Functioning of traditional ceramics $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ utilizing built-in nano-porous structure

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Abstract

This paper briefly reviews our approach to render active functions to micro porous crystal $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C12A7), which is known as a constituent of alumina cement, utilizing nano-space and topology of sub-nanometer-sized cages inherent to the crystal structure. Each cage with a positive charge is coordinated by 12 cages to form a three-dimensional structure. This structure is a similar to a close packing of sphere except that each opening wall of a cage is shared with a neighboring cage. Free oxygen ion $O_2^-$ accommodates in 1/6 of the cages to reserve electro neutrality in the stoichiometric state. We replaced this free oxygen ion by other active anions such as $O_2^-$, $H_2^+$, and electron, aiming at emergence of novel function. C12A7: $O_2^-$ exhibited strong oxidation power enough to oxide Pt, and field-assisted thermionic $O_2^-$ emission to several $\mu A$ levels, while conversion of insulator to persistent electronic conductor by illumination with ultraviolet radiation was discovered in C12A7: $H_2^+$ sample. Further, almost all of the free $O_2^-$ ions in the cages were successfully replaced by electrons by a chemical treatment using metallic Ca. The resulting material, which has a composition $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4-}(4e^+)$ and a high conductivity, $10^4 \text{ S cm}^{-1}$ at 300 K, is a first room-temperature stable electride, in which electrons work as anions. The present approach to novel function emergence by solely employing abundant oxide materials and fully utilizing nanostructure provides a way for material research for future to be done under severe circumstance of environment and resource.

1. Introduction

Oxide ceramics is probably among the oldest of man-made materials owing to the abundance and easy avail-ability of the ingredients. Although most oxides are optically transparent, important for optical applications, it has been believed that active functions based on excited electrons, such as in crystalline semiconductor materials, are not possible. For example, alumina and glasses, which are representative oxides, are optically transparent but electrically insulating. If novel active functionalities utilizing both optical transparency and electron activity in oxide materials are realized, one can expect that a new frontier of materials science will be opened in front of us because these oxides are abundant and environmentally compatible.

On the basis of this belief, we are exploring novel active properties based on excited electrons in transparent materials as well as novel electronic-active materials following a working hypothesis established based on a consideration of chemical bonding and point defects. In 1997, we reported CuAlO$_2$ as the first p-type transparent conductive oxide (TCO) [1] along with a chemical design concept for p-type TCOs. After that, a series of p-type TCOs were found based on our working hypothesis [2–5]. This discovery led to opening of a new frontier of transparent oxide semiconductors because a variety of active functions in semiconductors originate from the nature of pn-junction. Subsequently, we succeeded in fabrication of ultraviolet-light emitting diode, a representative devise utilizing both of optical transparency and electronic function by growing p-SrCu$_2$O$_2$ on n-ZnO heteroepitaxially [6]. Transparent transistor is also a device that can utilize the advantage of transparent oxide semiconductors. We fabricated a high performance of field effect transistor [7] employing single-crystalline thin films of InGaO$_3$ (ZnO)$_3$ [8] as the active layer. The resulting transistors exhibit a field mobility of $\sim 80 \text{ cm}^2(\text{ Vs})^{-1}$, which is comparable to that in polycrystalline Is-FET. Furthermore, an amorphous p-type oxide semiconductor was
found and an amorphous oxide pin-diode with good rectifying properties was fabricated just by depositing on glass substrates at room temperature [9]. This success is a milestone for practical application of oxide semiconductors to flexible electronics which is expected as an emerging field.

A wide material variety is a unique feature of oxide semiconductors. Semiconductive oxides are, however, restricted to transition metal or heavy metal cation-bearing materials. Representative light metal oxides, most abundant materials, are classified as typical electrical insulators in college textbooks and no one has succeeded in converting them to persistent electronic conductor until our report in 2002 utilizing nano-structures built-in crystal structure [10]. In this paper we briefly review our recent approach to functioning of traditional transparent oxide composed of naturally abundant and environmentally friendly materials, CaO and Al2O3. Both oxides are representative ingredients for traditional ceramics such as porcelain and cement, and have been believed to inactive.

2. Crystal structure of 12CaO·7Al2O3

This compound is easily prepared by a conventional solid-state reaction in air, but is not formed in O2 or moisture-free atmosphere. The crystal lattice of 12CaO·7Al2O3 (C12A7) with a micro porous structure has a cubic lattice constant of 1.199 nm, and the unit cell includes two molecules [11]. It is characterized by a positively charged lattice framework [Ca24Al28O64]4+ having 12 crystallographic cages with a per unit cell as shown in Fig. 1. Each cage with a formal +1/3 charge is coordinated by 12 cages to form a three-dimensional structure. This structure is a similar to a close packing of sphere except that each opening wall of a cage is shared with a neighboring cage. Free oxygen ion O2− accommodates in 1/6 of the cages to reserve electro neutrality in the stoichiometric state. The remaining two oxide ions (O2−), referred to as free oxygen ions, are entrapped in the cages in the stoichiometric composition. This is the origin of the fast oxygen ion conduction in this material [12]. Monovalent anions, such as hydroxyl ions (OH−) or halogen anions, X− (X− = F− and Cl−), are known to substitute for the free oxygen ion to form derivatives [Ca24Al28O64]4+·4(X−). The replacement of a free O2− ion by two monovalent anions likely stabilizes the structure through charge delocalization.

3. Experimental outline

C12A7 powers were synthesized by a conventional solid state reaction using CaCO3 and Al(OH)3. Single crystals

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Fig. 1. (a)Crystal structure of C12A7, (b) HR-TEM image along (111) direction, (c) expanded drawing of the two adjacent cages.
were grown by a floating-zone method. Samples bearing \( \text{O}^2^- \) or \( \text{H}^+ \) ions were prepared by heating C12A7 powders or single crystal in dry \( \text{O}_2 \) or dry \( \text{H}_2 \) atmosphere \[10,13–15\]. The concentrations of \( \text{O}^2^- \) and \( \text{O}_2^- \) ions were measured at 77 K by EPR \[13,16\], while the entrapped \( \text{H}^+ \) ion concentrations were evaluated by a combined use of SIMS and NMR\[10\]. Samples entrapping electrons instead of free \( \text{O}^2^- \) were prepared by heating a sealed silica glass containing C12A7 single crystals \[17\] with metal Ca shots at 700 °C \[18\]. The thermionic emission of \( \text{O}^2^- \) and \( \text{H}^+ \) ions was measured by a time-of-flight mass-spectrometer.

4. Active oxygen manipulation: C12A7:O\(^-\) + O\(_2\)\(^-\)

Active oxygen species such as \( \text{O}^- \), \( \text{O}_2^- \), and \( \text{O}_3^- \) are key chemical species in the oxidation of hydrocarbons or biochemical reactions. In particular, \( \text{O}^- \) has attracted much attention because of its extremely high oxidation power and high reactivity. Much effort has been made to create this species thus far. Generally, the active oxygen species are created on the surface of solid oxides with the aid of energetic photons. If the material containing a large amount of \( \text{O}^- \) is obtained in the chemically and thermally stable form, it is anticipated that it exhibits unique chemical properties, and thus has a huge potential for a variety of applications. The presence of the free oxygen ion provides us a novel opportunity to manipulate the active species by diffusing \( \text{O}_2 \) molecules into the dry C12A7. We reported that high concentration of active oxygen ion species with concentrations of more than \( 10^{20} \text{ cm}^{-3} \) can be generated in C12A7 by decreasing the OH content \[13,14\] as shown in Fig. 2. They are generated by the electron transfer expressed in the following reaction \[14,15\].

\[
\text{O}^2^-(\text{cage}) + \text{O}_2^-\text{(atmosphere)} \rightarrow \text{O}^-\text{(cage)} + \text{O}_2^-\text{(cage)} \quad (1)
\]

C12A7 compounds prepared under an ambient atmosphere inevitably trap a large amount of OH\(^-\) ions in the cage. This is the reason why the formation of a large amount of \( \text{O}^- \) and \( \text{O}_2^- \) has not found so far.

The resultant C12A7:O\(^-\) + O\(_2\)\(^-\) sample shows outstanding oxidative reactivity. We placed a Pt metal plate, which is known as the most stable metal against oxidation, in contact with the surface of C12A7. When a C12A7 pellet in contact with a metal Pt plate was annealed at 1300 °C in dry \( \text{O}_2 \) gas, the contacted area became brown (Fig. 3). The XPS measurement on the brown area revealed that Pt is oxidized to the tetravalent state \[13\]. No such an oxidation was observed for conventional C12A7 (i.e. C12A7:OH\(^-\)) and other calcium aluminate compounds.

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**Fig. 2.** ESR spectra of C12A7 ceramics prepared in different atmosphere. Spectra were measured at 77 K at an X-band. ND, denotes below sensitivity. Poor spectral resolution at high radical concentrations is due to dipolar broadening.

**Fig. 3.** Photographs of C12A7 ceramics sintered in wet air (left) and in dry oxygen (right). Star-shaped Pt plates were placed in contact with the samples. Brown color is due to the formation of Pt\(^{4+}\).
and the emission accompanied with electron, implying that emission current remained nano-ampere level at maximum electrode, essential for the YSZ to dissociate a drifted O$_2$ into C$_{12}$A$_7$:O$^-$ ion beam into vacuum by applying dc voltage to a C$_{12}$A$_7$:O$^-$ ion beam in a conductive state that persists after irradiation ceases.

5. Light-induced conversion into electronic conductor in C$_{12}$A$_7$:H$^+$ [10]

Materials that are good electrical conductors are not in general optically transparent, yet a combination of high conductivity and transparency is desirable for many emerging opto-electronic applications. To this end, various transparent oxides composed of transition or post-transition metals such as indium tin oxide are rendered electrically conducting by ion doping. However, such an approach does not work for the abundant transparent oxides of the main-group metals. We demonstrated a process by which the transparent insulating oxide C$_{12}$A$_7$ can be converted into an electronic conductor. H$^+$ ions are incorporated into the sub-nanometer-sized cages of the oxides by a thermal treatment in a hydrogen atmosphere at 1300 $^\circ$C; subsequent illumination of the C$_{12}$A$_7$:H$^+$ with ultraviolet light results in a conductive state that persists after irradiation ceases. The photo-activated material exhibits moderate electrical conductivity ($\sim$ 0.5 S cm$^{-1}$) at room temperature, with visible light absorption losses of only one percent for 200-nm-thick films. The formation of H$^+$ ions in the material was confirmed by NMR measurement and Time-of-flight mass spectrum of field-extracted ions from the sample. The incorporation of H$^+$ anions in the cage may be understood through the following chemical reactions:

\[
O_2^-(\text{cage}) + H_2(\text{atmosphere}) \rightarrow OH^- (\text{cage}) + H^- (\text{cage}),
\]

or

\[
O_2^-(\text{cage}) + H_2(\text{atmosphere}) \rightarrow 1/2O_2(\text{atmosphere}) + 2H^- (\text{cage}).
\]

The C$_{12}$A$_7$:H$^+$ looks white in the polycrystalline powder or colorless and transparent for single crystals and is insulating (conductivity $< 10^{-10}$ S cm$^{-1}$). However, upon irradiating with ultraviolet light, two absorption bands centered at 2.8 and 0.4 eV are induced as shown in Fig. 5(a). Simultaneously, a drastic increase in the conductivity was observed along with the coloration. The conductivity increased from $< 10^{10}$ S cm$^{-1}$ to 0.5 S cm$^{-1}$. The Seebeck coefficient of the conductive sample is negative ($\sim 360 \mu$VK$^{-1}$), indicating n-type conduction. Fig. 5(b) shows the temperature dependence of the conductivity ($\sigma$). Log $\sigma$ is proportional not to $T^{-1}$ but to $T^{-1/4}$ over a wide temperature range 300–50 K. This characteristic indicates that the conduction is not controlled by a simple thermal activation process but more probably by a variable-range hopping of carriers.

A possible mechanism for the photo-induced conversion of C$_{12}$A$_7$: H$^+$ from an insulator to a conductor is proposed as summarized in Fig. 6: First, the uv-irradiation induces an electron emission from the encaged H$^+$ ions (H$^+ \rightarrow H^0 + e^-$). Then, an empty cage electro-statistically captures the photo-induced electron to form an $F^+$-like center. As the electron is weakly bound in the cage, the wavefunction would spread spatially. Consequently, electrons may migrate throughout the crystal by variable-range hopping. The resultant H$^0$ atoms combine with each other to form H$_2$ molecules in a cage. The light-induced conduction is persistent below 320 $^\circ$C, indicating that the recombination
of the H₂ and the electron rarely occurs in such low temperature.

6. Room temperature stable electride: C12A7: e⁻ [18]

We removed ~100% of the free oxygen ions from the crystallographic cages in a single crystal of C12A7 by heating the crystal with a metal Ca shot in a vacuum-sealed SiO₂ glass. High density (~2 x 10²¹ cm⁻³) electrons were created in the cages following the reaction (3) and Fig. 7;

\[ [\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(2\text{e}^-) + 2\text{Ca} \rightarrow [\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4\text{e}^-) + 2\text{CaO}. \] (3)

The resulting electron forms a structure being interpreted as F⁺ center, and itinerates throughout the crystal by hopping to a neighboring cage with conductivity ~100 S cm⁻¹ at RT (Fig. 8), providing a view that the encaged electron behaves as anion. The electron anions couple anti-ferro-magnetically with each other, forming a diamagnetic pair or singlet bi-polaron. The resulting [Ca₂₄Al₂₈O₆₄]⁴⁺(4e⁻), schematically shown in Fig. 9, may be regarded as thermally and chemically stable single crystalline ‘electride’ in which electron works as anion. Electride was first created in 1983 by Dye, who synthesized it using metallic Cs and crown-ether [22]. Chemically, trapped electrons can be viewed as the smallest possible anion, and such materials could serve as strong reducing agent. From a physics standpoint, the stabilization of numerous bound electrons, or F centers, could provide new approaches to preparing conductive materials with unusual optical or magnetic properties, and there is interest in device applications for using such materials as low-temperature electron emitters. Most electrides have been either organic species, such as alkali metal adducts of
organic cage compounds or inorganic molecular sieves. However, the fatal drawback of electrides is thermal and chemical instability, i.e. stable only at cryogenic temperatures and are air and water sensitive. This is the reason why electrides have not attracted as materials aiming at practical applications.

Emergence of electronic conduction in C12A7 originates from mobile nature of electrons trapped in the sub-nanometer-sized cages with a positive formal charge. Each cage is neighbored by 12 cages like closed packing of sphere. These features lead to the formation of another conduction band, which is located below

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**Fig. 7. Synthetic route for electride utilizing C12A7 crystal.**

**Fig. 8. Photo of the samples treated with Ca and electrical conductivity.** Duration of Ca-treatment at 700 °C, a, before; b, 4 h; c, 12 h; d, 18 h; e, 40 h, and f, 240 h. The conductivity in sample a is \( \sim 10^{-10} \) S cm\(^{-1} \) at 300 K.
the conduction band derived from the cage framework as illustrated in Fig. 10 [23,24]. Electron doping into these cages are possible by two ways, i.e. photo-ionization of H$_2^+$ ion in C12A7:H$_2$ samples by UV-illumination and extraction of free O$_{2^-}$ ions in conventional C12A7 by the chemical treatment. High F$^+$-center concentration is insufficient for emergence of high conductivity as evidenced by data on Li-implanted MgO [25]. Although the F$^+$ center concentration in the implanted MgO is comparable or slightly higher that in the present electride, the conductivity in the former is lower by 5–7 orders of magnitude than that in the latter. It is evident that continuous connection of a sub-nanometer-sized cage, which is the precursor of F$^+$ center is indispensable for emergence of high conductivity.

7. Concluding remarks

Electronic properties of transition metal oxides have attracted much interest of researchers over past 2 decades and its enthusiasm is continuing to date by shifting a primary focus from Cu$^{2+}$-based high temperature superconductors to strongly electron correlated system. When viewed from standpoint of chemistry, a various novel active functions in transition metal oxides have been realized primarily by appropriate choice of a metal cation. However, this approach appears not effective for light metal oxides, which are major constituents of our environment. Our strategy for this issue is to utilize active anion species such as O$^-$ and H$^+$. Water is the most abundant oxide and an origin of life on our earth. When H$_2$O is dissociated into H$^+$ and OH$^-$, resulting ion species are not exciting to target novel material functions. If active anion species such as O$^-$ and H$^-$, which are unstable in an ambient atmosphere, are created readily from H$_2$O to a high concentration, we may expect a new frontier of abundant oxides as functional materials. Nanometer-sized cage with positive charge is the key for formation and stabilization of active anion species. Topology of cage connectivity is critically important for the emergence of electrical function. For practical application, various shapes of the sample such as fine powders, dense sintered bodies, thin films, and single crystals are required to meet the specific demand. We have established the fabrication method for densely sintered ceramics [26] and thin films [27,28] to date and started detailed examination for cold electron emitter using C12A7 electride and O$^-$ ion gun employing C12A7.O$^-$ dense ceramics.

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