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K^+ ion conducting properties in the R_2O_3-KNO_3 (R: Rare earths) solid solution series

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A new type of polycrystalline potassium ion conducting solid electrolyte doped with potassium nitrite as the starting material, was developed. Since cubic rare earth oxides hold reasonably enough interstitial space for bulky K^+ ion migration in the crystal lattice, an extraordinary high K^+ ion conductivity was successfully achieved by forming a polycrystalline $(1-x)R_2O_3$-$xKNO_3$ solid solution, which was realized by doping KNO_2 as the KNO_3 state into the interstitial site of cubic rare earth oxide crystal lattice. The potassium ion conductivity of the $(1-x)R_2O_3$-$xKNO_3$ (R: rare earths) solid solution linearly increased with expanding the R_2O_3 crystal lattice and the highest K^+ ion conductivity was obtained for the $0.653Gd_2O_3$-$0.347KNO_3$ solid solution, which is three orders of magnitude higher than that of a well-known polycrystalline K^+ ion conducting K_2SO_4 solid and the value exceeds that in the *ab* conducting plane of a K^+-β''-Al_2O_3 single crystal.

1. Introduction

In the solid electrolyte field, alkali metal ion such as Li^+ and Na^+ ions have been well known to easily conduct in solids because of their small ionic sizes and monovalent state. On the other hand, K^+ ion conductivity in solids is considerably low even if the crystal structure is preferably selected for obtaining a high ion conduction, because K^+ ion is, basically, too large in ionic size to migrate in solids, while the valency is equal to the monovalent Li^+ and Na^+. Among the K^+ ion conductors reported [1–3], only the K^+-β''-Al_2O_3 single crystal shows as high ion conductivity region as 10^{-1} $S \cdot cm^{-1}$ at 873 K [3], which is comparable to those of Li^+ and Na^+ ion conductors such as LISICON [4] and NASICON [5]. However, such a high K^+ ion conductivity was achieved only in the *ab* plane of the K^+-β''-Al_2O_3 single crystal, and the K^+ ion conductivity along *c*-axis was in several orders of magnitude lower than that in the *ab* plane. In addition, the K^+-β''-Al_2O_3 single crystal growth is also a time-consuming and trouble-some task. One of polycrystalline K^+ ion conducting solid electrolytes reported is K_2SO_4 [2]. However, the K^+ ion conductivity of the K_2SO_4 polycrystal is as low as 3.38×10^{-5} $S \cdot cm^{-1}$ even at 873 K and, therefore, the polycrystalline K^+ ion conductor whose ion conductivity reaches the practically application range of 10^{-1} $S \cdot cm^{-1}$, has not been realized yet.

For realizing a high K^+ ion conductivity in solids, a large conducting path length is necessary. However, it is easily speculated that such a large conducting path length can not be obtained for the conventional solids design. Rare earth oxides that are denoted as R_2O_3 hold three types of crystal structure, A, B and C-type. As can be easily speculated, the structures of the rare earth oxide series are based on fluorite (CaF_2) structure where one oxygen atom is empty among four oxygens to produce the interstitial open space in the crystal lattice. Among those three types, C-type structure is the lowest in its density, that is, the C-type structure holds the most open space among three types of the R_2O_3 structure.

In our previous study, a new type of K^+ ion conducting solid was successfully developed by applying the above described cubic C-type Gd_2O_3 as the host polycrystalline material which holds the reasonable large interstitial space for bulky ion migration like K^+ ions [6]. As a result, an extraordinary high K^+ ion conductivity was successfully realized by doping KNO_2 as the starting material to from KNO_3 in the interstitial site of the C-type Gd_2O_3 crystal lattice [7]. Since the size of the cubic crystal lattice is the key factor for the characterization of the K^+ ion conductivity in the solid solution, the cubic crystal lattice was intentionally varied by choosing three types of rare earth ions whose ionic radius increases in the order from Lu^{3+} (0.1001 nm [8]), Y^{3+} (0.1040 nm [8]), to Gd^{3+} (0.1078 nm [8]).

In this study, we investigated the lattice size effect of the host cubic C-type rare earth oxides on the K^+ ion conductivity in the series of R_2O_3-KNO_3 (R: Rare earths) solid solution electrolytes in detail.

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2. Experimental

Potassium nitrite (99.9%) and R_2O_3 ($R = Gd, Y, Lu$) (99.9%) were thoroughly mixed in a molar ratio of $KNO_2:R_2O_3 = x:(1-x)$ ($x = 0.182$–0.571). The mixture was made into pellets and heated at 723 K for 12 h in air (The heating temperature was determined to proceed the chemical reaction between R_2O_3 and KNO_2 to form a solid solution because of the low decomposition temperature of KNO_2 at around 732 K). The pellets were re-ground into powder by using an agate mortar and subsequently the resulting powder was made into pellets again. The pellets were calcined and sintered both at 873 K for 24 h in air. The content of potassium element in the samples was analyzed by an X-ray fluorescent spectrometer (Rigaku, ZEX-100e). The X-ray powder diffraction data were collected with an X-ray diffractometer (Rigaku, Multiflex) using Cu-Kα radiation in the 2θ range from 10° to 70° by a step width of 0.04°.

The ac conductivity (σ_{ac}) of the samples was measured by a complex impedance method at the frequency region from 5 Hz to 13 MHz (Hewlett Packard, Precision LCRmeter 8284A) in the temperature range from 473 to 873 K, using the sintered sample pellet with Pt sputtered electrodes on both center surface.

The dc electrolysis of the sample pellet was carried out by applying a dc voltage of 4 V for 144 h at 673 K in air with two Pt bulk electrodes. The cathodic surface of the electrolyzed pellet was examined by scanning electron microscope (SEM, S-800, Hitachi). The cross-sectional line analysis of the sample was done by electron probe microanalysis (EPMA-1500, Shimadzu) after the electrolysis. Modified Tubandt electrolysis (dc.3 V) was carried out by using three $0.653Gd_2O_3$-$0.347KNO_3$ pellets and two Pt electrodes at 1123 K for 46 h in air.

3. Results and discussion

Fig. 1 shows the X-ray powder diffraction patterns of the Gd_2O_3 samples doped with KNO_2 as the starting material and that of pure Gd_2O_3. The potassium content in the samples were determined by an X-ray fluorescent spectrometer and the x value calculated and listed in Fig. 1. In our previous communication [9], it was identified that KNO_2 is oxidized during the formation of interstitial solid solutions with Gd_2O_3 and exists as KNO_3 in the host Gd_2O_3 crystal lattice. It clearly shows that only peaks related to cubic Gd_2O_3 were obtained for the samples with $x \leq 0.347$. In the region of $x > 0.347$, an additional peak corresponding to KNO_3 was observed as well as those of the cubic Gd_2O_3 phase. Similar results were also obtained in the case of R_2O_3 samples ($R = Y$ and Lu) doped with KNO_2 as the starting material. Therefore, the general formula of the solid solutions prepared in this study is expressed as $(1-x)R_2O_3$-$xKNO_3$ ($R = Gd$, Y and Lu) hereafter.

The lattice constant variations of the $(1-x)R_2O_3$-$xKNO_3$ (R = Gd, Y and Lu) solid solutions calculated from the XRD peaks are depicted in Fig. 2(a–c), respectively. According to the Vergard's law, the lattice constants of the cubic $(1-x)R_2O_3$-$xKNO_3$ increase with the amount of potassium nitrate content in the solid solutions due to the larger K^+ ionic size

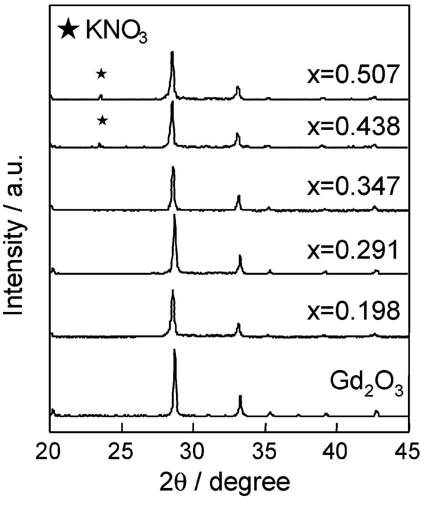
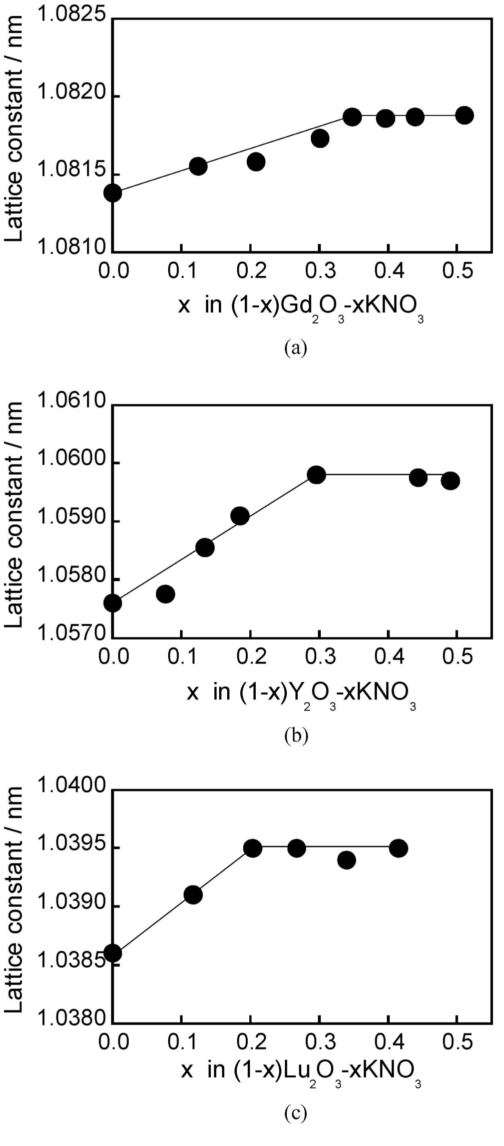


Figure 1 XRD patterns of the $(1-x)Gd_2O_3$-$xKNO_3$ with that of pure Gd_2O_3.



(a)

(b)

(c)

Figure 2 The lattice constant variations of the $(1-x)R_2O_3$-$xKNO_3$ ($R =$ (a) Gd, (b) Y and (c) Lu) solid solutions calculated from the XRD peaks.

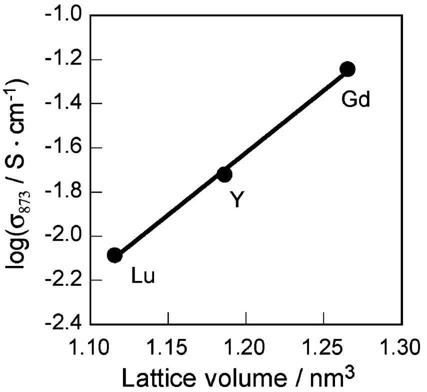


Figure 3 The relationship between the lattice volume and the ac conductivity at 873 K for $0.818R_2O_3$-$0.182KNO_3$ ($R = $ Gd, Y, Lu).

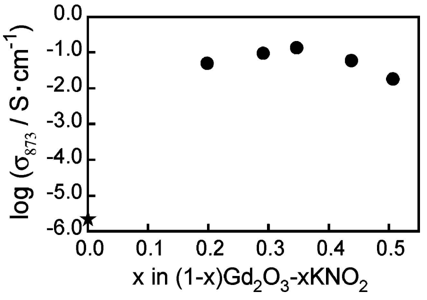


Figure 4 Compositional dependencies of the ac conductivity at 873 K for $(1-x)Gd_2O_3$-$xKNO_3$ (closed star: pure Gd_2O_3).

(0.152 nm [8] (6 coordinate)) compared with above three rare earth cations (Gd^{3+}: (0.1078 nm [8]), Y^{3+} (0.1040 nm [8]), Lu^{3+} (0.1001 nm [8]) (all in 6 coordinate)), up to $x = 0.347$, 0.291, and 0.198 for $R = $ Gd, Y, and Lu corresponding to their solid solution limits, respectively. This result strongly supports the idea that the solubility of KNO_3 in the interstitial site depends on the lattice volume of the host cubic rare earth oxides (Gd_2O_3: 1.2653 nm^3 > Y_2O_3: 1.1863 nm^3 > Lu_2O_3: 1.1158 nm^3) [8].

In order to investigate the influence of the crystal lattice volume to the K^+ ion conductivity, the conductivity measurement was carried out for the composition of $0.818R_2O_3$-$0.182KNO_3$ in which a cubic single phase is formed for all the three $(1-x)R_2O_3$-$xKNO_3$ ($R = $ Gd, Y, Lu) series. The relationship between the lattice volume and the conductivity at 873 K is shown in Fig. 3. The electrical conductivity linearly enhanced with the increase of the lattice volume, which clearly indicates that the conductivity directly depends on the lattice volume of the host cubic oxides.

Fig. 4 shows the KNO_3 content dependences of the electrical conductivity at 873K for $(1-x)Gd_2O_3$-$xKNO_3$ which shows the highest conductivity among the three types of $(1-x)R_2O_3$-$xKNO_3$ series. The conductivity increased monotonously in the region of $x \leq 0.347$, and reaches the maximum value of 1.72×10^{-1} S · cm^{-1}at $x = 0.347$. Further KNO_3 content in the crystal lattice results in the conductivity decrease due to the formation of the secondary KNO_3 phase as shown in Fig. 1.

For the purpose of identifying the conducting species in the $(1-x)Gd_2O_3$-$xKNO_3$ solid solutions, the dc electrolysis was carried out for the $0.653Gd_2O_3$-$0.347KNO_3$ solid solution which showed the highest conductivity in the $(1-x)Gd_2O_3$-$xKNO_3$ series. The schematic illustration of the electrolysis is presented in Fig. 5(a). From the preliminary I-V characteristics measurement, the decomposition voltage of the $0.653Gd_2O_3$-$0.347KNO_3$ solid solution was determined to be ca. 0.8 V. When the applied voltage exceeds the decomposition voltage, the solid electrolyte decomposes to generate the potassium ions that may contribute as the conducting ion species at the anode. Therefore, a dc voltage of 4 V that is considerably higher than the decomposition voltage of 0.8 V, was applied to carry out the dc electrolysis in order to supply the migrating ion species from the anode to cathode through inside the sample body continuously. In the case that the migrating ion species is cation, the conducting cation produced by the sample decomposition at the anode migrates into the $0.653Gd_2O_3$-$0.347KNO_3$ solid solution and reaches the interface between the sample pellet and the cathode, and as a result, the cation species deposits at the cathodic surface. On the other hand, if oxide anion migrates in the sample, no deposition is expected to appear on both sides. After the electrolysis, the elemental analysis in the electrolyzed sample was carried out by EPMA line analysis. Fig. 5(b) depicts the line analysis results in the electrolyzed pellet. Between the cation species of K^+ and Gd^{3+}, the K^+ segregation near the cathodic surface was clearly recognized as highlighted as the dotted circle. In addition, the formation of K_2O at the cathodic surface of the electrolyzed sample was clearly observed by the X-ray powder diffraction analysis. These results elucidate the fact that the potassium ions conduct from anodic to cathodic direction through the bulk and deposit as a potassium metal at the cathode and then immediately oxidized with ambient air atmosphere to form K_2O.

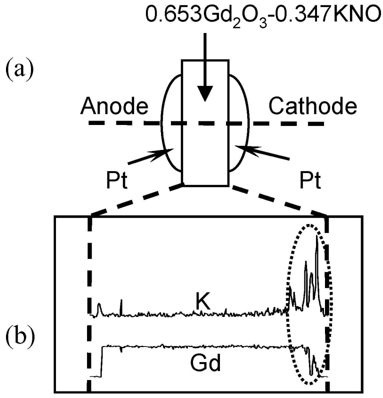


Figure 5 (a) The schematic illustration of the electrolysis of the $0.653Gd_2O_3$-$0.347KNO_3$ solid solution and (b) the elemental analysis results in the electrolyzed sample.

Modified Tubandt electrolysis was performed by using three $0.653Gd_2O_3$-$0.347KNO_3$ pellets and two Pt electrodes in order to quantitatively investigate the potassium ion conduction. As the same reason for the dc electrolysis mentioned above, the K^+ ion can migrate by applying the dc voltage higher than the decomposition voltage. In the case that the K^+ ions migrate from anodic to cathodic direction through the three pellets,

TABLE I Result of Tubandt electrolysis

	Mass changes (mg)			
		Expected for charge carriers		
	Observed	K^+	Gd^{3+}	O^{2-}, e^-
$0.653Gd_2O_3$-$0.347KNO_3$				
A (Anode side)	−0.38	−0.45	−0.27	0
B	−0.07	0	0	0
C (Cathode side)	+0.22	+0.21	+0.27	0

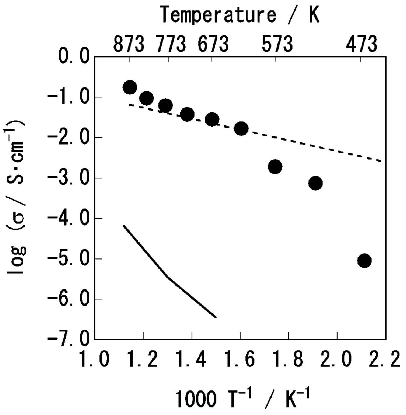


Figure 6 Temperature dependence of the $0.653Gd_2O_3$-$0.347KNO_3$ solid solution (●) with the data of representative K^+ ion conductors of the K^+-β''- Al_2O_3 single crystal (- - -)[3] and the K_2SO_4 polycrystal (—)[2].

the corresponding weight changes of the pellets on both the cathodic and anodic sides should be recognized. In the pellet on the anodic side, the weight loss should be observed due to the decomposition of KNO_3 into K^+ to conduct as well as the generation of the gaseous nitrogen oxides (NO and NO_2) and O_2. In contrast, the weight increase should be observed in the cathodic pellet due to the deposition of K^+species as the corresponding oxide state. In the case of the pellet located in the middle, no such a weight change should be recognized. The theoretical weight changes expected and the measured ones are tabulated in Table I. The actual weight changes observed, well agree with the theoretical ones (weight loss in both A and B: −0.45 mg, weight gain in C: 0.22 mg). This phenomenon clearly indicates the fact that the $0.653Gd_2O_3$-$0.347KNO_3$ solid solution is exactly a pure K^+ ion conducting solid.

Fig. 6 shows the temperature dependence of the $0.653Gd_2O_3$-$0.347KNO_3$ solid solution with the data of representative K^+ ion conductors of the K^+-β''-Al_2O_3 single crystal [3] and the K_2SO_4 polycrystal [2]. The K^+ ion conductivity of the polycrystalline $0.653Gd_2O_3$-$0.347KNO_3$ solid solution is not only three orders of magnitude higher than that of the well-known K_2SO_4 polycrystalline solid electrolyte but also exceeds that in the *ab* plane of the K^+-β''-Al_2O_3 single crystal and the enhancement of the K^+ ion conductivity at temperatures lower than 873 K will facilitate the application of the present K^+ ion conducting solid.

4. Conclusions

A new K^+ ion conducting solid electrolyte with high K^+ ion conductivity was successfully realized by doping KNO_2 as the starting material into the cubic C-type rare earth oxides (R_2O_3: R = Gd, Y, and Lu). The K^+ ion conductivity of the R_2O_3-KNO_3 solid solutions depends on both the lattice volume of the host R_2O_3 and the KNO_3 content in the interstitial site. The highest K^+ ion conductivity of $1.72 \times 10^{-1}\ S \cdot cm^{-1}$ at 873 K was obtained for the $0.653Gd_2O_3$-$0.347KNO_3$ solid solution. Since KNO_2 dissolves into the Gd_2O_3 crystal lattice with simultaneous oxidation of itself, the $0.653Gd_2O_3$-$0.347KNO_3$ solid formed is stable up to 873 K, which exceeds the melting point of KNO_3 (approximately 592 K). These characteristics are suitable for applying the present $(1 - x)R_2O_3$-$xKNO_3$ solid solutions to the functional materials such as chemical sensors and the improvement of the K^+ ion conductivity at temperatures lower than 873 K is highly expected.

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