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Direct Synthesis of Powdery Inorganic Electride $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$ and Determination of Oxygen Stoichiometry

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Electrides[1] are quasi-ionic crystals in which electrons serve as anions. The anionic electrons are spatially separated from molecular cations by cavity and/or channel structures formed by organic complexants or crystallographic cages or channel walls in zeolitic crystals. In 2003, we succeeded in the synthesis of an inorganic electride using a $Ca_{12}Al_{14}O_{33}$ crystal (C12A7), which is an air- and room-temperature-stable material in the category of the electride.[2] C12A7 has a mayenite-type crystal structure, whose chemical formula of the unit cell is expressed by $[Ca_{24}Al_{28}O_{64}]^{4+}(O^{2-})_2$. The "free oxygen ions" (O^{2-}) are trapped as counteranions in the cages embedded in the positively charged framework ($[Ca_{24}Al_{28}O_{64}]^{4+}$). The free oxygen ions can be selectively removed via appropriate reduction treatments or knock-on processes by energetic ions.[3] The removal results in the electron injection to the cage, which in turn imparts persistent electronic conductivity to C12A7. The electron-encaging C12A7 exhibits a metal–insulator transition at the critical electron concentration of $\sim 1 \times 10^{21}$ cm^{-3}, and the C12A7 electride with the theoretical maximum electrons (2.3×10^{21} cm^{-3}), i.e., $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$, undergoes superconducting transition at ~0.4 K.[4] Moreover, the skeleton structure of the electride provides an unique playground for various anionic chemical species stabilized by strong Madelung potential of the cages, which hardly exist under usual conditions. Typical examples are O_2^-, O^-, H^-, and Au^-.[5−7] Furthermore, several applications have been found for the C12A7 electride. Among them, one expects the electride usable for vacuum electronics as electron source materials for cold and thermo-field emissions by utilizing an small work function (2.4 eV).[8] Another promising application field is organic syntheses. It has been reported recently that the C12A7 electride acts as a selective reducing agent in organic reactions in water media, for instance, pinacol coupling of aromatic aldehydes.[9] These reactions are conventionally performed in nonaqueous solutions with an aid of reducing agents such as alkali and alkali-earth metal compounds.

The C12A7 electrides have been synthesized by reducing bulk C12A7 single crystals grown by Czochralski method and the electride powders have been prepared by grinding the bulk electride crystals. Thus, alternative mass productive methods for the powder, such as a direct synthesis from powder mixtures, are highly required to realize the chemical applications of the electride. Here we report a direct synthesis method for the preparation of the C12A7 electride powder with the electron density up to the theoretical maximum of 2.33×10^{21} cm^{-3}. Furthermore, we demonstrate a comprehensive technique for the precise determination of the oxygen stoichiometry of the C12A7 electride powders. The technique involves X-ray fluorescence (XRF), powder X-ray diffraction (XRD), neutron powder diffraction (NPD), thermo-gravimetric/differential thermal analyses (TG/DTA), and diffuse reflectance spectroscopy.

C12A7 electride powder was synthesized by a reaction of C12A7, $CaO \cdot Al_2O_3$ (CA), and Ca metal at 700−1100 °C: $0.8Ca_{12}Al_{14}O_{33} + 1.4CaAl_2O_4 + Ca \rightarrow Ca_{12}Al_{14}O_{32}$. More specifically, it was synthesized by the following seven-step procedure. First, a mixture of C12A7 and $CaO \cdot Al_2O_3$ (CA) was prepared by a reaction of $CaCO_3$ (99.99%, particle size of ~10 μm, Kojundo Chemical) and α-Al_2O_3 (99.99%, ~10 μm, Kojundo) with a molar ratio of 11:7 at 1300 °C for 6 h in an ambient air: $11CaCO_3 + 7Al_2O_3 \rightarrow 0.8Ca_{12}Al_{14}O_{33} + 1.4CaAl_2O_4 + 11CO_2\uparrow$ (i). The sintered mixture (C12A7 + CA) was ball-milled with a nylon pot (inner space: 10 cm in diameter)

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and yttria-stabilized zirconia balls (3 mm in diameter) (ii), and subsequently degreased at 700 °C for 2 h in air (iii). Further, it was heated at 1100 °C for 15 h in a dynamically evacuated silica tube ($\sim 1 \times 10^{-4}$ Pa) to eliminate excess oxygen species and hydroxyl groups incorporated in the cages and/or adsorbed on the powder surfaces (iv). The C12A7+CA and Ca metal shot (99.99%, ~2 mm, Aldrich) were sealed in an evacuated silica tube, and heated at 700 °C for 15 h. To compensate the deficiency of the Ca metal caused by its deposition on the inner surface of the glass tube, 2 times excess Ca metal were added to in the starting composition (v). The tube was then opened in a groove box filled with an Ar gas and the reacted material was grinded with an agate mortar to spread Ca within the mixture (vi). Finally, using a glass rod, the mixture was squeezed into a single-ended silica tube, which was subsequently evacuated and sealed. To prepare for possible cracking of the silica tube during the cooling process because of crystallization of the silica promoted by a reaction with the Ca metal, we further sealed the tube in another evacuated silica tube. The doubly sealed tube was then heated at 1100 °C for 2 h (vii).

Color of the products was black, much different from colorless C12A7 (See inset of Figure 1a). The chemical composition of synthesized powder determined by XRF was Ca:Al:O = 11.9 ± 0.1: 14.0: 31.0 ± 0.7. The Ca/Al ratio was almost equal to that in the ideal C12A7 electride ($Ca_{12}Al_{14}O_{32}$). However, the oxygen concentration was possibly underestimated because of an inaccuracy in XRF analysis for light elements such as oxygen.

Figure 1a shows an XRD pattern of the synthesized powder observed by Bruker D8 Advance diffract meter using CuK_α radiation from a rotating anode. All peaks in the pattern were attributed to those of the mayenite-type crystal (space group $I\bar{4}3d$) with the room-temperature lattice constant of a = 11.999 Å. Rietveld refinement using program TOPAS3 [10] revealed that the calculated pattern for C12A7 framework structure without the free oxygen ions, i.e., C12A7 electride was well-fitted to the observed pattern. Figure 1b is a neutron diffraction pattern observed by the high-resolution powder diffractometer (HRPD) installed at the JRR-3 reactor of JAEA (beam collimation of 35′-20′-(sample)-6′ with neutron wavelength λ = 1.8234 Å). Ten grams of sample powder was synthesized for the NPD measurement. Except small peaks due to $Ca_3Al_2O_6$ (C3A) impurity phase (mass fraction is < 5 wt %, see inset of Figure 1b), all the peaks were also assigned to those attributed to the mayenite-type structure. Figure 1c shows the residual factor in the Rietveld analysis (R_{wp}) using program RIETAN-2000[11] as a function of an occupancy number for the O3 site (g_{O3}). In this analysis, atomic parameters for the O3 site were fixed such that $(x, y, z) = (0.337, 1/4, 0)$ and B_{eq} = 1.15 Å^2, whereas g_{O3} was treated as a parameter.[12] Table 1 lists the structural parameters for the framework obtained by the Rietveld refinement. The maximum occupation of the cages by the oxygen ions (a cage per six cages) provides g_{O3} = 0.0833. The R_{wp} value decreased monotonically with a decrease in g_{O3}, and it became the minimum of 6.34% at g_{O3} = 0, indicating no free oxygen ions in the cages of the synthesized powders.

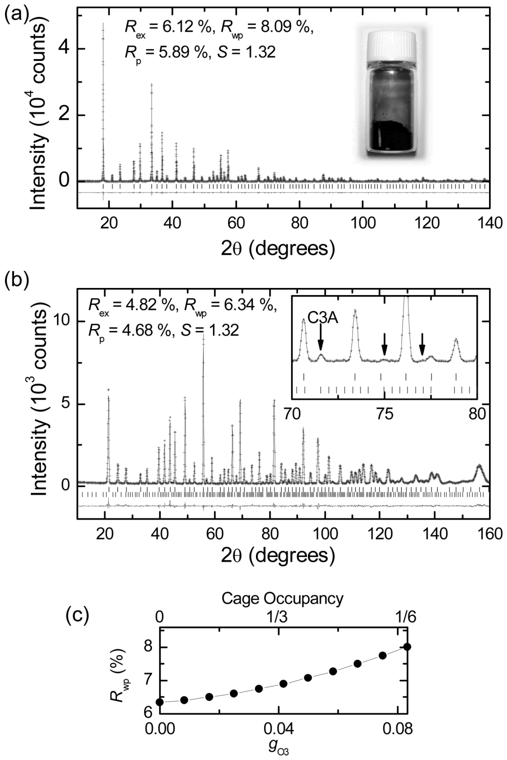

Figure 1. (a) Powder X-ray and (b) neutron diffraction patterns of C12A7 electride powder (+). Inset of (a) is a photograph of synthesized powder. Solid and gray lines are Rietveld fitting and residual patterns. Sticks below the observed patterns indicate diffraction positions of main and impurity phases. Inset of (b) is close-up view of small peaks assigned to $Ca_3Al_2O_6$ (C3A) impurity phase. (c) Residual factor of refinement R_{wp} for NPD pattern as a function of site occupancy for the O3 site (g_{O3}).

Table 1. Structural Parameters of C12A7 Electride Determined by Rietveld Refinements of Powder XRD and NPD Patterns

atom	site	*x*, *y*, *z*	*g*	B_{eq} (Å^2)
		XRD[a]		
Ca1/Ca^{2+}	24*d*	0.141528(42), 0, 1/4	1	0.684(10)
Al1/Al^{3+}	16*c*	0.017333(41), *x*, *x*	1	0.398(18)
Al2/Al^{3+}	12*b*	7/8, 0, 1/4	1	0.135(20)
O1/O^{2-}	48*e*	0.149301(81),0.963910(77), 0.055868(93)	1	0.539(24)
O2/O^{2-}	16*c*	0.935557(98), *x*, *x*	1	0.448(48)
		NPD[b]		
Ca1/Ca	24*d*	0.14017(14), 0, 1/4	1	0.697(27)
Al1/Al	16*c*	0.01794(12), *x*, *x*	1	0.210(54)
Al2/Al	12*b*	7/8, 0, 1/4	1	0.558(62)
O1/O	48*e*	0.15042(08), 0.96429(08), 0.0559(08)	1	0.583(18)
O2/O	16*c*	0.93407(08), *x*, *x*	1	0.905(33)

[a] a = 11.998560(13) Å. [b] a = 12.00472(24) Å.

Figure 2 is TG/DTA traces for the synthesized powder (30 mg) observed by Rigaku Thermo Plus under 80%-He/20%-O_2 carrier gas with a dew point of −56 °C (H_2O molar fraction: 14 ppm). Emissions of H_2O molecules (mass peak of m/e = 18) from sample were detected with a quadrupole mass spectrometer (Q-Mass) (see Figure 2b).

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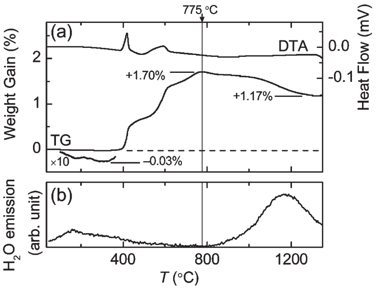

Figure 2. (a) TG/DTA profiles of C12A7 electride powder (heating rate 20 K min^{-1}) under 80%-He/20%-O_2 gas flow. (b) H_2O molar fraction in evolved gas monitored by Q-Mass during TG/DTA measurement.

Below 300 °C, weight loss of 0.03% accompanied with the H_2O emission was observed. The loss is attributable to detach of H_2O from the sample. On the other hand, the weight gain up to 1.70% was observed with exothermic peaks at 420 and 585 °C. These temperatures were almost the same as those in previous report.[13] Further, additional weight loss was observed above 775 °C and integrated net weight gain from 300 to 1350 °C is determined to be 1.20%, which is close to the theoretical one due to the oxidation of C12A7 electride to form stoichiometric C12A7 (weight gain of +1.17%). This observation, together with change in the sample color from black to white in spite of keeping the mayenite-type crystal structure unchanged after the TG/DTA measurement, revealed that the oxidation reaction of $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4 + O_2 \rightarrow [Ca_{24}Al_{28}O_{64}]^{4+}(O^{2-})_2$ took place. It further indicates that the prepared powder contains almost no "free oxygen ion" or they are the ideal C12A7 electride with the maximum electron density.

The excess weight gain of 0.53% (= 1.70 − 1.17) at 600−1350 °C suggests incorporation of oxygen species such as O^- and O_2^-.[14] If formation of O_2^- is dominant, its concentration at 775 °C is 5.3×10^{20} cm^{-3}, which reasonably agrees with the previous data on the C12A7 heating in an O_2-bearing atmosphere.[5] On the other hand, H_2O emission above 775 °C is attributable to dissociation of encaged OH^-.[15] The OH^- is likely to be produced by a reaction of the free oxygen ion with impurity H^- in the cages ($O^{2-} + H^- \rightarrow OH^- + e^-$). Provided that the integrated intensity of the H_2O emission peak below 600 °C corresponds to the weight loss of 0.03%, the intensity of the 1170 °C peak provides a weight loss of ~0.1% due to the OH^- dissociation, which in turn indicates the encaged H^-concentration is 3×10^{20} cm^{-3} at most.

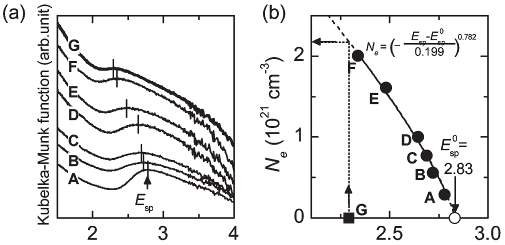

Figure 3. (a) Absorption spectra of C12A7 powders encaging electrons in cages. Spectra A−F are for electron-encaging C12A7 samples with various electron concentration (N_e) (A, 0.26; B, 0.56; C, 0.77; D, 1.0; E, 1.6; and F, 2.0×10^{21} cm^{-3}). G is the spectrum in C12A7 electride prepared by the direct synthetic method in this study. (b) Relation between the absorption peak position (E_{sp}) and N_e.

Finally, we have confirmed the formation of the ideal C12A7 electride by evaluating the electron concentration (N_e). Absorption spectra (obtained by Kubelka−Munk transformation of diffuse reflectance spectra) of the electron-encaging C12A7 powders with various N_e are shown in Figure 3a. The powders were prepared by grinding single crystals whose electron concentration was tuned by varying the heating time and temperature of reducing treatment with Ti metal. Their N_e were estimated from analyses of optical reflectance spectra using Drude−Lorentz model.[16] The powders were diluted in dehydrated MgO powders with a weight ratio of 1:25. The absorption band centered at 2−4 eV has been assigned as associated with the s−p transition of the electron bound to the cage. The peak position (E_{sp}) shifts to a lower energy with an increase in N_e. (Figure 3b) with a relation of $N_e = [-(E_{sp} - E_{sp}{}^0)/0.119]^{0.782}$, where the low-$N_e$ limit $E_{sp}{}^0 = 2.83$ eV at $N_e \approx 1 \times 10^{18}$ cm^{-3}.[2] The N_e value in the synthesized powders evaluated from the above relation is 2.3×10^{21} cm^{-3}, which is in good agreement with the positive charge density (2.33×10^{21} cm^{-3}) of the lattice framework $[Ca_{24}Al_{28}O_{64}]^{4+}$, further confirming that all the free oxygen ions were replaced with the anionic electrons.

In summary, we have found a straightforward method for the synthesis of C12A7 electride powder using commercially available chemical ingredients, providing an opportunity for facilitating exploration of C12A7 electride applications in various fields including electron emission and chemical reaction.

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Supporting Information Available: The details of XRF analysis (PDF); CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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