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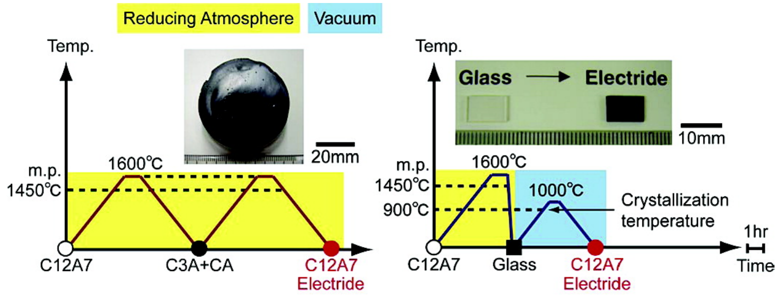

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Simple and Efficient Fabrication of Room Temperature Stable Electride: Melt-Solidification and Glass Ceramics

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Electrides[1] are ionic compounds in which electrons act as anions. These compounds are promising for practical applications such as reducing agents, cold-cathode electron-field emissions, thermionic power generation, and refrigeration devices.[2−4] However, fatal drawbacks such as the thermal and chemical instability of organic electrides[5−8] at room temperature (RT) have impeded their applications. Although these problems can be overcome by synthesizing RT stable single crystal $12CaO{\cdot}7Al_2O_3$ (C12A7) electrides, the fabrication process is not suitable for the practical applications because a single crystal C12A7 is needed as the starting material and because of the long duration of the Ca treatment in the synthesis process.[9] Practical applications and research of electrides may be facilitated by a simple synthetic procedure. Here we show that RT stable C12A7 electrides can be simply synthesized via a strongly reducing C12A7 "melt", i.e., a direct solidification of the melt (melt-solidification) or a crystallization of the transparent glass (glass ceramics[10]).

The C12A7 contains two types of oxygen ions: O^{2-} ions that construct a positively charged three-dimensional framework and extra-framework O^{2-} ions that are loosely bound to the cages embedded in framework in order to adjust the charge balance. The latter is selectively extracted by a strong reduction treatment, which leaves electrons localized in the cages and forms a C12A7 electride. Thus, our attention is focused on melting C12A7 under a reduction atmosphere to extract the extra-framework O^{2-} ions and to simultaneously leave electrons in the cages. However, the process is thought to be almost impossible because the crystallographic phase of the C12A7 has not been synthesized in a reducing atmosphere, even from stoichiometric melt.

Insulating C12A7 powders, which were synthesized by a conventional solid-state reaction in a stoichiometric mixture of high-purity $CaCO_3$ and γ-Al_2O_3 at 1300 °C for 12 h in air, were melted in a carbon crucible with a carbon cap at 1600 °C in air ($PO_2 \approx 10^{-16}$ atm) for 1 h and then slowly cooled (Figure 1a). As expected from the phase diagram,[11] the solidified C12A7 melt was the mixed phase of $3CaO{\cdot}Al_2O_3 + CaO{\cdot}Al_2O_3$ (C3A+CA) (Figure 1b), but the remelt-solidification of the resultant mixture in the same atmosphere unexpectedly resulted in a dark green C12A7 phase that had an electronic conduction. We also quenched the C12A7 melt in a carbon crucible with a carbon cap in air to form a transparent reduced glass (Figure 1c). Differential thermal analysis revealed that the glass was converted to crystalline C12A7 at the onset of the crystallization temperature, T_c, 900 °C. Then the glass was encapsulated in a SiO_2 glass ampule under a vacuum and heated at 1000 °C for 30 min. The resultant crystallized glass also showed an electronic conduction with a dark green color similar to the remelt and solidified C12A7 (Figure 1d). On the other hand, the C12A7 samples obtained from the remelt-solidification and the crystallization of the glass prepared in air using an alumina crucible, i.e., under an oxidative atmosphere, yielded white, electrically insulating C12A7.

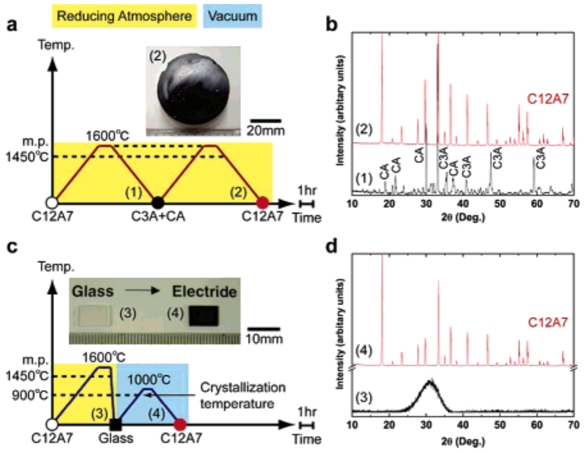

Figure 1. Fabrication of a C12A7 electride via melt under a reducing atmosphere. The reducing atmosphere (yellow box) is achieved using a carbon crucible with a carbon cap in air. (a) Fabrication procedure for the electride by the solidification of the reduced C12A7 melt and the photograph (inset) of the obtained dark green electride (ϕ50 mm × 10 mm), which indicates that a large electride sample in a desired shape can be easily fabricated. (b) Powder X-ray diffraction patterns of (1) C3A+CA and (2) crystalline single phase C12A7. (c) Fabrication procedure for the C12A7 electride by the crystallization of the transparent reduced glass under a vacuum (blue box). The photograph (inset) shows that the crystallization converts (3) the transparent reduced glass to (4) a dark green polycrystalline electride. (d) Powder X-ray diffraction patterns of (3) the transparent glass and (4) the crystalline single phase C12A7.

Both the electronic conductive C12A7 samples show an electron paramagnetic resonance (EPR) signal with an isotropic shape that appeared at $g = 1.994$ (Figure 2b), which is assigned to an F^+-like center where an electron is captured by six Ca^{2+} ions attached to the cage wall. This F^+-like center is the same as the one observed in the UV-irradiated electronic conductive C12A7:H[12] and the Ca-treated single crystal electride.[9] Thus, we conclude that both the electronic conductive C12A7 samples containing a large amount of entrapped electrons in the cages are electrides.

Figure 2a shows the correlation between the electrical conductivity and the concentration of the F^+-like centers (entrapped electrons) of the melt-derived polycrystalline C12A7 and the Ca-treated single crystal C12A7 electride. The data from log σ and log N_{F+} in the polycrystalline electride are almost identical to those of a single crystal electride. It is favorable that the melt-derived C12A7 electrides have nearly the same carrier mobility (0.1 $cm^2/V{\cdot}s$) as the single crystal sample. This feature may be understood by the tightly connected large grains (~3 mm) of the polycrystalline sample (Figure 2c), which largely reduces the deteriorative grain boundary effects on the electronic transport.

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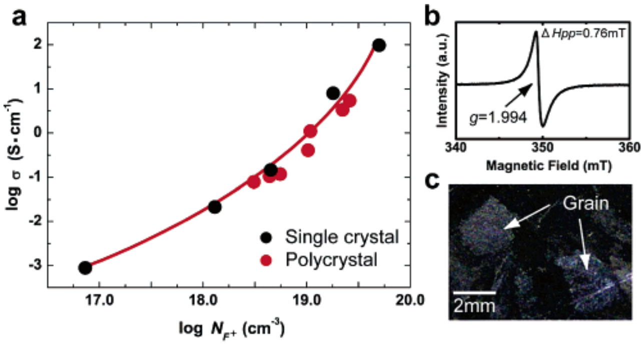

Figure 2. (a) Electrical conductivity (σ) versus F^+-like center concentration (N_{F+}) as determined by EPR at 300 K for polycrystalline (red circles) and single crystal electrides (black circles). It indicates that the electron mobility of the polycrystalline electrides obtained via the melt is comparable to that of single crystal electrides. (b) EPR spectrum of polycrystalline electride (microwave frequency = 9.7 GHz). (c) HCl-etched fracture surfaces of the polycrystalline electride obtained via the melt.

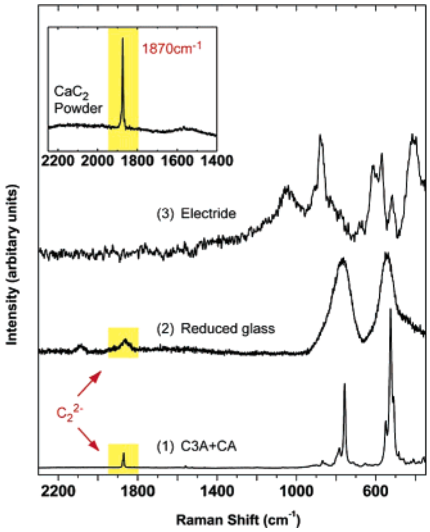

Figure 3. Raman spectra of C12A7 relevant samples. Light source: second harmonics (532 nm) of CW-Nd:YAG laser. (1) C3A+CA precipitated from the first melt-solidification, (2) the reduced glass obtained by quenching the reduced melt, and (3) C12A7 electride derived from the melt. A band at around 1870 cm^{-1}, which may be assigned as C_2^{2-} from the reference spectrum of CaC_2 in the inset, is seen for (1) and (2) but not (3).

However, it is still unclear why the C12A7 phase and not the mixed phase of C3A+CA precipitates in the final state from the strongly reduced melt. It has been reported that the nanoporous C12A7 phase is successfully prepared from a melt with a C12A7 composition in an oxidative atmosphere.[13−15] This is attributed to the existence of O^{2-} template anions bound to the positively charged cages, which maintain the neutrality of structure.[13−15] Thus, our finding indicates that new template anions, which function under a reducing atmosphere, exist in the melt in order to stabilize the nanoporous C12A7 phase and leave electrons in the cages during the cooling process.

To identify the template species, we measured the Raman spectra of the electride and the precursors, i.e., the precipitated C3A+CA and the transparent reduced glass. Figure 3 shows the distinct difference between the two precursors and the electride. A band near 1870 cm^{-1}, which may be assigned as C_2^{2-} from the reference spectrum of CaC_2 powder (inset of Figure 3), is seen for two precursors, but not for the electride. It is believed that the C_2^{2-} ions dissolve into the melt from the carbon crucible to compensate for the oxygen deficiency, which occurs because of the strongly reducing atmosphere. C_2^{2-} (1.2 Å) and O^{2-} (1.4 Å) have a similar anion size, which further suggests that the C_2^{2-} anion also works as a template under a reducing atmosphere instead of extra-framework O^{2-} ions in the cages. The disappearance of the Raman band at 1870 cm^{-1} after crystallization implies that the encaged C_2^{2-} ions are only stable in the nucleation and/or initial stage of the crystallization and are released from the cages during the cooling process. Thus, the total processes are expressed by the following chemical reactions:

$$C_2^{2-}\ (\text{melt or glass}) \rightarrow C_2^{2-}\ (\text{cage}) \rightarrow C_2\ (\text{atmosphere}) + 2e^-\ (\text{cage})$$

and/or

$$C_2^{2-}\ (\text{cage}) + 2O^{2-}\ (\text{cage}) \rightarrow 2CO\ (\text{atmosphere}) + 6e^-\ (\text{cage})$$

Thermal desorption measurements confirmed that CO gas is evolved from the C3A+CA around ∼800−1000 °C or from the crystallization process of the glass at ∼1000 °C.

This successful fabrication of C12A7 in a reducing atmosphere is attributed to the discovery of a new template anion, C_2^{2-}, which may be responsible for the formation of C12A7 electride. The present work provides crystallized glass characteristics such as shape flexibility, partially fabricates the electronic conductive crystalline phase in a transparent insulating glass, and can be used to mass produce RT stable electrides for various applications.

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