

Thin film and bulk fabrication of room-temperature-stable electride C12A7:e⁻ utilizing reduced amorphous 12CaO · 7Al₂O₃(C12A7)

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Abstract

Heavily electron-doped 12CaO · 7Al₂O₃(C12A7) exhibits unique electronic properties such as high electronic conductivity of 1500 S cm⁻¹ (to superconductor via metal–insulator transition) and a very small work function (2.4 eV) arising from electrons entrapped in sub-nanometer-sized cages inherent to the crystal structure. We report the efficient synthetic processes of bulk and thin film C12A7:e⁻ using the reduced C12A7 melt or a-C12A7. Solidification of the melt produced in carbon crucibles and crystallization of the reduced C12A7 glass (insulating) in vacuum yielded bulk C12A7:e⁻. It was suggested that C₂²⁻ ions work as a template to form the nano-cages in the crystallization processes. The films of C12A7:e⁻ were fabricated by the reduction treatment of crystalline C12A7 thin films with reduced a-C12A7. By applying this process, heavily electron-doped thin films of 12SrO · 7Al₂O₃ with the same crystal structure as C12A7 but a non-equilibrium phase was first realized.

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1. Introduction

In 2003, we synthesized heavily electron-doped 12CaO · 7Al₂O₃ crystal (C12A7) with the chemical composition of [Ca₂₄Al₂₈O₆₄]⁴⁺(4e⁻) by chemical treatments [1]. C12A7 has a cubic unit lattice with two chemical formulas. The unit cell contains 12 sub-nanometer-sized cages (inner diameter ~ 0.4 nm) composed of tetrahedral coordinated Al³⁺, bridging and non-bridging oxygens, and Ca²⁺ ions. Each cage is connected with eight neighboring cages by sharing a mono-layer open mouse. Since the cage wall hav-

ing a composition of [Ca₂₄Al₂₈O₆₄]⁴⁺ is positively charged, 2O²⁻ ion are accommodated randomly in the two cages out of 12 cages. The inner diameter of the cage is larger by ~50% than the diameter of O²⁻. Thus, these O²⁻ ions are loosely bounded by six Ca²⁺ ions attaching to the cage wall, and are called ‘free oxygen ions’ [2]. Hereafter, electron-doped C12A7 obtained by replacement of the free O²⁻ ions is called C12A7:e⁻ (C12A7 electride).

Exceptional functionalities have been discovered for C12A7:e⁻ in last several years [3]. Although the material is comprised of typical insulating oxides, CaO and Al₂O₃, they exhibit high electronic conductivity at RT (the maximum conductivity is 1500 S cm⁻¹) and show metal–insulator transition at a critical electron concentration of =1 × 10²¹ cm⁻³ [4]. Metallic C12A7:e⁻ exhibits a superconducting transition at 0.2–0.4 K [5]. In general, low work

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function and chemical inertness are not compatible in metals. However, C12A7:e^- has a low work function of 2.4 eV [6], which is the same as metal K, but is chemically inert in an ambient atmosphere (one can touch with hands!). These unique properties are expected for applications in various fields such as electronic devices and chemical reaction reagents. For facilitating applications, efficient fabrication methods are required for both bulk and thin film C12A7:e^- .

In this paper we report the fabrication methods of bulk and thin films of C12A7:e^- utilizing amorphous C12A7 . For the bulk synthesis of C12A7:e^- , solidification of C12A7 melt prepared in the strongly reducing atmosphere or crystallization of the reduced C12A7 glass was successful. Chemical reduction process with metal Ca [3] or Ti [4] cannot be applied for the fabrication of C12A7:e^- thin films because the thickness of reaction layers is comparable to the thin film thickness desired for device application.

2. Experimental

2.1. Bulk synthesis

Two synthetic routes from the strongly reduced C12A7 melt were examined, i.e. melt-solidification and recrystallization of the glass from the reduced melt (glass-ceramic process). Fig. 1 shows the concrete synthetic procedures, which were successful, for each process. The stoichiometric mixture of CaCO_3 and Al_2O_3 was melted in carbon crucibles with carbon caps at a temperature $\sim 1600^\circ\text{C}$. The resulting melt is called *reduced melt*, hereafter. When this melt was quenched, clear transparent C12A7 glasses were obtained. The resulting glass abbreviated as the *reduced glass* was insulating as conventional glasses. When the reduced melt was cooled to room-temperature, the white-colored, solidified product composed of $3\text{CaO} \cdot \text{Al}_2\text{O}_3(\text{C3A})$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3(\text{CA})$ was obtained. When this product was reheated to $\sim 1600^\circ\text{C}$ in a carbon crucible, kept it for 1 h and was cooled to recrystallize,

the black-colored, massive agglomerate (see Fig. 1) was obtained. The phase of this product was C12A7 and *electronic conducting*.

2.2. Thin film fabrication

First, amorphous thin films of ~ 400 nm thick were deposited at RT by pulsed laser deposition (PLD) method using ceramic C12A7 targets. The partial O_2 pressure was $\sim 1 \times 10^{-3}$ Pa during the depositions. The substrates employed were $\text{MgO}(100)$. Polycrystalline(p-) C12A7 thin films were obtained by heating the resulting amorphous(a-) C12A7 thin films to 1100°C in an ambient atmosphere. Next, a- C12A7 (~ 30 nm thick) layers were deposited on the p- C12A7 thin films at 700°C in an O_2 pressure of $\sim 1 \times 10^{-3}$ Pa by PLD. Last, the over-layered a- C12A7 layer was removed by chemical-mechanical polishing (CMP). Fig. 2 summarizes the fabrication processes described above. $12\text{SrO} \cdot 7\text{Al}_2\text{O}_3$ (S12A7) with the same crystal structure as C12A7 is known as a meta-stable phase [6]. We applied this method to S12A7 and successfully obtained S12A7:e^- thin films by tuning the temperature and atmosphere for the post-annealing of a- S12A7 . The carrier mobility and concentrations were evaluated by Hall voltage measurements in a Van der Pauw configuration.

3. Results

3.1. Bulk preparation

The product from the first solidification from the reduced melt was the composite of C3A and CA and electrically insulating. However, the product obtained by the second melt-solidification was C12A7:e^- . This result was highly reproducible, indicating the events occurring during the second solidification process is the essence for the fabrication of C12A7:e^- in this method. The conductivity of the C12A7:e^- was $1\text{--}10 \text{ S cm}^{-1}$ and the electron carrier concentration was of the order of 10^{19} cm^{-3} . The color of

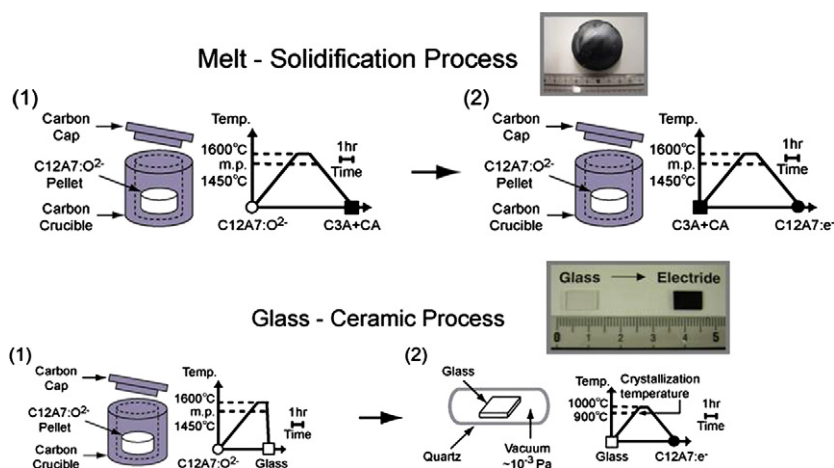


Fig. 1. Fabrication of bulk C12A7:e^- via melt. Photos show the final products in (1), and reduced glass (insulating) & crystallized glass (conducting).

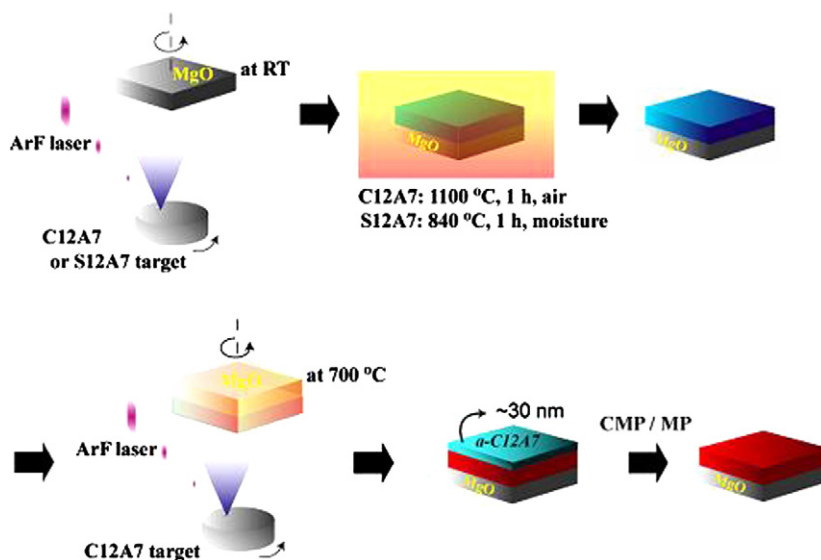


Fig. 2. Fabrication process of C12A7:e⁻ and S12A7:e⁻ thin films. The process consists of thin film deposition, subsequent reduction by reduced a-C12A7 layer and the final removal over-layered a-C12A7 by chemical mechanical polishing.

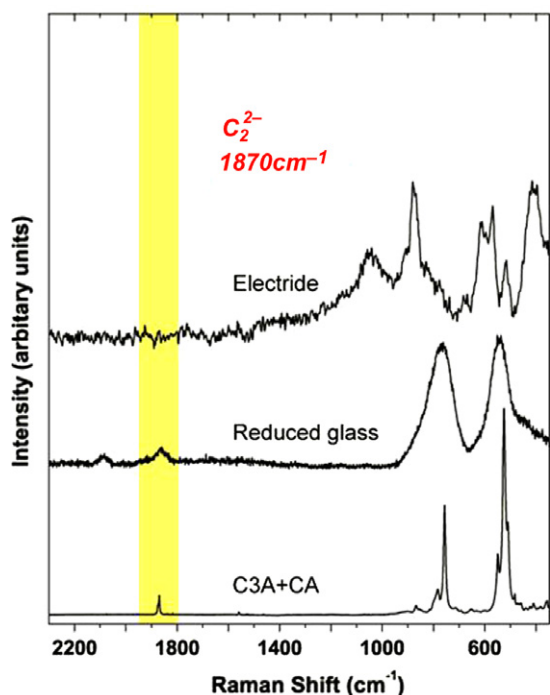


Fig. 3. Raman spectra of C12A7:e⁻, reduced C12A7 glass, and product first solidified from the reduced melt.

the powders obtained by crushing the agglomerate was green, which was consistent with a relation between the color and the conductivity [1].

Fig. 3 shows Raman spectra of the relevant samples. It is noted that a peak appears at 1860 cm^{-1} for the first melt-solidified product and the reduced glass but is not observed for the C12A7:e⁻ obtained by the second solidification. This peak was identified as C₂²⁻ ions on the basis of comparison with the spectrum of CaC₂ crystal and polarized Raman measurements.

3.2. Thin film fabrication

As-deposited thin films were amorphous for C12A7 and S12A7. Polycrystalline thin films were obtained by post-annealing the as-deposited a-thin films for C12A7 at a temperature $>900\text{ °C}$ in air.

For S12A7, annealing temperature and atmosphere were explored because this phase is not an equilibrium phase in the SrO–Al₂O₃ system [7]. Eventually, p-S12A7 thin films were obtained by post-annealing at 700 °C in a moist atmosphere, suggesting the OH⁻ ions stabilize the cage structure.

These p-C12A7 and S12A7 thin films were insulating. However, when a-C12A7 layers ($\sim 30\text{ nm}$) were deposited on these p-thin films at 700 °C , the insulating C12A7 or S12A7 layers were converted to highly conducting states. Fig. 4 shows the DC conductivities of resulting C12A7:e⁻ and S12A7:e⁻ thin films as a function of temperature. It is evident that both samples exhibit metallic conduction. The Hall mobility and carrier concentrations in the C12A7:e⁻ film were evaluated to be $2.5\text{ cm}^2\text{ (V s)}^{-1}$ and $1.3 \times 10^{21}\text{ cm}^{-3}$, respectively. Similar values ($1.0\text{ cm}^2\text{ (V s)}^{-1}$ and $1.4 \times 10^{21}\text{ cm}^{-3}$) were obtained for the S12A7:e⁻ thin films. No carrier doping was observed in the same conditions without deposition of a-C12A7 on the p-C12A7 or -S12A7. Deposition of Au layers or Ti layers was examined for carrier generation. The former did not work, whereas the latter did. These observations imply that the role of a-C12A7 deposition on p-C12A7(S12A7) is to exact free O²⁻ accommodated in the cages and inject electrons to the cages.

4. Discussion

First, the formation mechanism of C12A7:e⁻ from the melt is considered. It is known that the physical properties of C12A7 melt vary with temperature and atmosphere

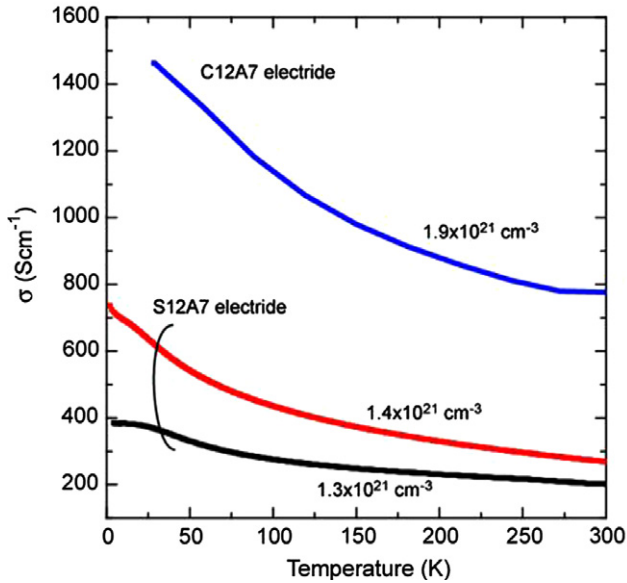
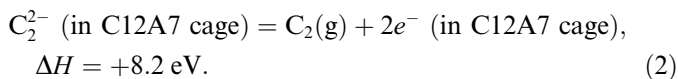
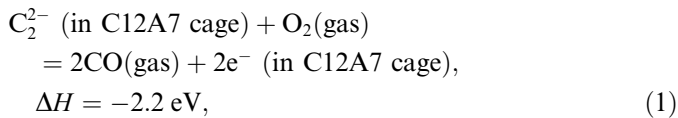


Fig. 4. DC conductivities in C12A7:e⁻ and S12A7:e⁻ thin films as a function of temperature. Numbers in the figure denote doped electron concentrations.

[8,9]. Crystalline phases precipitated vary with the melting histories; the melt equilibrated at a temperature >1550 °C in the reducing atmosphere gives the mixture of C3A and CA instead of C12A7. Thus, the phase constitution for the first solidified product is as-expected. However, the C12A7 phase was obtained as the second solidified product. We may understand this formation of C12A7:e⁻ by considering the essential role of C₂²⁻ ions; C12A7 and S12A7 are exceptional crystals in the MO–Al₂O₃ systems (M: alkaline earth metal) because their crystal structure is composed of sub-nanometer-sized cages with a positive charge. If some appropriate anions species such as O²⁻ and OH⁻ do not accommodate in the cages, these crystals cannot be stabilized, thus are decomposed to MO + M3A. The diameter of C₂²⁻ ion is almost the same as that of O²⁻ and the charge state of both ions is the same. It is thus plausible that C₂²⁻ ions in the first solidified product work as a template and C12A7 phase is stabilized. According to a quantum chemical calculation on C12A7 encaging various anions species [10], the following enthalpy changes are obtained for the possible reactions:



This means the reactions (1) and (2) are not so unfavorable. If these reactions occur, the generation of electrons in the cages and disappearance of C₂²⁻ ion in the resulting C12A7:e⁻ may be reasonably understood. Fig. 5 illustrates a tentative model for the formation of C12A7:e⁻ by solid-

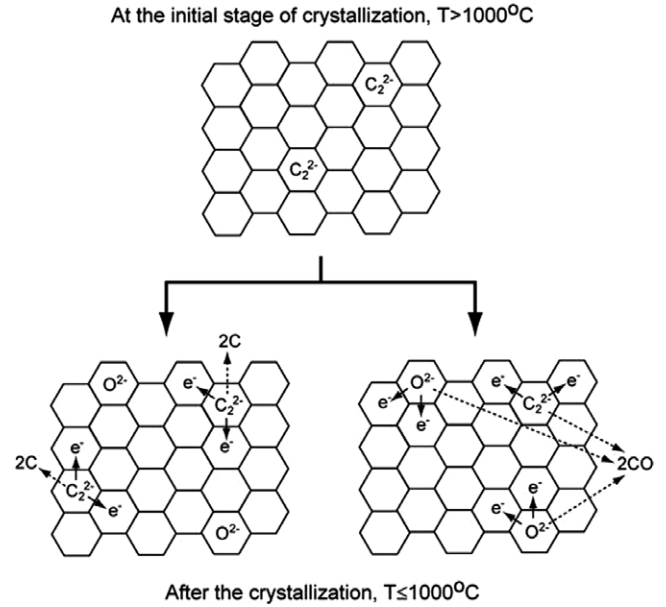


Fig. 5. A mechanism for the formation of C12A7:e⁻ and S12A7:e⁻ from the reduced melts. C₂²⁻ ions work as templates to form a sub-nanometer-sized cage in C12A7 in the crystallization of the melt and entrapped C₂²⁻ ions react with O₂ to yield electron and CO which escapes from the cages during subsequent cooling processes.

ification of reduced C12A7 melts. This mechanism is also applicable for the crystallization of the reduced glasses (containing C₂²⁻ ions).

It is quite interesting to note that there are many reports on the crystallization of C12A7 glasses but no such formation of C12A7:e⁻ has been found to date. The C12A7:e⁻ glass-ceramics can be obtained by crystallization of the reduced glass in an O₂/H₂O free atmosphere. When the crystallization occurs in an ambient atmosphere, electrons cannot remain in the cages as a result of competition with O²⁻ or OH⁻. Thus white-colored, insulating C12A7 ceramics are obtained.

Second, we mention the C12A7:e⁻ and S12A7:e⁻ thin film fabrication in the present work. It was already reported that electrons can be injected into cages by extracting O²⁻ ions entrapped in the cages of C12A7 [3,9]. Extraction of the O²⁻ ion was performed by using chemical reactions of metal with strong affinity to oxygen, such as Ti, at an elevated temperature. However, this process cannot be applied to the thin films because the reaction layer is comparable for the film thickness. Such a reaction layer was not observed in the present method and highly conductive C12A7:e⁻ and S12A7:e⁻ thin films were obtained by removing a-C12A7 layers with CMP. It is surprising for us that a-C12A7 deposited on p-C12A7 at 700 °C is very effective to extract the O²⁻ ion from a-C12A7 thin films. Since this deposition temperature is so lower than the glass transition temperature (830 °C) and the on-set crystallization (~900 °C), the over-layered a-C12A7 remains uncrystallized. Remembering that the bulk reduced C12A7 glass exhibits photochromism based on oxygen vacancies [11], we may expect a-C12A7 deposited

in a vacuum chamber contains a large amount of oxygen vacancies in amorphous structures.

Finally, the possibility of application of C12A7:e⁻ thin films is described. The unique feature of C12A7:e⁻ has both of a low work function of 2.4 eV and chemical inertness. In addition, these metallic conducting thin films have optical transparency, ~70% for the 100 nm thick sample. These properties are favorable for the application of the cathode material in organic LEDs. Low work function contact is required to reduce the electron-injection barrier between the cathode and electron-transport organic layers. The chemical inertness is, of course, needed as the contact. Since C12A7:e⁻ is transparent, light emission can be taken out from both sides in the device structure using ITO as the anode and C12A7:e⁻ as the cathode [12].

5. Summary

- (1) Bulk C12A7:e⁻ was synthesized by solidification of reduced C12A7 melts produced in carbon crucibles. Reheating the transparent glass (insulating) obtained from the reduced C12A7 melt in vacuum resulted in the formation of C12A7:e⁻ ceramics, as well.
- (2) A mechanism, in which C₂²⁻ ions work as the template in the formation of C12A7:e⁻ in the reducing condition, was proposed to explain the results.
- (3) Metallic conducting C12A7:e⁻ thin films were fabricated by depositing amorphous C12A7 thin layer on insulating crystalline C12A7 thin films. Electron concentrations of $1.9 \times 10^{21} \text{ cm}^{-3}$ could be doped and the conductivity of $\sim 800 \text{ S cm}^{-1}$ was obtained.
- (4) The thin films of S12A7:e⁻ (S12A7 is a non-equilibrium phase with the same crystal structure as C12A7) were first fabricated by the same proce-

dures with (3) at the tuned temperature and atmosphere in the reduction treatment by a-C12A7 deposition.

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