K\(^+\) ion conducting properties in the R\(_2\)O\(_3\)-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\(_2\)O\(_3\)-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\(_2\)O\(_3\)-xKNO\(_3\) solid solution linearly increased with expanding the R\(_2\)O\(_3\) crystal lattice and the highest K\(^+\) ion conductivity was obtained for the 0.653Gd\(_2\)O\(_3\)-0.347KNO\(_3\) solid solution, which is three orders of magnitude higher than that of a well-known polycrystalline K\(^+\)ion conducting K\(_2\)SO\(_4\) solid and the value exceeds that in the ab conducting plane of a K\(^+\)-β"-Al\(_2\)O\(_3\) 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\(_2\)O\(_3\) single crystal shows as high ion conductivity region as 10\(^{-1}\) S 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\(_2\)O\(_3\) 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\(_2\)O\(_3\) single crystal growth is also a time-consuming and trouble-some task. One of polycrystalline K\(^+\) ion conducting solid electrolytes reported is K\(_2\)SO\(_4\) [2]. However, the K\(^+\) ion conductivity of the K\(_2\)SO\(_4\) polycrystal is as low as 3.38 \times 10^{-5} \text{ S cm}^{-1} even at 873 K and, therefore, the polycrystalline K\(^+\) ion conductor whose ion conductivity reaches the practically application range of 10^{-1} \text{ S 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\(_2\)O\(_3\) 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\(_2\)O\(_3\) 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\(_2\)O\(_3\) 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\(_2\)O\(_3\) 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\(_2\)O\(_3\)-KNO\(_3\) (R: Rare earths) solid solution electrolytes in detail.
2. Experimental

Potassium nitrite (99.9%) and R$_2$O$_3$ (R = Gd, Y, Lu)(99.9%) were thoroughly mixed in a molar ratio of KNO$_2$:R$_2$O$_3$ = 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$_2$O$_3$ 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-K$_\alpha$ radiation in the 2θ range from 10° to 70° by a step width of 0.04°.

The ac conductivity ($\sigma_{ac}$) 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$_2$O$_3$-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$_2$O$_3$ samples doped with KNO$_2$ as the starting material and that of pure Gd$_2$O$_3$. 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$_2$O$_3$ and exists as KNO$_3$ in the host Gd$_2$O$_3$ crystal lattice. It clearly shows that only peaks related to cubic Gd$_2$O$_3$ 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$_2$O$_3$ phase. Similar results were also obtained in the case of R$_2$O$_3$ 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$_2$O$_3$-$x$KNO$_3$ ($R = $ Gd, Y and Lu) hereafter.

The lattice constant variations of the (1 − $x$)R$_2$O$_3$-$x$KNO$_3$ ($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$_2$O$_3$-$x$KNO$_3$ increase with the amount of potassium nitrate content in the solid solutions due to the larger K$^+$ ionic size