{3+} ion migration along a or b axis direction, the effect of expansion and the decrease of the mobile Al^{3+} cation content works in the opposite direction and as a result, there appears no appreciable change in the ion conducting characteristics.

4. Conclusions

By comparing the Al^{3+} ion conducting characteristics in the single crystals of pure $Al_2(WO_4)_3$ and the $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ solid solution, it becomes clear that the expansion of the $Al_2(WO_4)_3$ crystal lattice is considerably effective for the enhancement of the Al^{3+} ion conduction along c axis and the conductivity increases approximately one order of magnitude, while the conductivity along a or b axis remains unchanged due to the competing effects of the expansion and the decrease in the number of mobile Al^{3+} ions. The enhancement of trivalent Al^{3+} ion conductivity for the $Al_2(WO_4)_3$-$Sc_2(WO_4)_3$ solid solution polycrystalline phase in comparison to the $Al_2(WO_4)_3$ single phase polycrystal can be attributed mainly to a considerable increase in its ion migration in grains along c axis and to the improvement of ion conductivity at the grain boundaries. The evaluation of the ionic conduction along each axis can be accomplished only by successfully growing a solid solution in a single crystal form, and our findings lead us in the right direction not only to enhance trivalent ion migration in the bulk crystal grain of $Sc_2(WO_4)_3$-type structure but also to elucidate profound existing effects by excluding the grain boundaries influence on the ion conducting characteristics.

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