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# Potassium ion conductivity of $KNO_2$ mixed oxides

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## Abstract

Two types of polycrystalline solids, $KNO_2$ mixed $Gd_2O_3$ and $KNO_2$ mixed $Nb_2O_5$, were prepared. In the case for $KNO_2$ mixed $Gd_2O_3$, a remarkable enhancement in $K^+$ ion conductivity was successfully realized by interstitially dissolved $KNO_3$ formed during the preparation process in the C-type cubic $Gd_2O_3$ crystal lattice. In contrast, the conductivity of $KNO_2$ mixed $Nb_2O_5$ was more than three orders of magnitude below that of the $Gd_2O_3$–$KNO_3$ solid solution due to the $KNO_3$ decomposition during the preparation procedure. The $K^+$ ion conductivity of the polycrystalline $Gd_2O_3$–$KNO_3$ solid solution is more than three orders of magnitude higher than that of the $K^+$ ion conducting $K_2SO_4$ polycrystal and the value exceeds that of $K^+$-$\beta''$-alumina single crystal in *ab* plane, realizing the highest ion conductivity among the $K^+$ ion conducting solid electrolyte series. The superior ion conducting properties are realized by forming the interstitially $KNO_3$ dissolved $Gd_2O_3$ solid solution, without decomposing the mixed salt with $K^+$.

*Keywords:* Solid electrolyte; Potassium ion; C-type rare earth oxide; Gadolinium oxide; Niobium oxide

## 1. Introduction

$K^+$ ion is one of conducting ion species in solids [1,2]. However, the $K^+$ ion (ionic radius (four-coordinate): 0.137 nm) conductivity is appreciably below the practical application region compared with those of $Li^+$ (ionic radius (four-coordinate): 0.059 nm) and $Na^+$ (ionic radius (four-coordinate): 0.099 nm) ion conductors, such as $Li^+$ ion super ionic conductor of LISICON [3] and $Na^+$ ion super ionic conductor of NASICON [4], according to its relatively large ionic size. One exception is the single crystal of $K^+$-$\beta''$-alumina [5] and its $K^+$ ion conductivity (in the *ab* plane) is as high as $10^{-1}$ S cm$^{-1}$ at 600 °C and the value is comparable to those of well-known $Li^+$ or $Na^+$ ion conducting solids. However, the $K^+$ ion conductivity of $K^+$-$\beta''$-alumina single crystal along *c*-axis is several orders of magnitude lower than that in *ab* plane, indicating that the $K^+$ ion conductivity of the polycrystalline $K^+$-$\beta''$-alumina is considerably below that of the $K^+$-$\beta''$-alumina single crystal. One of the other $K^+$ ion conductors is polycrystalline potassium sulfate ($K_2SO_4$). However, the $K^+$ ion conductivity of $K_2SO_4$ polycrystal is as small as $3.38 \times 10^{-5}$ S cm$^{-1}$ at 600 °C [2] and still three orders of magnitude lower than that of the practical application region (>$10^{-2}$ S cm$^{-1}$) of the representative $Li^+$ and $Na^+$ ion conducting solids. In order to obtain practical $K^+$ ion conductors, the realization of polycrystalline $K^+$ ion conducting solid showing the ion conductivity which enters into the application region, is highly requested. In our previous communication [6], C-type $Gd_2O_3$ was selected as the mother polycrystalline solid which possesses the highest symmetric cubic phase and holds reasonable space for bulky ion conduction like $K^+$ ions.

In this study, two types of oxides, cubic $Gd_2O_3$ (C-type rare earth oxide) and monoclinic $Nb_2O_5$, were selected as the mother phase candidates and the mixing of $KNO_2$ was carried out to clarify the formation of the oxide–$KNO_3$ solid solution and their $K^+$ ion conducting characteristics were compared in detail.

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## 2. Experimental

$Gd_2O_3$ and $KNO_2$ powders were mixed by ball milling method (FRITSCH GmbH, Pulverisette 7). The mixture was pelletized and heated at 450 °C for 12 h in air. The pellets were pulverized and the resulting powder was pelletized again, and heated at 600 °C for 12 h in air, and then sintered at 600 °C for 12 h in air. The preparation of the $KNO_2$ mixed $Nb_2O_5$ solids was also carried out in a similar manner.

The sample characterization was conducted by X-ray powder diffraction using Cu Kα radiation (Rigaku, Multiflex). The XRD data were collected by a step-scanning method in the $2\theta$ range of 10–70°. The composition was identified by X-ray fluorescence analysis (Rigaku, ZSX100e). Fourier transform-IR spectrometer (JASCO International Co. Ltd., FT/IR-430) was used to obtain the infrared spectra of the samples. The electrical ac conductivity was measured using the sample pellet with the two Au electrodes by the complex impedance method (Hewlett-Packard, impedance analyzer 4192A) at the frequency region 5 Hz–13 MHz in the temperature range between 200 and 500 °C.

## 3. Results and discussion

Figs. 1(a) and 2 present the X-ray powder diffraction patterns of the $KNO_2$ mixed $Gd_2O_3$ and the $KNO_2$ mixed $Nb_2O_5$ series, respectively. Up to $x = 0.405$ in $(1-x)Gd_2O_3$–$xKNO_3$, only C-type cubic $Gd_2O_3$ phase was observed, while additional peak corresponds to $KNO_3$ was observed for $x > 0.405$. Furthermore, the lattice parameter of C-type cubic $Gd_2O_3$ monotonously increases with the $KNO_3$ content in $(1-x)Gd_2O_3$–$xKNO_3$ as shown in Fig. 1(b), suggesting the formation of the $Gd_2O_3$–$KNO_3$ solid solution. From Fig. 1, it becomes clear that the solid solution limit in the series is estimated to be ca. $x = 0.405$. In contrast, for the $KNO_2$ mixed $Nb_2O_5$ series, all samples prepared show peaks corresponding only to mother $Nb_2O_5$ phase without any peak shift in the XRD patterns.

From IR measurements of $(1-x)Gd_2O_3$–$xKNO_3$ with $x = 0.405$ and 0.469 (Fig. 3), the bands at 1384 $cm^{-1}$ ($\nu_3$ asymmetric stretching mode of $NO_3^-$) and 827 $cm^{-1}$ (out-of-plane $\nu_2$ deformation mode of $NO_3^-$) were observed for both samples, suggesting that $NO_3^-$ anion exists in both solids. Furthermore, we have confirmed that the IR spectra of mother $Gd_2O_3$ did not change by $KNO_2$ doping. Therefore, it is considered that $KNO_2$ may be oxidized by ambient oxygen during the heating process. Since it is evident from Fig. 1 that the solids for $x \leq 0.405$ are the single solid solution, while the solid is the mixture phase of the $Gd_2O_3$–$KNO_3$ solid solution and $KNO_3$ phases for $x \geq 0.469$, the IR spectrum for the solid solution of $x = 0.405$ is the $NO_3^-$ anion existing in the interstitial sites of the solid solution. From the IR measurements for the $KNO_2$ mixed $Nb_2O_5$ series, there appears no peak corresponding to $NO_3^-$ anion, indicating that all the samples prepared in the $KNO_2$ mixed $Nb_2O_5$ series do not

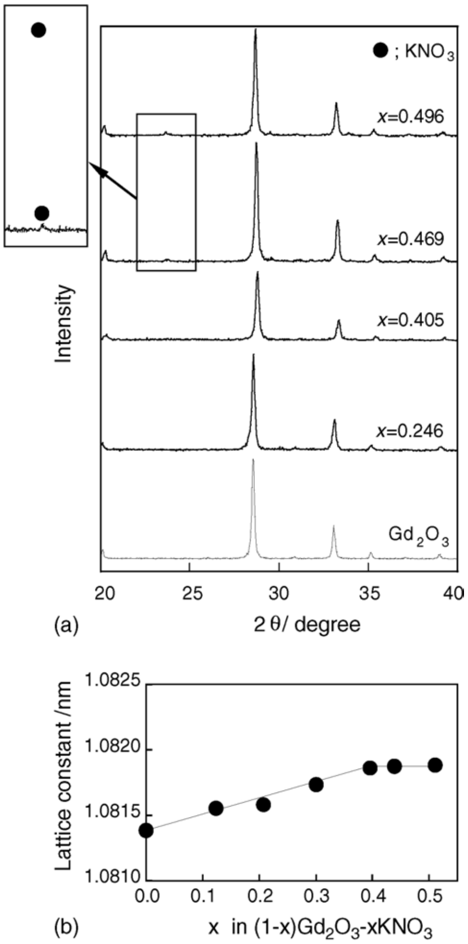

Fig. 1. (a) The X-ray powder diffraction patterns of $KNO_2$ mixed $Gd_2O_3$ and (b) the relationship between lattice parameter and the $KNO_3$ content in the $Gd_2O_3$–$KNO_3$ solids.

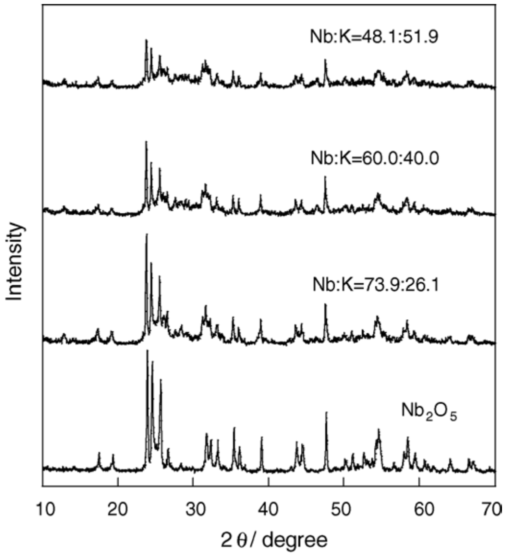

Fig. 2. The X-ray powder diffraction patterns of $KNO_2$ mixed $Nb_2O_5$.

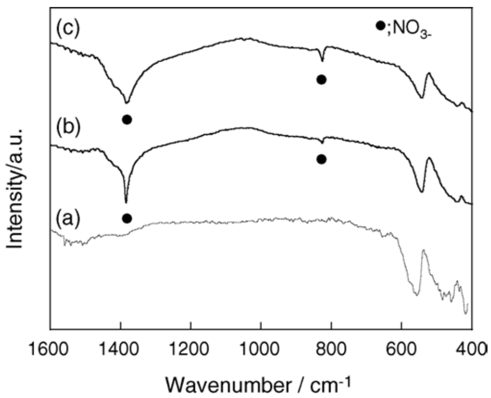

Fig. 3. FT-IR spectra of (a) $Gd_2O_3$, (b) $0.595Gd_2O_3$–$0.405KNO_3$ and (c) $0.531Gd_2O_3$–$0.469KNO_3$.

contain $NO_3^-$ at all. Although a peak shift in XRD and the IR bands corresponding to $NO_3^-$ anion were not recognized at all, the K content in the $KNO_2$ mixed $Nb_2O_5$ system was the same as that of the mixing ratio from the X-ray fluorescence analysis. The results indicate the fact that $KNO_3$ produced from the oxidation of $KNO_2$ decomposes during preparation procedure.

The $KNO_3$ content dependencies of the electrical conductivity at 500 °C for the $Gd_2O_3$–$KNO_3$ series are presented in Fig. 4. The electrical conductivity increases with the $KNO_3$ content in the $Gd_2O_3$–$KNO_3$ solids and shows the maximum conductivity at around $x = 0.405$. As the sample with $x = 0.469$ was the mixed phase (see Fig. 1), the highest conductivity of $10^{-1}$ S cm$^{-1}$ was obtained for the sample with $x = 0.405$ among the samples having the single solid solution phase. On the other hand, the conductivities for the $KNO_2$ mixed $Nb_2O_5$ series were independent of the mixing ratio of $KNO_2$.

Fig. 5 shows the temperature dependencies of the conductivity for the $0.595Gd_2O_3$–$0.405KNO_3$ solid solution and the $0.4KNO_2$ mixed $0.6Nb_2O_5$ solid, together with the data of $K^+$-$\beta''$-$Al_2O_3$ single crystal (in *ab* plane) and polycrystalline $K_2SO_4$. The conductivity of the $0.595Gd_2O_3$–$0.405KNO_3$ solid solution is three orders of magnitude higher than that of $KNO_2$ mixed $Nb_2O_5$, indicating the formation of the solid solution by introducing $K^+$ cation and $NO_3^-$ anion simultaneously in the $Gd_2O_3$ crystal lattice. The conductivity of $0.595Gd_2O_3$–$0.405KNO_3$ is two times higher than that of the $K^+$-$\beta''$-$Al_2O_3$ single crystal (in *ab* plane) having the highest $K^+$ ion conductivity among the $K^+$ ion conducting solids reported so far. The solid solution formation is also effective to avoid decomposition of $KNO_3$, which is clearly observed in the case for the $Nb_2O_5$–$KNO_3$ series.

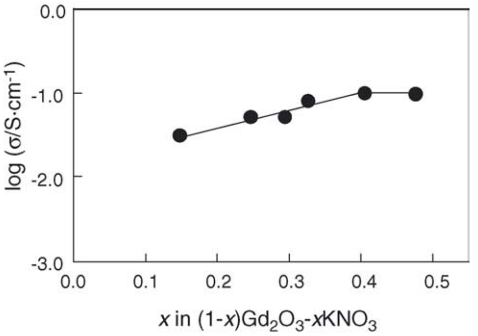

Fig. 4. The $KNO_3$ content dependence of the electrical conductivity for the $Gd_2O_3$–$KNO_3$ series at 500 °C.

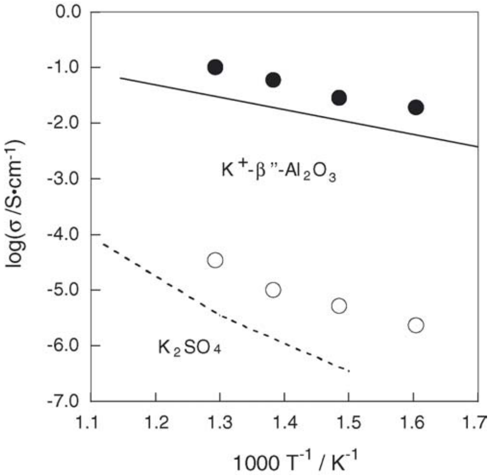

Fig. 5. The temperature dependencies of the conductivity for the $0.595Gd_2O_3$–$0.405KNO_3$ solid solution (●) and $0.4KNO_2$ mixed $0.6Nb_2O_5$ (○) with the corresponding data of $K^+$-$\beta''$-$Al_2O_3$ single crystal [5] (in *ab* plane) (solid line) and polycrystalline $K_2SO_4$ [2] (dotted line).

## 4. Conclusions

Two types of solid mixtures, $KNO_2$ mixed $Gd_2O_3$ and $KNO_2$ mixed $Nb_2O_5$, were studied as the starting materials for the synthesis of new type of $K^+$ ion conducting solids. The formation of the solid solution with holding both $K^+$ cation and $NO_3^-$ anion in the interstitial $Gd_2O_3$ crystal lattice was explicitly observed in the case for $Gd_2O_3$–$KNO_3$, and the $K^+$ ion conductivity was as high as $10^{-1}$ S cm$^{-1}$ at 500 °C, while decomposition of the salt with $K^+$ occurred in the case for the $KNO_2$ mixed $Nb_2O_5$ series, resulting in the great conductivity decrease compared with the cases for the $Gd_2O_3$–$KNO_3$ solids and the $K^+$-$\beta''$-$Al_2O_3$ single crystal (in *ab* plane). The results described above clearly support the idea that the $Gd_2O_3$–$KNO_3$ solid is the superior $K^+$ ion conducting solid solution electrolyte which contains not only $K^+$ cation but also $NO_3^-$ anion in the polycrystalline C-type cubic $Gd_2O_3$ crystal lattice.

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