The Rare-Earth Dependence on the Solid Solution Formation and Electrical Properties of $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ (R=Nd, Sm, Gd and Ce)

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$\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ (R=Nd, Sm, Gd, 及び Ce) の固溶体生成及び電気的性質の希土類依存性

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The solid solution $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ (R=Nd, Sm, Gd and Ce) was prepared by solid-state reaction using $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, KNbO_3 , Nb_2O_5 , Nb and rare-earth oxides. The solubility limit of the solid solutions was extended with an increase in the ionic radii of the rare earths. All the solid solutions exhibited similar semiconductive behavior with a linear $\log \rho$ - T relationship over a wide temperature range. These results suggest that the conduction mechanism is independent of the type of rare earths and also the unit-cell parameters, which agrees well with the tunneling conduction model with a vibrating barrier.

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1. Introduction

The electrical properties of transition-metal (TM) oxides which possess the perovskite structure are basically determined by the concentration of d electrons and the structural parameters.¹⁾ The electron correlation between the f electrons of rare earths R and d electrons of the TM can be neglected because the $4f$ electrons of R are screened by $5s$ and $5p$ shells. Thus, by using various R with different ionic radii, it is possible to control the structural parameters that govern the electrical properties of perovskite oxides such as RTMO_3 .

The perovskite niobate A_xNbO_3 (A=Sr,²⁾⁻⁴⁾ Ba,^{5),6)} Eu,⁷⁾⁻¹³⁾ Sr-Eu¹⁴⁾ and Sr-Ca¹⁴⁾) exhibits metallic conduction with niobium valence in the range from 4.5+ to 4+. On the other hand, perovskite-related oxides with niobium valence in the range from 5+ to 4.5+, for example, $\text{Na}_{1-x}\text{Sr}_x\text{NbO}_3$,^{15),16)} $\text{K}_{1-x}\text{Ba}(\text{Sr})_x\text{NbO}_3$,¹⁷⁾ $\text{R}_{1+x}\text{Nb}_3\text{O}_9$ (R=La, Ce and Nd),¹⁸⁾ ANbO_y (A=Ca and Sr-La)¹⁹⁾ and niobium phosphates²⁰⁾ are all semiconducting or semimetallic.

Recently, $\text{M}[\text{A}_{n-1}\text{Nb}_n\text{O}_{3n+1}]$ possessing a structure closely related to the Ruddlesden-Popper phase has been reported.²¹⁾ This series of compounds can be considered as two-dimensional layered perovskites. Carrier doping in $\text{M}[\text{A}_{n-1}\text{Nb}_n\text{O}_{3n+1}]$ by intercalation of excess M ions (M=Li,^{22),23)} H²⁴⁾ and Rb²⁵⁾) to the interlayer space has been reported, but the electrical properties of these compounds were not studied. We have succeeded in synthesizing $\text{KCa}_{2-x}\text{La}_x\text{Nb}_3\text{O}_{10}$ ($0.1 \leq x \leq 0.4$), which corresponds to the $n=3$ compound of $\text{M}[\text{A}_{n-1}\text{Nb}_n\text{O}_{3n+1}]$, and have reported the first example of electrical conduction of this series.²⁶⁾ $\text{KCa}_{2-x}\text{La}_x\text{Nb}_3\text{O}_{10}$ is semiconducting exhibiting a linear $\log \rho$ - T relationship and was discussed in terms of the tunneling conduction by the vibrating barrier model,²⁷⁾ where the d electrons of niobium act as small polarons. However, since both the structure and the d electron concentration change simultaneously with the substitution of La^{3+} , the discussion of the relationship between the structure and the electrical property was insufficient.

Here, we report the synthesis and electrical properties of $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ (R=Y, Nd, Sm, Gd, Yb and Ce). Emphasis is placed on the change in the structural parameters with

the various rare earths and its dependence on the electrical properties.

2. Experimental

2.1 Sample preparation

Polycrystalline $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ was prepared from $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, KNbO_3 , Nb_2O_5 , Nb and R_2O_3 (R=Y, Nd, Sm, Gd and Yb) or CeO_2 by solid-state reaction according to

$$1/2 x \text{KNbO}_3 + 2/5 x \text{Nb}_2\text{O}_5 + 1/5 x \text{Nb} + 1/2 x \text{R}_2\text{O}_3 + (1-x/2) \text{KCa}_2\text{Nb}_3\text{O}_{10} \rightarrow \text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10},$$

or

$\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was synthesized by the solid-state reaction of stoichiometric amounts of K_2CO_3 , CaCO_3 and Nb_2O_5 at 1100°C for 20h under an ambient atmosphere. KNbO_3 was obtained by the solid-state reaction of stoichiometric amounts of K_2CO_3 and Nb_2O_5 at 1000°C for 1h under an ambient atmosphere. La_2O_3 was preheated at 1000°C for 1h under an ambient atmosphere to avoid contamination in the form of hydroxides. After thorough mixing in an agate mortar with acetone, the powder was pressed into pellets of 13 mmφ. The pressed pellets were then placed in an alumina boat surrounded by powder having the same composition in order to prevent contamination from the boat. To minimize oxidation during synthesis under an argon atmosphere, the reactor tube was evacuated to $\sim 8.5 \times 10^{-3}$ Pa before argon purging and titanium powder was set in the tube as an oxygen getter. All samples were fired at 1200°C for 10h under an argon atmosphere at the heating and cooling rate of 5°C/min.

2.2 Analyses

Crystalline phases were identified using a Mac Science MXP3 diffractometer (monochromated $\text{Cu K}\alpha$ radiation). Unit-cell parameters were refined from the positions of 15-21 peaks which were indexed reasonably by the nonlinear least squares method. The amounts of potassium, calcium, rare-earths and niobium were determined by inductively coupled plasma emission spectroscopy (ICP) (Nippon Jarrell Ash, ICAP575 Mark II). For the ICP measurements, samples were decomposed in a mixture of HF, H_2SO_4 and

HNO₃ by heating at 200°C for at least 3h. The resistivity measurements were performed using a standard dc four-probe method from 5 to 280 K.

3. Results and discussion

3.1 Solid solution formation

Table 1 summarizes the compositional analysis results of the samples obtained as single phases. The compositions of the products were essentially consistent with the corresponding nominal ones, indicating that volatilization of the starting components was negligible.

X-ray powder diffraction (XRD) patterns for the neodymium-doped samples are shown in Fig. 1. The single-phase products ($0 \leq x \leq 0.3$) were indexed according to a pseudotetragonal orthorhombic structure, thus indicating successful substitution. On the other hand, for $x \geq 0.4$, NdNbO₄ and an unidentified phase were evident in the samples. The solubility limit for the samarium-, gadolinium- and cerium-doped samples were also determined in the same manner, and are shown in Fig. 2 as open circles. Syntheses of yttrium- and ytterbium-doped samples were also attempted, but single-phase samples could not be obtained even for $x=0.1$. All the multiphase samples contained RNbO₄ as an impurity phase regardless of the type of rare earth. Unreacted R₂O₃ was occasionally observed in addition to RNbO₄ for the smaller rare earths.

The unit-cell parameters of the single-phase samples are shown in Table 2. The ionic radius²⁸⁾ for each rare-earth decreases in the order; La³⁺ (0.136 nm) > Ce²⁺ (0.134 nm) > Nd³⁺ (0.127 nm) > Sm³⁺ (0.124 nm). Considering the ionic radius of 9-coordinated Gd³⁺ and Sm³⁺,²⁸⁾ the

Fig. 2. The solubility limit as a function of the ionic radii. The × mark represents the plot for the solubility limit based on the ionic radius of Ce⁴⁺.

No single-phase samples were obtained for Y and Yb substitution. The data on La are from Ref. 26.

Table 2. The Unit-Cell Parameters of KCa_{2-x}R_xNb₃O₁₀

rare earth	x value	unit-cell parameter / nm		
		a	b	c
-	0	0.3875	0.3859	2.951
Ce	0.1	0.3880	0.3863	2.952
	0.2	0.3880	0.3865	2.956
	0.3	0.3885	0.3870	2.959
	0.4	0.3893	0.3881	2.958
Nd	0.1	0.3875	0.3858	2.952
	0.2	0.3880	0.3864	2.955
	0.3	0.3882	0.3866	2.958
Sm	0.1	0.3874	0.3860	2.954
	0.2	0.3876	0.3860	2.955
Gd	0.1	0.3874	0.3859	2.951

Table 1. The Composition of the Single-Phase Products

rare earth	x value	composition ^{a,b}
-	0	K _{0.96} Ca _{1.96} Nb ₃ O ₁₀
La ^c	0.1	K _{1.06} Ca _{1.86} La _{0.11} Nb ₃ O ₁₀
	0.2	K _{1.00} Ca _{1.75} La _{0.23} Nb ₃ O ₁₀
	0.3	K _{1.08} Ca _{1.68} La _{0.32} Nb ₃ O ₁₀
	0.4	K _{1.01} Ca _{1.59} La _{0.47} Nb ₃ O ₁₀
Ce	0.1	K _{1.08} Ca _{1.92} Ce _{0.10} Nb ₃ O ₁₀
	0.2	K _{1.07} Ca _{1.83} Ce _{0.17} Nb ₃ O ₁₀
	0.3	K _{1.01} Ca _{1.68} Ce _{0.27} Nb ₃ O ₁₀
	0.4	K _{1.07} Ca _{1.55} Ce _{0.40} Nb ₃ O ₁₀
Nd	0.1	K _{1.08} Ca _{1.88} Nd _{0.10} Nb ₃ O ₁₀
	0.2	K _{1.07} Ca _{1.79} Nd _{0.20} Nb ₃ O ₁₀
	0.3	K _{1.03} Ca _{1.65} Nd _{0.29} Nb ₃ O ₁₀
Sm	0.1	K _{1.09} Ca _{1.97} Sm _{0.11} Nb ₃ O ₁₀
	0.2	K _{1.08} Ca _{1.81} Sm _{0.21} Nb ₃ O ₁₀
Gd	0.1	K _{1.07} Ca _{1.86} Gd _{0.10} Nb ₃ O ₁₀

^a The compositions are normalized by setting the amount of niobium to 3.

^b The amount of oxygen is set to a nominal value.

^c Data from Ref. 26.

Fig. 1. The XRD patterns of KCa_{2-x}Nd_xNb₃O₁₀.

ionic radius of 12-coordinated Gd³⁺ is presumably smaller than that of Sm³⁺. The tendency of the increment of the unit-cell volume also decreased in this order (Fig. 3). Although Nd³⁺ and Sm³⁺ are smaller than Ca²⁺, the unit-cell volume tends to increase when they are substituted for Ca²⁺. This can be explained by the simultaneous increase in the B-site ionic radius from Nb⁵⁺ (0.064 nm²⁹⁾) to Nb⁴⁺ (0.068 nm²⁸⁾) with the substitution of the rare earth. An increase in the unit-cell parameters was also observed for K_{1-x}Ba_xNb₃O₁₀,¹⁷⁾ in this system, the substitution of potassium decreases the average ionic radius of the A-site, but the simultaneous decrease of the niobium valence with substitution increases the average ionic radius of the B-site. The solubility limit was strongly dependent on the ionic radius of the rare earth, such that single-phase products are more

Fig. 3. The variation of the unit-cell volume. The data on La are from Ref. 26.

apt to be obtained when the average ionic radius of the A site is larger. The fact that $\text{KSr}_2\text{Nb}_3\text{O}_{10}$ ²⁹⁾ ($\text{R}_{\text{Sr}^{2+}}$ is larger than $\text{R}_{\text{Ca}^{2+}}$ by 0.006 nm²⁹⁾) is known to exist also supports this tendency.

Due to the $4f^{15}d^{16}s^2$ electronic configuration of cerium, compared to the other lanthanides, the valence of cerium can be either 3+ or 4+. The ionic radius of Ce^{4+} is 0.114 nm and that of Ce^{3+} is 0.134 nm.²⁸⁾ As can be seen from Fig. 2, the Ce^{3+} plot follows the tendency of the substitution limit for the other rare-earths, while the Ce^{4+} (shown as an X mark) plot does not. Thus, the valence of cerium is most likely close to 3+. Similar results have been obtained in our preliminary study on the synthesis of $\text{KLa}_{1-x}\text{Ce}_x\text{Nb}_2\text{O}_7$ using CeO_2 as one of the starting materials. The product was insulating probably because the valence of niobium was 5+ and that of cerium was 3+. Furthermore, Abakumov et al.¹⁸⁾ reported that Ce^{4+} was reduced to Ce^{3+} in $\text{Ce}_{1+x}\text{Nb}_3\text{O}_{10}$ synthesized from CeO_2 , NbO_2 and Nb_2O_5 under an inert atmosphere.

3.2 Electrical properties

The room temperature resistivities of the samples with various R at $x=0.1$ was in the order of 10^2 – $10^4 \Omega \cdot \text{m}$ and decreased with an increase in x . The resistivity behavior for the neodymium-substituted samples is shown in Fig. 4. The single-phase samples for other rare-earths showed similar semiconducting behavior, thus suggesting a localization of electrons.

The localization of electrons in $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ can be argued based on the disorder of the periodic potentials. Since $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ contains perovskite slabs, conduction should originate from the overlapping of Nb $4d$ t_{2g} and O $2p$ orbitals. Conduction of other solid-solution compounds, such as $\text{Na}_{1-x}\text{Sr}_x\text{Nb}_3\text{O}_{10}$ ¹⁶⁾ and $\text{K}_{1-x}\text{Ba}(\text{Sr})_x\text{NbO}_3$,¹⁷⁾ was also discussed with the presence of electrons in the π^* conduction band formed by the overlapping of Nb $4d$ t_{2g} and O $2p$ orbitals. The conduction model in these Ba- or Sr-substituted compounds was discussed based on a one-electron energy diagram, which is similar to the conduction model proposed by Goodenough³⁰⁾ for Na_xWO_3 and ReO_3 . The niobium d electrons were suggested to localize because of the non-periodic potentials resulting from the random distribution of Na^+ and Sr^{2+} or that of K^+ and Ba^{2+} . With the random distribution of Ca^{2+} and R^{3+} and the different crystallographic environments expected for niobium,^{21),31)} the generation of a nonperiodic potential is reasonable.

The resistivity behavior of $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ ($\text{R}=\text{Ce}, \text{Nd}$ and Sm ; $x=0.2$) is shown in Fig. 5. The resistivity of the single-phase $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ exhibited semiconducting behavior with a $\log \rho$ – T dependence. The same dependence was observed for the $x=0.1$ and 0.3 samples. Such behavior was also observed in $\text{KCa}_{2-x}\text{La}_x\text{Nb}_3\text{O}_{10}$,²⁶⁾ and was interpreted

Fig. 4. The temperature dependence of the normalized resistivity for $\text{KCa}_{2-x}\text{Nd}_x\text{Nb}_3\text{O}_{10}$.

Fig. 5. The temperature dependence of the normalized resistivity for $\text{KCa}_{1.8}\text{R}_{0.2}\text{Nb}_3\text{O}_{10}$ ($\diamond \text{R}=\text{Ce}$, $\triangle \text{R}=\text{Nd}$ and $\circ \text{R}=\text{Sm}$).

ed by the tunneling conduction of small polarons with vibrating barriers model,²⁷⁾ which is based on the incoherent tunneling of electrons between the nearest neighboring sites with an oscillating barrier. The transfer rate R (which dominates the conductivity σ) in the vibrating barrier model is expressed as

$$\sigma (= \rho^{-1}) \approx R \approx \text{constant} \times \exp(-2\alpha S_0) \times \exp(-U/k_B T) \exp(2\alpha^2 k_B T / m\omega^2) \quad (1)$$

where $\exp(-2\alpha S_0)$ is the overlap term, $\exp(-U/k_B T)$ is the coincidence term and $\exp(2\alpha^2 k_B T / m\omega^2)$ is the tunneling term. α is related to the expansion of the wave function, S_0 is the equilibrium width of the barrier, U is the activation energy for the displacement of sites, m is the mass of the ions involved, and ω is the oscillating frequency of the barrier. The overlap term is nearly independent of the temperature, thus the remaining two exponential terms dominate the temperature dependence of conduction. When the tunneling term, which is due to the oscillation of the barrier, is dominant, the resistivity is expressed as

$$\log \rho \sim (-2\alpha^2 k_B / m\omega^2) \times T \quad (2)$$

thus giving the $\log \rho$ – T linear behavior.

Regardless of the structural change (change in unit-cell parameters) with the various rare earths, there is no apparent change in the temperature dependence of resistivity. This agrees with the fact that no variables concerning the ion position or the barrier width are included in the tunneling term in Eq. (2).

The site-localization parameter α^{-1} represents the degree of the penetration of the electron wave function into the forbidden region and can be calculated from the slope in Fig. 5. The α^{-1} values of $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ are summarized in Table 3. When comparing the compounds with the same amount of substituted rare earth in $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$, there was no substantial difference in the value of α^{-1} . On the con-

Table 3. The Site-Localization Parameter α^{-1}

rare earth	x value	α^{-1} / nm
La ^b	0.2	0.105
	0.3	0.123
Ce	0.1	0.088
	0.2	0.097
	0.3	0.125
	0.4	0.177
Nd	0.1	0.074
	0.2	0.093
	0.3	0.124
Sm	0.1	0.071
	0.2	0.097
Gd	0.1	0.078

^a $\omega = 1 \times 10^{12} \text{ s}^{-1}$, $m = 1.5 \times 10^{-25} \text{ kg}$ used for calculation.

^b Data from Ref. 26.

trary, with the increase in the average niobium valence, α^{-1} increased; thus the electrical properties are influenced mainly by the carrier concentration and the effect by the structural parameters can be neglected.

4. Conclusion

The isostructural series $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ ($\text{R}=\text{Nd}, \text{Sm}, \text{Gd}$ and Ce) has been synthesized by solid-state reactions and the electrical properties are discussed based on the changes in structural parameters and electron concentration. The maximum amount of rare-earth substitution in $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ increased with the increase in the ionic radii of the rare earths. The introduction of various rare earths altered the unit-cell parameters of $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$, but all samples showed similar $\log \rho$ - T semiconducting behavior. This indicates that the electrons in $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ behave as small polarons and conduction can be interpreted by the tunneling conduction through the vibrating barrier model. The values of α^{-1} did not differ for the various rare earths but varied with the change in niobium valence; this observation shows that the electrical properties in $\text{KCa}_{2-x}\text{R}_x\text{Nb}_3\text{O}_{10}$ are mainly dominated by the carrier concentration.

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