Floating Zone Growth and Characterization of (Ca$_{1-x}$Nd$_x$)$_{12}$Al$_{14}$O$_{33}$+6x ($x \sim 0.001$) Single Crystals

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Supporting Information

ABSTRACT: Rare earth Nd$_{3+}$ ion-doped Ca$_{12}$Al$_{14}$O$_{33}$ single crystals were grown at a rate of 1 mm/h by the floating zone technique in an oxygen atmosphere. The Nd concentration in the central area of the as-grown crystals was higher than that in the peripheral area due to the highly concave growth interface shape. The average Nd concentration in the as-prepared parallelepiped slices of $\sim 6 \times 3 \times 2$ mm$^3$ for electrode fabrication was $\sim 0.095 \pm 0.011$ atom \% Nd in contrast to the nominal 0.1 atom \% Nd concentration. The Nd-doped C12A7:Nd single crystalline electrode prepared by thermal treatment with a Ti metal at 1100 °C for 48 h induced an insulator–metal transition with the highest conductivity of approximately 1165 S/cm. These annealing conditions provide an approach to completely remove clathrated oxide ions from the crystallographic cages, leading to the formation of C12A7:Nd(e$^-$) and C12A7:tc$^-e^-$ electrides with high-density electrons ($\sim 2.4 \pm 0.2 \times 10^{21}$ and $\sim 1.8 \pm 0.1 \times 10^{21}$ cm$^{-3}$) localized in the cages. The carrier mobility at room temperature in C12A7:Nd(e$^-$) was very similar to that in C12A7:tc$^-e^-$, even though it was very high at temperatures below $\sim$150 K.

1. INTRODUCTION

Light metal oxide 12CaO·7Al$_2$O$_3$ (abbreviated as C12A7) has attracted attention for use in functional ceramics. The crystal structure of C12A7 is cubic with a unit cell composed of a positively charged lattice framework [Ca$_{12}$Al$_{14}$O$_{33}$]$^{4+}$ and two extraframework oxide ions (called free O$^{2-}$ ions) that compensate the positive lattice framework.$^{1-3}$ C12A7 can be regarded as a clathrate compound due to its three-dimensionally connected subnanometer-sized cage structure.$^4$ It is also known as a novel functional material with applications in catalysis, fuel cells, hydrogen storage, and CO$_2$ atmosphere.$^{18}$ In the chemical reduction processes, four electrons in C12A7 were injected into 4 of the 12 cages by extracting two of the O$^{2-}$ ions for the free oxide ions in C12A7 to compensate the positive lattice framework [Ca$_{24}$Al$_{28}$O$_{64}$]$^{4+}$ and two positronium cages.15

However, theoretical studies$^{21-25}$ as well as experimental research,$^26$ have revealed that the three-dimensionally connected cages form an additional conduction band known as the conduction band (CCB) in the bottom of the framework conduction band. Because of the low electron concentration in the cages, conduction occurs through the hopping of the electrons from a localized deformed cage to the CCB. The electron-doped C12A7:tc$^-e^-$ electrode is stable under ambient conditions,$^{10}$ and it has recently been used in electronic devices as an electron-emitting source or a low electron injection barrier due to its combination of a low work function ($\sim$2.4 eV) comparable to that of the potassium metal and chemical inertness that is in contrast with the reactive nature of potassium.$^{29}$ In addition, the C12A7:tc$^-e^-$ electrode can be used as a cathode material in organic light-emitting diodes (OLEDs), as an electrode in fluorescent lamps, as a chemical reducing reagent, for ammonia synthesis,$^{27,28}$ and so on.

The effect of cationic substitution on the structure and electrical properties of C12A7 is much less known than that of anionic substitution. Bertoni et al. investigated Mg substitution in the Ca$_{12-x}$Mg$_x$Al$_{14}$O$_{33}$ system and found that electrical conductivity was decreased.$^{29}$ They also studied a Si-substituted Ca$_{12}$Al$_{14-x}$Si$_x$O$_{33+x/2}$ structure that catalyzes hydrocarbon decomposition at high temperatures.$^{30,31}$ Stefan et al. grew C12A7 single crystals with the substitution of 1 mol \% Fe in the Al site by the floating zone (FZ) method, obtaining a reduction

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of the electrical conductivity relative to that of C12A7:Ce\textsuperscript{3+}.\textsuperscript{32} However, the framework and channel modifications in the mayenite Ca\textsubscript{12}Al\textsubscript{14}O\textsubscript{33} nanocages were investigated theoretically by cationic doping.\textsuperscript{33}

To the best of our knowledge, to date, trivalent cation substitution in the Ca sites of a C12A7 single crystal has not been studied yet. The substitution of trivalent cations into the divalent Ca\textsuperscript{2+} sites in C12A7 is one possible method for doping a high density of electrons by neutralizing the increased positive charge within the lattice framework. We previously studied the solid solubility limit of rare earth ions (Y\textsuperscript{3+}, Ho\textsuperscript{3+}, Eu\textsuperscript{3+}, and Nd\textsuperscript{3+}) into the C12A7 phase by the FZ technique, and maximum solubility was found for Nd.\textsuperscript{34} The present work reports C12A7 single crystal growth by the FZ method with 0.1 atom % Nd substitution in the Ca site, the electride fabrication of the as-grown single crystal with optimum annealing conditions, and investigations of the electrical conductivity, carrier concentration, and carrier mobility of the as-prepared electrides.

2. RESULTS AND DISCUSSION

2.1. Crystal Growth. The neodymium-doped C12A7:Nd single crystals were grown with a nominal concentration of 0.1 atom % Nd, as shown in Figure 1A. Before the C12A7:Nd single crystal growth, we also grew a nondoped transparent C12A7 single crystal (see Figure S1d). The as-grown C12A7:Nd crystal is transparent and bluish in color. The bulk XRD pattern along the growth direction is shown in Figure 1B. The reflection peaks were identified as (332) and (664). The presence of this single family of peaks confirms the single domain nature of the grown crystal; it was also found that the growth direction was slightly tilted by approximately 1.63° from the (111) direction. The regular and periodic set of the Laue reflection points pattern also confirms the single crystallinity.

2.2. Neodymium Distribution in As-Grown Single Crystals. Figure 3 shows the Nd concentration distribution in the as-grown crystal measured by using electron probe microanalysis (EPMA). The Nd concentration was not uniform along the radial direction as shown in Figure 3A. The Nd concentration in the central region is higher than the nominal concentration of 0.1 atom % Nd, whereas the Nd concentration in the peripheral area is very low compared to the nominal concentration. This inhomogeneity of the Nd distribution may be due to a highly concave shape of the growth interface (shown in Figure 2A). Because of the concave interface shape, the crystallization starts from the peripheral area and proceeds toward the center. Consequently, if the crystal growth starts along the growth direction from time t\textsubscript{1} to t\textsubscript{2}, the crystallization occurs along the radial direction from the peripheral area at time t\textsubscript{1} to the central area at time t\textsubscript{2} as shown in Figure 2B. This means that the crystallization starts in the peripheral area earlier than in the central area. Because of the highly concave growth interface and a low effective distribution coefficient of Nd (~0.14),\textsuperscript{34} the Nd dopant in the diffusion layer in the melt is concentrated as a normal freezing process during crystallization from the peripheral area to the central area. Consequently, the Nd concentration is very high at the central area in contrast to that in the peripheral area and is even higher than the nominal concentration. The Nd concentration along the longitudinal direction in the as-prepared parallelepiped slice was estimated to be 0.093 ± 0.011 atom % by EPMA as shown in Figure 3B. The Nd distribution inhomogeneity along the growth direction was low as compared to that in the radial direction. This result agrees with our previous reported results that the Nd concentration along the vertical growth direction in the central and the peripheral areas was not significantly changed, in contrast to the results observed in the radial direction.\textsuperscript{34} Therefore, we have prepared the parallelepiped-shaped slice for the electride fabrication by cutting the crystal neither exactly in the central area nor exactly in the peripheral area but in between as indicated by the red line in Figure 3A. In a similar

Figure 1. As-grown Nd-doped C12A7:Nd single crystal (A) and bulk X-ray diffraction (XRD) pattern of the crystal grown along the growth direction (B). The crystal was cut cross-sectionally along the growth direction necessary for performing the bulk XRD measurement.

Figure 2. Nd concentration map at the growth interface (A) and schematic diagram of crystallization during growth (B). t\textsubscript{1} and t\textsubScript{2} indicate successive crystallization times; white arrow in the crystal indicates crystallization from the peripheral to the center areas.
manner, we have prepared several parallelepipeds of approximately $6 \times 3 \times 2$ mm$^3$ slices for annealing.

2.3. Electrical Conductivity of Single Crystal Electrides. Because of the annealing of C12A7:Nd single crystals at 1100 °C for 36−72 h, the color of all samples changed from transparent bluish to black (see Figure S1). The nondoped sample also became black after the annealing at 1100 °C for 48 h. The temperature dependence of the electrical conductivity of the C12A7:Nd single crystals annealed at 1100 °C for various annealing times is shown in Figure 4A. The conductivity (300−2 K) increases as the annealing time increases from 36 to 48 h and decreases for the further increase of the annealing time up to 72 h, with the highest conductivity at 300 K found for the Nd-doped sample annealed for 48 h (sample c). At a temperature range lower than ∼150 K, the conductivity for sample c was very high compared to that of all other samples except for the Nd-doped sample annealed for 72 h (sample e). This may be due to the high electron density ($\sim 2.4 \times 10^{21}$ cm$^{-3}$) over the cages in the C12A7:Nd single crystal electride.

However, in the case of the long (more than ∼48 h) annealing process at 1100 °C, the sample becomes more brittle, and the sample thus showed an increased tendency to break during the removal of the TiO$_2$ layer that completely covered the sample surface. The out-diffusion of the free oxide ions from the crystallographic cages during the annealing is continued despite the formation of a thick titanium oxide layer over the sample’s surface, which is advantageous in contrast to the Ca-metal treatment. Furthermore, the long-time annealed sample may contain some cracks and may partly decompose in several places, making holes/voids on the surface as is evident from the scanning electron microscopy (SEM) image and compositional analysis using EPMA (shown in Figure 5A,B). Because of these holes and cracks, the conductivity decreased drastically to an even lower value than that for the nondoped sample and became almost constant even at very low temperatures of up to 2 K. Thus, it is shown that a 48 h annealing time is expected to be optimal at 1100 °C. To optimize the annealing temperature, we measured the conductivity of the C12A7:Nd single crystals annealed at 900−1200 °C for 48 h of the annealing time (see Figure S2).

Figure 4B shows the Arrhenius plot of the electrical conductivities ($\sigma$) of Ti-heated single crystals annealed for 36−72 h at 1100 °C. The Arrhenius plot has no negative slope, indicating no thermally activated mechanism through variable range hopping conduction, and the electron concentration is higher than $1 \times 10^{21}$ cm$^{-3}$. In contrast, we have obtained positive slopes for all annealed samples resulting in the insulator-to-metal transition. In all conductive samples, log $\sigma$ is exponentially increased up to ∼50 K and becomes almost constant and insensitive to temperatures below ∼50 K.

The sample annealed at 1200 °C for 48 h was very brittle, and its color changed to yellowish in contrast to black as shown in Figure 5C. The color change may be due to the decomposition to another phase instead of C12A7 confirmed by the compositional analysis using EPMA. The SEM image of the sample annealed at 1200 °C for 48 h (Figure 5D) also shows many cracks. Therefore, the Ti-metal vapor treatment for 48 h at 1100 °C would be the optimum annealing condition for C12A7:Nd single crystals for obtaining the highest conductive electrides.

Room temperature (RT) conductivity $\sigma_{300 K}$ of C12A7:Nd single crystals annealed at 1100 °C for 48 h (sample c) showed a maximum value of approximately ∼1165 S/cm, compared to
that of samples on which other annealing conditions were applied as well as nondoped C12A7 (sample a) as shown in Figure 6. For the long annealing of more than ~60 h (Figure 6A), the obtained RT conductivity decreases sharply. The RT conductivity was not significantly changed in the 36−60 h range of annealing times, and the doping electron concentration (2.3 ± 0.2 × 10^{21} \text{cm}^{-3}) for 36 h annealed at 1100 °C (sample b) was also nearly equal to that of sample c (2.4 ± 0.2 × 10^{21} \text{cm}^{-3}) (shown in Table 1), indicating the complete replacement of the free O^{2−} ions by the electrons. Further, at 900 °C (sample f), 1000 °C (sample g), and 1100 °C (sample c) and an annealing time of 48 h, the RT conductivity was slightly changed (Figure 6B), even though the carrier concentration in the corresponding samples was significantly lower than that for the annealing temperature of 1100 °C (sample c) (Table 1).

Figure 7 shows the resistivity curves (ρ−T) for the nondoped and Nd-doped single crystal electrides, wherein the sample annealed at 1100 °C for 48 h (sample c) shows the lowest resistivity. In the low-temperature range of below ~100 K, ρ is governed because of the electron−electron interaction that follows the ρ−ρ_{0} ∝ T^{n} law with n ∼ 2 (see Figure S4). In contrast, at temperatures greater than ~100 K, the resistivity follows the ρ−ρ_{0} ∝ T^{n} law with n ∼ 1 (see Figure S5), wherein resistivity is controlled by the phonon scattering. ρ_{0} is the temperature-independent residual resistivity observed at temperatures lower than ~15 K, which may be due to the imperfection of the crystals. These resistivity characteristics agree with the previously reported results.18 Similar resistivity behavior was observed for samples f and g (see Figure S3).

2.4. Carrier Concentration and Mobility. The electron density introduced in the cages and the carrier mobility were investigated using Hall coefficient measurements. In the Hall coefficient measurement, a four-point probe was set up around the perimeter of the sample. When the magnetic flux through the sample and the current along the length of the sample are applied perpendicular to each other, a Hall voltage, V_{H}, that is perpendicular to both the magnetic flux and the current is developed. The Hall coefficient, R_{H}, can be calculated using the equation

\[
\sigma_{RT}(\omega_{K}) = \text{C12A7 single crystals for 48 h (a) and C12A7:Nd single crystals for 36 h (b), 48 h (c), 60 h (d), and 72 h (e) annealed at 1100 °C. (B) RT conductivity of C12A7:Nd single crystals annealed at 900 °C (f) and 1000 °C (g) for 48 h.}
\]
The electrical resistivity ($\rho$) of the samples a, b, c, and d linearly increases with increasing temperature and follows the $\rho = \rho_0 + \alpha T^2$ law with $n = 2$ at lower temperatures of below $\sim 100$ K resulting in typical metals.

$$R_H = \frac{V_{hf} d}{IB} = \frac{1}{qN_e}$$  \hspace{1cm} (1)

where $d$ is the sample thickness, $B$ is the magnetic field, $I$ is the electrical current, $q$ is the charge of the carrier, and $N_e$ is the carrier density. In our experiment, we measured the resistance, $R = V_{HF}/I$, of the sample for the magnetic field varying between $\pm 9$ T. The measured resistance was plotted as the ordinate against the magnetic field as the abscissa. The multiplication of the slope of the plot and the sample thickness gives the Hall coefficient value. Using this Hall coefficient value, we calculated the carrier concentration, $N_e$, of the annealed samples (Table 1). The carrier mobility, $\mu_H$, was calculated by using the equation

$$\mu_H = \frac{R_H}{\rho}$$  \hspace{1cm} (2)

where $\rho$ is the resistivity of the sample.

Figure 8 shows the data for carrier concentration $N_e$ and carrier mobility $\mu_H$ at RT (300 K) of the as-prepared C12A7$\cdot$Nd$^-$ (e$^-$) and C12A7$\cdot$e$^-$ single crystal electrodes. The standard deviation for the measurements of carrier concentration and carrier mobility in sample d is very high because of the partial decomposition in part or microcracking during removal of the titanium oxide layer. The maximum carrier concentration corresponding to $N_e \sim 2.4 \pm 0.2 \times 10^{21}$ cm$^{-3}$ was found for sample c annealed at 1100 °C for 48 h, which is consistent with the theoretically calculated value of $\sim 2.37 \times 10^{21}$ cm$^{-3}$. This implies the removal of $\sim 100\%$ of the clathrated oxide ions from the crystallographic cages, leading to the formation of the complete electride, C12A7$\cdot$Nd$^-$ (e$^-$). The carrier concentration of sample b is almost equal to that of sample c (Figure 8A and Table 1), indicating the nearly complete replacement of the free oxide ions by the electrons, whereas the carrier mobility of sample b is lower than that of sample c. It was found that the carrier mobility in C12A7$\cdot$Nd$^-$ (e$^-$) tends to increase with increasing annealing time, whereas the carrier concentration in C12A7$\cdot$Nd$^-$ (e$^-$) is independent of the annealing time below 60 h. However, for the annealing time of 48 h, the carrier concentrations in samples f and g that annealed at 900 and 1000 °C were lower than that in sample c that annealed at 1100 °C, even though the carrier mobilities in the corresponding samples were almost the same (Figure 8B).

The lower carrier concentration than that of sample c annealed at 1100 °C for 48 h indicates that some free oxide ions still remain inside the crystallographic cages. The carrier mobility in C12A7$\cdot$Nd$^-$ (e$^-$) and C12A7$\cdot$e$^-$ for the annealing time of 48 h at 1100 °C at RT was quite similar, whereas the carrier concentration in C12A7$\cdot$Nd$^-$ (e$^-$) was very high, implying a higher electrical conductivity with respect to C12A7$\cdot$e$^-$.
increased sharply below \(~150\) K in \(\text{C12A7:Nd}(e^-)\) for the annealing time of \(48\) h at \(1100\) °C (see Figure S6).

For the \(\text{C12A7:}e^-\) electride, our measured carrier concentration and carrier mobility values were \(~1.8 \times 10^{21}\) cm\(^{-3}\) and \(~3.02\) cm\(^2\) V\(^{-1}\) S\(^{-1}\), respectively, consistent with the previously reported values of \(~2.0 \times 10^{21}\) cm\(^{-3}\) and \(~4\) cm\(^2\) V\(^{-1}\) S\(^{-1}\).\(^{10,18}\) However, in the previously reported work,\(^{10,18}\) the optical spectra, different annealing conditions, and different measurement environment were used to measure the carrier concentration and carrier mobility. In addition, for the Hall effect measurement, the sample should be homogenous, crack-free, and hole-free and must exhibit a uniformly thick flat shape, possibly giving rise to the difference in the measurement results.

3. EXPERIMENTAL SECTION

Single-phase polycrystalline \(12\text{Ca}_{1-x}\text{Nd}_x\text{O}_{7}\text{Al}_2\text{O}_3\) powder was prepared by solid-state synthesis from \(\gamma\text{-Al}_2\text{O}_3\) (99.99% purity, Taimei Chemical Co., Japan), \(\text{CaCO}_3\) (99.99% purity, Rare Metallic Co., Japan), and \(\text{Nd}_2\text{O}_3\) (99.9% purity, Rare Metallic Co., Japan) powders in a stoichiometric ratio. The powders were mixed with the appropriate amounts of ethanol using a mortar and pestle. The obtained powder mixture was calcined for \(12\) h at \(1200\) °C in an \(\text{O}_2\) atmosphere. The synthesized product was checked by powder XRD for phase purity, and no secondary phases were detected in the product. To make the feed rod, the fine powder was placed in the rubber tube and pressed under a hydrostatic pressure of \(300\) MPa and subsequently sintered at \(1300\) °C for \(12\) h in an \(\text{O}_2\) atmosphere to obtain the high-density feed rod.

The crystal growth was performed by using an optical floating zone furnace (FZ-T-10000-H-III-VPS-YT; Crystal Systems Inc., Japan) equipped with four \(1000\) W halogen lamps as the heat source. The growth conditions were as follows: a growth rate of \(1\) mm/h, a growth atmosphere of \(0.1\) MPa oxygen, feed and seed rotation rates of \(25\) rpm, and a growth direction of \(111\). The crystals were cut using a diamond wheel saw and polished with \(1\) μm diamond dispersion. The neodymium content along the growth and radial directions of the as-grown crystal was determined using a wavelength dispersive XRD pattern. For the resistivity and Hall coefficient environment were used to measure the carrier concentration and carrier mobility. For the Hall effect measurement, the sample should be homogenous, crack-free, and hole-free and must exhibit a uniformly thick flat shape, possibly giving rise to the difference in the measurement results.

4. CONCLUSIONS

In conclusion, the Nd-doped \(\text{C12A7:Nd}\) single crystals were grown by the FZ method, and the electrical properties of the electride-treated \(\text{C12A7:Nd}\) single crystals were characterized. An inhomogeneous Nd distribution along the radial direction was observed, which is likely due to the highly concave growth interface shape. There is further room for the flat or convex growth interface shape to obtain a uniform dopant distribution. The Ti-metal vapor annealing treatment was optimized at \(1100\) °C for \(48\) h for which the highest electrical conductivity (\(\sim 1165 \text{S/cm}\)) and carrier concentration (\(\sim 2.4 \pm 0.2 \times 10^{21} \text{cm}^{-3}\)) values were obtained. This high electron density in \(\text{C12A7:Nd}(e^-)\) is quite similar to the theoretically calculated value (\(\sim 2.37 \times 10^{21} \text{cm}^{-3}\)), indicating that all clathrated oxide ions were removed from the crystallographic cages through electron doping. The RT carrier mobilities in \(\text{C12A7:Nd}(e^-)\) and \(\text{C12A7:e^-}\) were the same (\(\sim 3.04 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}\)), in good agreement with the previous report,\(^{10,18}\) even though it increases rapidly in the low-temperature region (<\(150\) K) for the \(\text{C12A7:Nd}(e^-)\) annealed at \(1100\) °C for \(48\) h.

■ ASSOCIATED CONTENT

 Supporting Information
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Ti-metal vapor treatment, temperature-dependent electrical resistivity, conductivity, and carrier mobility, electron–electron interaction resistivity, and phonon-scattering controlled resistivity (PDF)

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