

## ARTICLE

# Preparation and Characterization of Storage and Emission Functional Material of Chlorine Anion: $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot (\text{Cl}^-)_{3.80}(\text{O}^{2-})_{0.10}$

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A storage and emission functional material of  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot (\text{Cl}^-)_{3.80}(\text{O}^{2-})_{0.10}$  (C12A7-Cl<sup>-</sup>), was prepared by the solid-state reactions of CaCO<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and CaCl<sub>2</sub> in Cl<sub>2</sub>/Ar mixture atmosphere. The anionic species stored in the C12A7-Cl<sup>-</sup> material were dominated by Cl<sup>-</sup>, about  $(2.21 \pm 0.24) \times 10^{21} \text{ cm}^{-3}$ , accompanied by a small amount of O<sup>2-</sup>, O<sup>-</sup>, and O<sub>2</sub><sup>-</sup>, measured via ion chromatography, electron paramagnetic resonance, and raman spectra measurements. These results also corroborate identification of time-of-flight mass spectroscopy—the anionic species emitted from the C12A7-Cl<sup>-</sup> surface were dominated by the Cl<sup>-</sup> (about 90%) together with a small amount of O<sup>-</sup> and electrons. The structure and morphological alterations of the material were investigated via X-ray diffraction and field emission scanning electron microscope, respectively.

**Key words:** Chlorine anion, Storage-emission material, C12A7-Cl<sup>-</sup>, Characterization

## I. INTRODUCTION

The chlorine anion (Cl<sup>-</sup>) is a monovalent anion through the attachment of an electron to a chlorine atom. The Cl<sup>-</sup> is potentially useful in many fields including the semiconductor industry, material modifications, atmospheric chemistry, and biochemistry [1–5]. For example, Cl<sup>-</sup> can remarkably enhance the plasma-etching of polycrystalline silicon in semiconductor chemistry [1,2]. Halogen anions have also been used as an alternative to positive ions for ion fusion drivers in inertial confinement fusion [6]. The conventional method to form Cl<sup>-</sup> is through the attachment of a free low-energy electron to the chlorine atom or through anion-molecule reactions that can occur in a plasma process, electron impact, or laser irradiation on chlorine-containing molecules in gas phase [7,8]. Generally, it is difficult to generate pure Cl<sup>-</sup> anions via the above processes, because various complex species such as electrons, positive ions, and other anions are formed synchronously [9].

Recently, we have developed a new approach to generate pure O<sup>-</sup>, where the O<sup>-</sup> are emitted from the anionic storage-emission material  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot 4\text{O}^-$  (C12A7-O<sup>-</sup>) [10–14]. The C12A7-O<sup>-</sup> nanoporous material, prepared by the solid-state reaction of CaCO<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under dry oxygen environment, can store

and emit the O<sup>-</sup> [12,13]. The structure of C12A7-O<sup>-</sup> is characterized by a positive charged lattice framework  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}$  including 12 sub-nanometer sized cages with a free space of about 0.4 nm in diameter [14]. The number of O<sup>-</sup> stored in C12A7-O<sup>-</sup> was in the order of  $10^{20} \text{ cm}^{-3}$  [13–16]. In addition, the O<sup>-</sup> can be emitted into the gas phase through heating the material [10–13]. The emitted species from C12A7-O<sup>-</sup> were about 90% O<sup>-</sup> together with a trace amount of electrons [12,13]. Thus, it allows one to generate pure O<sup>-</sup> anions in the gas phase via the C12A7-O<sup>-</sup> material. More recently, we have also synthesized various derivatives of C12A7 such as C12A7-OH<sup>-</sup> [15,16], C12A7-H<sup>-</sup> [17,18], C12A7-F<sup>-</sup> [19,20] and found that these materials or the modified ones would be potentially used in a one-step synthesis of phenol from benzene [21], the reduction of NO [22], fast microorganisms' inactivation [23], the stream reforming or oxidation of oxygenated organic compounds [24–26], and increasing the surface hydrophilicity of polymer by producing hydrophilic hydroxyl and carbonyl compounds through the reactions of the O<sup>-</sup> [27]. In 2003, Hosono's group first synthesized an important inorganic electrode C12A7:e<sup>-</sup> [28], which has attracted much interest in its unique physical and chemical properties [29–32].

As one of the derivatives of C12A7, the material of Ca<sub>12</sub>Al<sub>14</sub>O<sub>32</sub>Cl<sub>2</sub> (also named C11A7-CaCl<sub>2</sub>) was first prepared by co-sintering C12A7 with CaCl<sub>2</sub> at 900–1300 °C by Jeevaratnam *et al.*, with a lattice constant of 1.2004 nm [33]. Its crystal structure was further revealed by Pollmann *et al.* and Iwata *et al.*, and Ca<sub>12</sub>Al<sub>14</sub>O<sub>32</sub>Cl<sub>2</sub>, belonging to *I43d* space group, pos-

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sessed a body-centered cubic structure and the value of its lattice constant is around 1.201 nm [34,35]. This material also has a typical positively charged framework of C12A7 with a unit-cell content of  $\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}\text{Cl}_4$  [33]. On the other hand, because it plays an important role in the setting and hardening of chlorine-bearing cement, C11A7-CaCl<sub>2</sub> has attracted much attention recently [36]. The compound  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$  is one of the main constituents of a new type of Portland cement, termed "Eco-cement" [37], which has been recently developed in order to solve the municipal waste problems caused by limited availability of landfill sites.

In this work, we synthesized and characterized the Cl<sup>-</sup> emission material of C12A7-Cl<sup>-</sup> ( $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot (\text{Cl}^-)_{3.80}(\text{O}^{2-})_{0.10}$ ), which was able to selectively emit the Cl<sup>-</sup>. We also provide a flexible method to generate pure Cl<sup>-</sup> via the C12A7-Cl<sup>-</sup> material, which should be useful in etching and sterilization.

## II. EXPERIMENTS

### A. Sample preparation

The emission material of C12A7-Cl<sup>-</sup> was synthesized by the solid-state reaction of CaCO<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and CaCl<sub>2</sub>. The powders of CaCO<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and CaCl<sub>2</sub> with the average particle diameter of 20–30  $\mu\text{m}$  were mixed and grained at a molar ratio of CaCO<sub>3</sub>: $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:CaCl<sub>2</sub>=11:7:1. The powder mixture was pressed to a slice with a diameter of 15 mm and a thickness of 1 mm by a pressure of 150–200 kg/cm<sup>2</sup>, and then put into a ceramic tube (length: 1 m, inner diameter: 20 mm). The slice samples were temperature-programmed to 1350 °C with heating rate of 10 °C/min, sintered at 1350 °C for 8 h and cooled to room temperature under flowing argon atmosphere. Then, the sample was annealed at 700 °C under flowing Cl<sub>2</sub>/Ar mixture (Cl<sub>2</sub>:Ar=0.1:0.9; flow rate: 100 mL/min) atmosphere for 10 h. Finally, the sintered samples were naturally cooled to room temperature. For comparison, the C12A7-O<sup>-</sup> sample was also prepared by the solid-state reaction of CaCO<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under flowing dry O<sub>2</sub> environment, as has been previously described [13].

### B. Sample characterization

The experimental apparatus, described previously [13], consists essentially of a sampling chamber and an ion detection chamber equipped with a time-of-flight (TOF) mass spectrometer. The sample (diameter: 1.5 cm, thickness: 1.5 mm) was supported by a quartz tube (length: 60 cm, diameter: 3 cm), which had a circular flat (diameter: 1.5 cm, depth: 1.8 mm) with a hole of 2.5 mm in the center of the flat. The quartz tube was installed in the sample chamber, ensuring that the sample was located in the center of the sample cham-

ber. The anions and electrons emitted from the frontal surface were extracted by an extraction electrode, then analyzed by the TOF mass spectrometry.

Electron paramagnetic resonance (EPR) measurements were performed to investigate the anionic species (O<sup>-</sup> and O<sub>2</sub><sup>-</sup>) in the C12A7-Cl<sup>-</sup> bulk. EPR experiments were conducted at ~9.1 GHz (X-band) using a JES-FA200 spectrometer at 77 K. Spin concentrations were determined from the second integral of the spectrum using CuSO<sub>4</sub>·5H<sub>2</sub>O as a standard with an error of about 20%. A detailed description of EPR measurements of the oxygen species in C12A7-O<sup>-</sup> can be found in Ref.[14].

The absolute Cl<sup>-</sup> concentrations in the C12A7-Cl<sup>-</sup> samples (after dissolving in the deionized water) were analyzed by ion chromatography (IC; DX-120, Dionex Co.) method and calibrated with a standard NaCl solution of 0.4 mmol/L.

Raman spectra (RS) was measured with Confocal Laser MicroRaman Spectrometer (LABRAM-HR, Jobin Yvon) at room temperature using a Ar<sup>+</sup> laser ( $\lambda=514.532$  nm) as the excitation light source.

X-ray diffraction (XRD) measurements were carried out to investigate the structure of C12A7-Cl<sup>-</sup>. The synthesized C12A7-Cl<sup>-</sup> samples were crushed into an average diameter of 20–30  $\mu\text{m}$ . Powder XRD patterns were recorded on an X'pert Pro Philips diffractometer with a Cu K $\alpha$  source ( $\lambda=1.540598$  Å). The measurement conditions were in the  $2\theta$  range of 10°–90°, with step counting time of 5 s, and step size of 0.017° at 298 K. The measurement of the lattice constant was made from diffractometer traces using Si as the internal standard.

To investigate the morphology and microstructure, the C12A7-Cl<sup>-</sup> sample was first coated with a gold layer about 10 nm thick (SCD 050 Sputter Coater, BAL-TEC) and then observed by field emission scanning electron microscopy (FESEM; Sirion-200, FEI, American).

## III. RESULTS AND DISCUSSION

### A. Emitted species measured by TOF

The anions emitted from the C12A7-Cl<sup>-</sup> surface were identified by anionic TOF mass spectrometry. As shown in Fig.1(a), there are two emission peaks for C12A7-O<sup>-</sup>: the dominant peak has the mass number of 16, which corresponds to O<sup>-</sup>, and the weak peak has the mass number of about 0, which corresponds to electrons. It is quite different from the emission of the C12A7-Cl<sup>-</sup> sample. As shown in Fig.1(b), for the latter we clearly observe four emission peaks; the dominant peaks have the mass numbers of 35 and 37, which correspond to chlorine isotopes of <sup>35</sup>Cl<sup>-</sup> and <sup>37</sup>Cl<sup>-</sup>, respectively, and the other two weak peaks at mass numbers of about 0 and 16 correspond to electrons and O<sup>-</sup>. The isotopic ratio of  $I(^{35}\text{Cl}^-)$  to  $I(^{37}\text{Cl}^-)$  is about 3.0. No

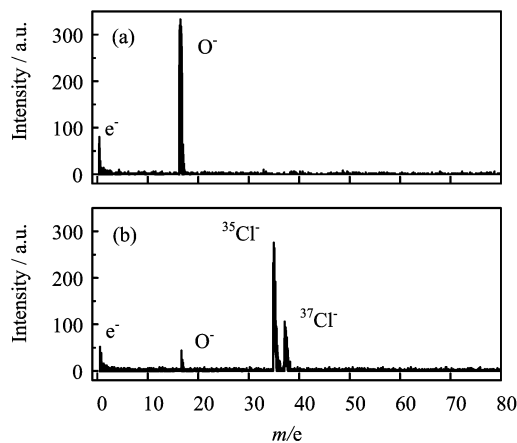


FIG. 1 Typical TOF mass spectra for anions emitted from different sample surfaces at 700 °C and 1 kV/cm: (a) C12A7-O<sup>-</sup> sample and (b) C12A7-Cl<sup>-</sup> sample. The isotopic ratio of  $I(^{35}\text{Cl}^-)$  to  $I(^{37}\text{Cl}^-)$  is about 3.0.

$\text{Cl}_2^-$  emission was observed within our experimental detection limitation. The alteration of the anionic distribution emitted from the C12A7-Cl<sup>-</sup> would indirectly demonstrate that Cl<sup>-</sup> should be the major anions stored in the materials of C12A7-Cl<sup>-</sup>.

### B. Characteristics of storage of C12A7-Cl<sup>-</sup>

Present results show that the anionic species emitted from the C12A7-Cl<sup>-</sup> material surface were dominated with the Cl<sup>-</sup> together with a small amount of O<sup>-</sup>, indicating that the possible anionic species encaged in the C12A7-Cl<sup>-</sup> material may include Cl-containing anionic species such as Cl<sup>-</sup> and the O-containing anionic species such as O<sup>-</sup>, O<sub>2</sub><sup>-</sup>, O<sup>2-</sup>, etc. In order to clarify these species, we carried out the material characterization by EPR, IC, and RS measurements.

First, EPR measurements were performed to investigate the anionic species in the C12A7-Cl<sup>-</sup> bulk. Figure 2 show the EPR spectra of the C12A7-O<sup>-</sup> material and the C12A7-Cl<sup>-</sup>. By simulating the EPR spectra and using CuSO<sub>4</sub>·5H<sub>2</sub>O as a spin concentrations standard, we can estimate the anionic oxygen species concentrations in the body. For the fresh C12A7-Cl<sup>-</sup>, the concentrations of O<sup>-</sup> and O<sub>2</sub><sup>-</sup> are about  $4.4 \times 10^{17}$  and  $2.5 \times 10^{17}$  cm<sup>-3</sup>, respectively. It has been confirmed that the concentrations of O<sup>-</sup> and O<sub>2</sub><sup>-</sup> in the fresh C12A7-O<sup>-</sup> material were in the order of 10<sup>20</sup> cm<sup>-3</sup> [13,15]. As compared with the C12A7-O<sup>-</sup>, it was found that the concentration of O<sup>-</sup> and O<sub>2</sub><sup>-</sup> in the C12A7-Cl<sup>-</sup> material was much lower than those in the C12A7-O<sup>-</sup> material. This agrees with the TOF results, which shows that the anionic species emitted from the C12A7-Cl<sup>-</sup> material surface were dominated by the Cl<sup>-</sup>, and the anionic species emitted from the C12A7-O<sup>-</sup> surface were dominated by the O<sup>-</sup>. After

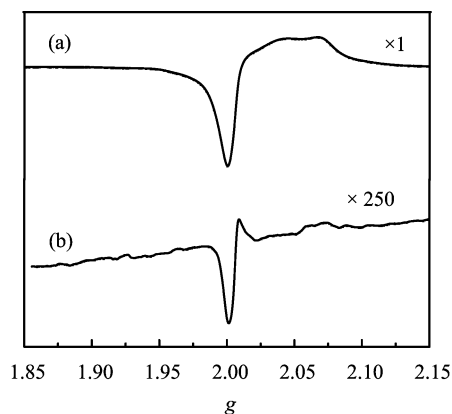


FIG. 2 EPR spectra for (a) the C12A7-O<sup>-</sup> material and (b) the C12A7-Cl<sup>-</sup> material. The amplified times of the EPR signal are 1 and 250 respectively.

running emission for 10 h at 800 °C and 800 V/cm, the concentrations of O<sup>-</sup> and O<sub>2</sub><sup>-</sup> in C12A7-Cl<sup>-</sup> sharply decreased to  $1.0 \times 10^{17}$  and  $0.6 \times 10^{17}$  cm<sup>-3</sup>, respectively, which is only about 25% of that in fresh C12A7-Cl<sup>-</sup>.

Note that this EPR method can not measure the Cl<sup>-</sup> species in the C12A7-Cl<sup>-</sup> material because there are no unpaired electrons for the Cl<sup>-</sup>. The absolute Cl<sup>-</sup> concentration in the C12A7-Cl<sup>-</sup> was analyzed by using IC method and calibrated with a standard NaCl solution of 0.4 mmol/L, Figure 3 shows the IC spectra for standard NaCl solution of 0.4 mmol/L, the fresh C12A7-Cl<sup>-</sup> aqueous solution, and the aqueous solution for the C12A7-Cl<sup>-</sup> sample after running the emission at 800 °C and 800 V/cm for 10 h. All the C12A7-Cl<sup>-</sup> aqueous solutions were obtained in the same way, *i.e.* dissolving 28.8 mg C12A7-Cl<sup>-</sup> sample into 100 mL deionized water. It can be clearly seen that the Cl<sup>-</sup> peaks are present both in the fresh C12A7-Cl<sup>-</sup> aqueous solution and the used ones by comparing the retention time and peak shape with those of NaCl solution. Absolute Cl<sup>-</sup> concentrations for the above C12A7-Cl<sup>-</sup> samples were estimated by the integral of the calibrated IC peaks using NaCl solution as a standard. The Cl<sup>-</sup> concentration for the fresh C12A7-Cl<sup>-</sup> material was  $2.21 \times 10^{21}$  cm<sup>-3</sup> and decreased to  $1.53 \times 10^{21}$  cm<sup>-3</sup> for the used C12A7-Cl<sup>-</sup> sample after running the emission for 10 h. Due to the total negative charge concentration ( $2.33 \times 10^{21}$  cm<sup>-3</sup>) [13,14], the above IC results further confirmed that the Cl<sup>-</sup> are dominating anionic species stored in the C12A7-Cl<sup>-</sup>.

The RS measurement was performed to investigate the diatomic anionic species (*e.g.*, O<sub>2</sub><sup>-</sup>), probably, existing in the C12A7-Cl<sup>-</sup> material. Figure 4 show the RS of the C12A7-O<sup>-</sup> and the C12A7-Cl<sup>-</sup>. For C12A7-O<sup>-</sup> material, besides three peaks at 324, 518, and 777 cm<sup>-1</sup>, a peak at 1130 cm<sup>-1</sup> was also observed in the range between 200 and 1400 cm<sup>-1</sup>; In contrast, there is no peak around 1130 cm<sup>-1</sup> observed for

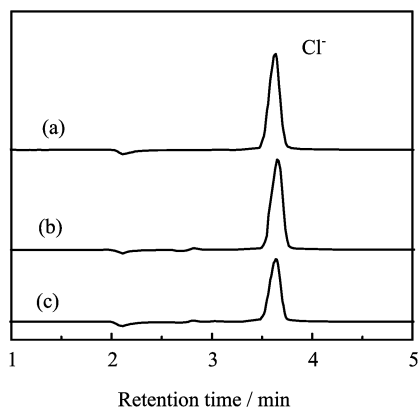


FIG. 3 IC spectra for (a) standard NaCl solution of 0.4 mmol/L, (b) the fresh C12A7-Cl<sup>-</sup> aqueous solution (the fresh C12A7-Cl<sup>-</sup>: 28.8 mg, deionized water: 100 mL), and (c) the used C12A7-Cl<sup>-</sup> aqueous solution (the used C12A7-Cl<sup>-</sup> samples after running the emission at 800 °C and 800 V/cm for 10 h: 28.8 mg, deionized water: 100 mL).

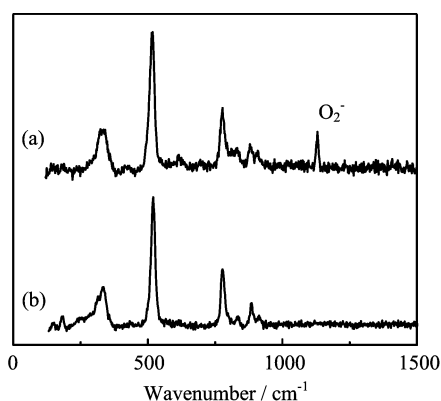


FIG. 4 Raman spectra for (a) the C12A7-O<sup>2-</sup> material and (b) the C12A7-Cl<sup>-</sup> material.

C12A7-Cl<sup>-</sup> material. Raman bands located at 200–1000 cm<sup>-1</sup> would arise from the lattice framework, which is composed of tetrahedrally coordinated Al<sup>3+</sup> [38]. The strong Raman band at 518 cm<sup>-1</sup> would be assigned to symmetric vibrations of Al–O–Al bridged oxygen between tetrahedral AlO<sub>4</sub> groups. Bands in the 700–900 cm<sup>-1</sup> region would be assigned to aluminum-oxygen stretching vibrations of AlO<sub>4</sub> tetrahedrons [38]. It has been reported that the Raman band (stretching vibration) of O<sub>2</sub><sup>2-</sup> should be located around 1130 cm<sup>-1</sup>. No observable peak appeared near 1130 cm<sup>-1</sup> for the present C12A7-Cl<sup>-</sup> materials. This indicates that the anionic species of O<sub>2</sub><sup>2-</sup> in the C12A7-Cl<sup>-</sup> material was below the detection limit.

The species of O<sup>2-</sup> was about  $0.6 \times 10^{20}$  cm<sup>-3</sup> in C12A7-Cl<sup>-</sup>, which was estimated by the charge balance, total positive charge concentration ( $2.33 \times 10^{21}$  cm<sup>-3</sup>) [13,14] as well as all anionic species was measured by EPR and IC. Accordingly, the anionic species in the

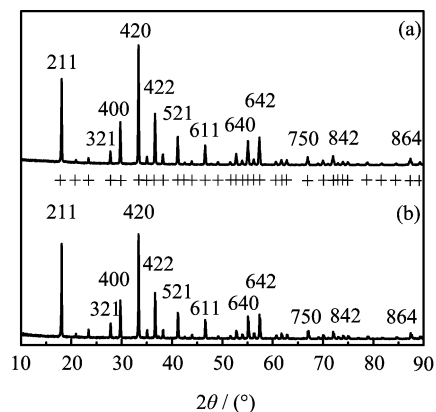


FIG. 5 XRD pattern from (a) the fresh C12A7-Cl<sup>-</sup> material and (b) the used C12A7-Cl<sup>-</sup> material for 10 h' emission at 800 °C and 800 V/cm. The tick marks indicate the positions of the diffraction peaks given in the PDF 45-0568 card [34].

synthesized material was dominated by the Cl<sup>-</sup>, accompanied by small amounts of O<sub>2</sub><sup>2-</sup>, O<sup>-</sup>, and O<sup>2-</sup>, which also agrees with the distribution of the emitted anions via the TOF observations. The chemical formula of present material is approximately described as C12A7-Cl<sup>-</sup>.

### C. Characteristics of structure of C12A7-Cl<sup>-</sup>

The XRD measurement was carried out to investigate the structure of C12A7-Cl<sup>-</sup> and possible alternation after running the Cl<sup>-</sup> emission (Fig.5). By comparing the measured peak positions and intensities of the XRD pattern with the standard data in the PDF 45-0568 card (International Centre for Diffraction Data (ICDD), Grant-in-Aid, 1994), the diffraction structure of the fresh C12A7-Cl<sup>-</sup> material is in complete accord with that of C11A7·CaCl<sub>2</sub> (with a unit-cell content of Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>Cl<sub>4</sub>), belonging to the *I*4̄3*d* space group. No other phases such as Ca<sub>5</sub>Al<sub>6</sub>O<sub>14</sub> (C5A3), Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (C3A), and CaAl<sub>2</sub>O<sub>4</sub> (CA) were observed. Thus, the impurity phase in the C12A7-Cl<sup>-</sup> material is negligible beside the Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>Cl<sub>4</sub> phase. The lattice constant derived from twenty stronger diffraction peaks is about 1.2015±0.0005 nm, which agrees well with the previous reported data (around 1.201 nm) [34–36]. Although the lattice framework is unchanged, the lattice constants slightly decrease to 1.2010±0.0007 nm for 10 h emission. The decreases of the lattice constants may be caused by the consumption of the Cl<sup>-</sup> in the cages during the emission process.

The XRD was also used to measure the crystallite size. The crystallite sizes calculation was based on the Scherrer equation:

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

TABLE I The characterization results of  $\text{C12A7-Cl}^-$  obtained from two different samples, *i.e.*, sample 1: the fresh  $\text{C12A7-Cl}^-$  sample, and sample 2: the used  $\text{C12A7-Cl}^-$  sample after emission at  $800\text{ }^\circ\text{C}$  and  $800\text{ V/cm}$  for 10 h.

Sample	$a^a/\text{nm}$	$d^b/\text{nm}$	$n_b(\text{Cl}^-)^c/10^{21}\text{cm}^{-3}$	$n_b(\text{O}^-)^d/10^{17}\text{cm}^{-3}$	$n_b(\text{O}_2^-)^d/10^{17}\text{cm}^{-3}$
1	$1.2015\pm 0.0005$	72	$2.21\pm 0.24$	$4.4\pm 1.0$	$2.5\pm 0.5$
2	$1.2010\pm 0.0007$	83	$1.53\pm 0.25$	$1.0\pm 0.4$	$0.6\pm 0.2$

<sup>a</sup> The lattice constants  $a$  were measured via XRD.

<sup>b</sup> The average crystallite sizes  $d$  were calculated by the Warren-Averbach method.

<sup>c</sup> The concentration of  $\text{Cl}^-$  in the  $\text{C12A7-Cl}^-$  bulk was measured via IC.

<sup>d</sup> The concentration of  $\text{O}^-$  and  $\text{O}_2^-$  in the  $\text{C12A7-Cl}^-$  bulk was measured via EPR.

where  $d$  is the crystallite sizes,  $\lambda$  is the wavelength of  $\text{Cu K}\alpha 1$  X-ray source,  $\beta$  is the full-width at half maximum (FWHM), and  $\theta$  is the diffraction angle of the XRD. Applying conventional methods in line-broadening analysis of the Warren-Averbach method to calculating quantities as the average crystallite size, effects of the crystal size and internal strains on broadening were separated by plotting  $(\beta \cos \theta / \lambda)^2$  versus  $(\sin \theta / \lambda)^2$  and taking the square root of the intercept as the measure of the particle size [39]. As can be seen in Table I, the average crystallite size of the particles increased from 72 nm to 83 nm after 10 h emission.

The microstructure on the fresh  $\text{C12A7-Cl}^-$  surface and its morphological alterations after running the emission were also observed by the FESEM images. Figure 6(a) shows the typical FESEM image of the fresh sample where a high density of voids is present with a random distribution, indicating that the prepared  $\text{C12A7-Cl}^-$  is a nanoporous material. No obvious morphological alteration was observed after running the emission at  $800\text{ }^\circ\text{C}$  and  $800\text{ V/cm}$  for 10 h (Fig.6(b)).

To develop  $\text{C12A7-Cl}^-$  material into application, we have carried on a primary investigation in etching and sterilization by using  $\text{C12A7-Cl}^-$ . The process needs further work, which is in progress.

#### IV. CONCLUSION

In conclusion, a storage and emission functional material of chlorine anion:  $\text{C12A7-Cl}^-$  ( $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot (\text{Cl}^-)_{3.80}(\text{O}^{2-})_{0.10}$ ) was prepared by the solid-state reactions of  $\text{CaCO}_3$ ,  $\gamma\text{-Al}_2\text{O}_3$ , and  $\text{CaCl}_2$  in  $\text{Cl}_2/\text{Ar}$  mixture atmosphere. The anionic species emitted from the  $\text{C12A7-Cl}^-$  surface were dominated by the  $\text{Cl}^-$  (about 90%) together with a small amount of the  $\text{O}^-$  and electrons, identified by TOF mass spectroscopy. The anionic species stored in the  $\text{C12A7-Cl}^-$  material were dominated by the  $\text{Cl}^-$ , accompanied by a small amount of  $\text{O}^{2-}$ ,  $\text{O}^-$ , and  $\text{O}_2^-$ , measured via ion chromatography, electron paramagnetic resonance and Raman spectra measurements. The structure and morphological alterations of the material were investigated via XRD and FESEM, respectively. Potentially, the present method may be useful to develop a rela-

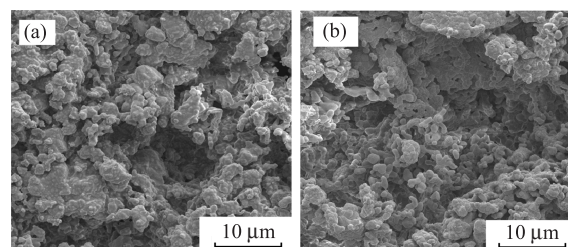


FIG. 6 FESEM images of the fractured surfaces of (a) the fresh  $\text{C12A7-Cl}^-$  sample; (b) the  $\text{C12A7-Cl}^-$  sample after emission at  $800\text{ }^\circ\text{C}$  and  $800\text{ V/cm}$  for 10 h. Magnification: 5000.

tively pure beam source of  $\text{Cl}^-$ , which may be applied to the fields such as etching, sterilization, film preparation, material modification, atmospheric chemistry, anion mass spectrometer, and particle accelerator.

#### V. ACKNOWLEDGMENTS

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