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溶胶-凝胶法制备多孔晶体材料 C12A7-Cl⁻

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摘要: 利用溶胶-凝胶法制备了多孔晶体材料 C12A7-Cl⁻ (Ca₁₂Al₁₄O₃₂Cl₂), 制备凝胶的原料是四水合硝酸钙、九水合硝酸铝、氯化钙、尿素和乙二醇. 混合溶液经过搅拌 2–3 h 形成溶胶, 再经 350 °C 热处理后形成凝胶体, 最终在流动氩气气氛中 1000 °C 烧结后得到材料. 用 X 射线衍射, 场发射扫描电子显微镜, 热重分析, 电子顺磁共振和离子色谱等方法表征合成的 C12A7-Cl⁻ 多孔晶体材料. 结果表明, 利用溶胶-凝胶法成功地生成了 C12A7 结构, 氯负离子是材料中存储的主要负离子. 此外, 从 C12A7-Cl⁻ 晶体材料表面发射的氯负离子也被飞行时间质谱观测到. 上述结果说明溶胶-凝胶法可被用于制备 C12A7-Cl⁻ 晶体材料.

关键词: 溶胶-凝胶; C12A7-Cl⁻; 表征; 发射

中图分类号: O647; O648

Sol-Gel Preparation of Porous C12A7-Cl⁻ Crystals

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Abstract: Present study provides an approach to produce porous crystal material of C12A7-Cl⁻ (Ca₁₂Al₁₄O₃₂Cl₂) by sol-gel method. Reactants for the gel were Ca(NO₃)₂·4H₂O, Al(NO₃)₃·9H₂O, CaCl₂, urea, and ethylene glycol. The mixture solution was stirred for 2–3 h to form the sol, after thermal treatment at 350 °C, the formed gel was then sintered under flowing argon at 1000 °C. The prepared porous crystal material was investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA), electron paramagnetic resonance (EPR), and ion chromatography (IC). Results indicated that the C12A7-Cl⁻ material was successfully prepared *via* sol-gel method and the Cl⁻ anions were the dominant anions stored in the bulk of the material. The emission of Cl⁻ anions from the C12A7-Cl⁻ surface was detected by time-of-flight mass spectrometry (TOF-MS). Our results show that the sol-gel method can be potentially useful in the development of C12A7-Cl⁻ materials.

Key Words: Sol-gel; C12A7-Cl⁻; Characterization; Emission

As one of the important chemical intermediates, the chlorine anion (Cl⁻) has attracted much attention in many fields including atmospheric chemistry, biochemistry, material modifications, electrochemistry, and semiconductor industry^[1–6]. For example, the presence of two isotopes (³⁵Cl⁻ and ³⁷Cl⁻) favors the interpretation of anionic mass spectra, which has been of considerable value in chemical ionization mass spectrometry^[1]. Because the major reactions between Cl⁻ and organic substances are generally

to form the anionic attachment products [MCl]^{-[1,4–6]}, Cl⁻ has been considered to identify saccharides^[5], and to monitor barbiturates^[6]. On the other hand, it has been reported that Cl⁻ can enhance the plasma etching of polycrystalline silicon (poly-Si) in semiconductor chemistry^[8]. More recently, halogen anions have been proposed as an alternative to positive ions for ion fusion drivers in inertial confinement fusion^[9], because electron accumulation would be prevented in negative-ion beams.

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The material of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$ (or named C12A7- Cl^-), one of the derivate of C12A7, was first prepared from co-sintering C12A7 with CaCl_2 by Jeevaratnam *et al.* and reported a lattice constant of 1.2004 nm^[10]. Its chemical character was further investigated by Sango *et al.*^[11]. Similar to C12A7^[12], the material of C12A7- Cl^- , belonging to $\bar{I}43d$ space group, possesses a body-centered cubic structure and also has typical positively charged framework of $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}$ with a unit-cell content of $\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}\text{Cl}_4$ ^[10]. Besides conventional method, C12A7 has also been successfully synthesized by sol-gel method^[13-16], which was utilized to prepare C12A7- Cl^- sample in this article.

Recently, we have developed an approach to generate high pure and sustainable chlorine anion flux, which is emitted from the surface of the synthesized C12A7- Cl^- material^[17]. But both of the high sintering temperature (up to 1350 °C) and the using of chlorine gas, which is harmful to the environment and human body, were disadvantages of application. In this work, we confirmed experimentally that the sol-gel method could be useful in preparing C12A7- Cl^- material and avoid the two disadvantages mentioned above.

1 Experimental

1.1 Sample preparation

The material of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$ (C12A7- Cl^-) was prepared by the sol-gel method. The starting solution was prepared from hydrated calcium nitrate (AR), hydrated aluminum nitrate (AR), calcium chloride (AR), urea (AR), ethylene glycol (AR), and distilled water. Molar ratio of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}:\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}:\text{CaCl}_2:\text{CO}(\text{NH}_2)_2:\text{HOCH}_2\text{CH}_2\text{OH}$ is 11:14:1:76:380. Firstly, appropriate amounts of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and CaCl_2 were dissolved in distilled water. The solution was stirred for 2–3 h. Then, a given amount of urea was added into the above solution, stirring for 2–3 h too. At last, ethylene glycol was added to the solution, stirring in the same condition to form the sol. The resulting sol was aged for 24 h to form gel. Thermal treatment was done in air at 350 °C for 2 h. The resulting powder sample was further temperature-programmed with a heating rate of 10 °C·min⁻¹, sintered at 1000 °C for 6 h, and finally cooled to room temperature under flowing argon atmosphere (flowing rate: 100 mL·min⁻¹).

1.2 Characterization

X-ray diffraction (XRD) measurement was carried out to investigate the structure of C12A7- Cl^- . Powder X-ray diffraction patterns were recorded on a MAC Science MXP18AHF diffractometer with a $\text{Cu-K}_{\alpha 1}$ source ($\lambda=0.154056$ nm) in the 2θ range of 15°–75°. The crystal morphology was investigated using the field emission scanning electron microscopy (FESEM; FEI, Sirion-200, America).

Thermogravimetric analysis (TGA) (Shimadzu DTG-60H thermal analyzer) was carried out with a heating rate of 10 °C·min⁻¹ in nitrogen atmosphere for the precursor powder which was obtained by thermally treating the dried gel in air at 350 °C for 2 h.

The absolute Cl^- concentration in the C12A7- Cl^- sample (after

dissolving in the deionized water) was analyzed by ion chromatography (IC; DX-120, Dionex Co.), and the IC results were calibrated with a standard NaCl solution of 4×10^{-4} mol·L⁻¹. Electron paramagnetic resonance (EPR) measurement was performed to investigate the anionic species (e.g., O^- and O_2^-) in the C12A7- Cl^- bulk. The experiment was conducted at ca 9.1 GHz (X-band) using a JES-FA200 spectrometer at 120 K. Spin concentrations were determined from the second integral of the spectrum using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a standard with an error of about 20%.

For time-of-flight (TOF) observation, the powder of precursor was pressed to a slice with a diameter of 15 mm and a thickness of 2 mm under a pressure of $(1.5-2) \times 10^{10}$ Pa, and then were temperature-programmed to 1000 °C with a heating rate of 10 °C·min⁻¹, sintered at 1000 °C for 6 h and cooled to room temperature under flowing argon atmosphere. The TOF experimental apparatus, described previously^[18], consists essentially of a sampling chamber and an ion detection chamber equipped with a 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 chamber. The anions and electrons emitted from the frontal surface were extracted by an extraction electrode, and then analyzed by the TOF mass spectrometer.

2 Results and discussion

2.1 XRD/SEM analysis

The XRD analysis was carried out to investigate the structure of the as-prepared C12A7- Cl^- . Fig.1 shows the XRD pattern obtained from the C12A7- Cl^- sample sintered at 1000 °C. The results of comparing the measured positions and intensities of the XRD patterns with the standard data in the PDF 05-4568 card (International Centre for Diffraction Data (ICDD), 2002) are as follows: all the diffraction peaks have appeared, the X-ray diffraction structure for the samples completely accords with that of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$. This means that the material structure prepared by the sol-gel method has a cubic structure with a unit-cell content of $\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}\text{Cl}_4$ and belongs to $\bar{I}43d$ space group. The unit cell constant for the sample sintering at 1000 °C, derived from the stronger diffraction peaks, was about (1.2002 ± 0.0006) nm.

The mean particle size (d) was estimated by analyzing the broadening of the diffraction peaks. The mean particle size was calculated by the Scherrer equation:

$$d = K\lambda / \beta \cos\theta \quad (1)$$

where K is a constant (0.89), λ is the wavelength of X-ray source ($\text{Cu K}_{\alpha 1}$, $\lambda=0.154056$ nm), β is the full-width at half maximum (FWHM), and θ is the diffraction angle of the X-ray diffraction. The mean particle diameter of the C12A7- Cl^- sample calculated by Eq.(1) was 48.95 nm.

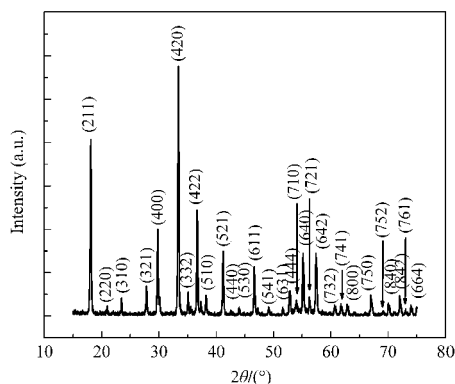


Fig.1 XRD pattern of C12A7-Cl⁻ sample prepared by sol-gel method (sintered at 1000 °C for 6 h)

The microstructure of the as-prepared C12A7-Cl⁻ sample was observed by the FESEM. Fig.2 shows typical FESEM image of the sample which was formed in further sintering temperature at 1000 °C for 6 h. From the SEM image, the C12A7-Cl⁻ sample had high density of voids presented with a random distribution, indicating that the prepared C12A7-Cl⁻ is a porous material.

2.2 TGA analysis

The TGA analysis was carried out to study the phase transformation during the formation of C12A7-Cl⁻. Fig.3 shows the TGA diagram of the precursor powder of the material. For the dried gel has been thermally treated in air at 350 °C for 2 h, the mass loss in the temperature region lower than 360 °C is slight. The mass loss between 50 and 150 °C was assigned to the loss of the residual water^[19]. The mass loss in the range from 360 to 690 °C was obviously identified from the TGA curve. This mass loss would mainly response for the combination of the decomposition of the residual aluminum nitrate into Al₂O₃^[20-21] and calcium nitrate into CaO with the existence of Al₂O₃^[22-23]. The mass loss over 800 °C may be attributed to the gasification of small amount solid residuals such as carbon^[24].

2.3 EPR/IC analysis

The EPR measurement was performed to investigate the active oxygen species such as O⁻ and O₂⁻ in the C12A7-Cl⁻ material. Fig.4 shows the EPR spectrum from the C12A7-Cl⁻ sample. The experimental spectrum was simulated by a simple superpo-

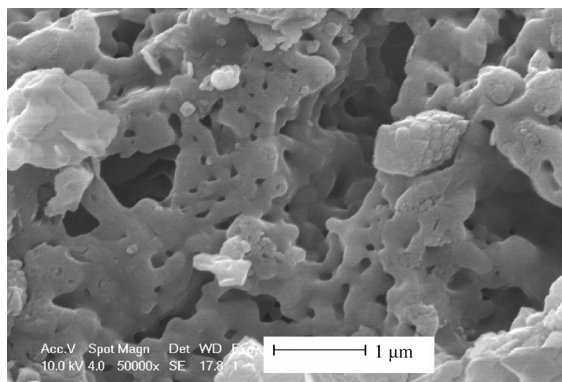


Fig.2 Typical FESEM image of the C12A7-Cl⁻ material prepared by sol-gel method (sintering at 1000 °C for 6 h)

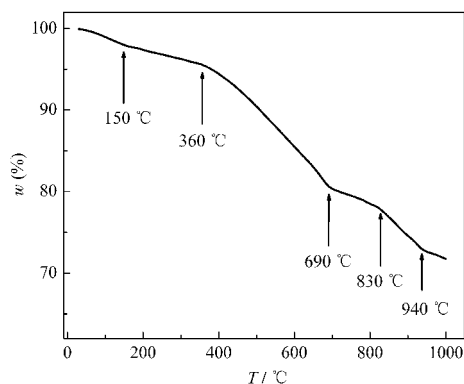


Fig.3 TGA of the material precursor powder

sition with the Lorentzian line shape of O⁻ ($g_{xx}=g_{yy}=2.043$ and $g_{zz}=1.997$) and O₂⁻ ($g_{xx}=2.001$, $g_{yy}=2.009$, and $g_{zz}=2.071$)^[12] in common set of g -values and different intensity ratios. By simulating the EPR spectrum and using CuSO₄·5H₂O as a spin concentration standard, we estimated the O⁻ and O₂⁻ concentrations in the C12A7-Cl⁻ sample to be about $2.39 \times 10^{17} \text{ cm}^{-3}$ and $1.91 \times 10^{17} \text{ cm}^{-3}$, respectively.

Note that this EPR method can not measure the Cl⁻ species in the C12A7-Cl⁻ material because there are no unpaired electrons for the Cl⁻. The absolute Cl⁻ concentration in the C12A7-Cl⁻ was analyzed by using IC method and calibrated with a standard NaCl solution of $4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, the C12A7-Cl⁻ aqueous solution was obtained by dissolving 28.8 mg C12A7-Cl⁻ sample into 100 mL deionized water. Absolute Cl⁻ concentration for the sample was estimated by the integral of the calibrated IC peaks using NaCl solution as a standard. The Cl⁻ concentration in the C12A7-Cl⁻ sample was $1.88 \times 10^{21} \text{ cm}^{-3}$. Due to the total negative charge concentration ($2.33 \times 10^{21} \text{ cm}^{-3}$)^[18], the above IC result further confirmed that the Cl⁻ anions were dominating anionic species stored in the C12A7-Cl⁻ material.

2.4 TOF observations

The anions emitted from the C12A7-Cl⁻ surface were identified by anionic TOF mass spectrometer. Fig.5 shows a typical anionic TOF-MS from the C12A7-Cl⁻ sample at a emission temperature of 700 °C and extraction electric field of 800 V·cm⁻¹. The

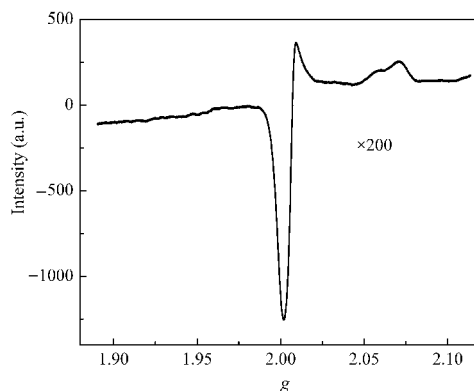


Fig.4 EPR spectrum from the C12A7-Cl⁻ sample sintered in flowing argon ambience at 1000 °C for 6 h

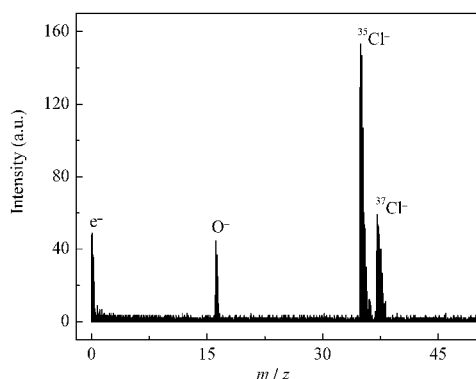
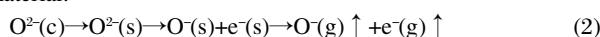


Fig.5 Typical TOF mass spectrum for anions emitted from C12A7-Cl⁻ sample (sintered at 1000 °C for 6 h) surfaces at 700 °C and 800 V·cm⁻¹

dominant peaks have the mass numbers of 35 and 37, which correspond to chlorine isotopes of ³⁵Cl⁻ and ³⁷Cl⁻, respectively, and the other two peaks at $m/z=0$, 16 were simultaneously observed, attributed to emission of the electrons and O⁻ anions, respectively. It was found that the anionic species emitted from the C12A7-Cl⁻ material surface were dominating with the Cl⁻ anions together with an amount of O⁻ anions and electrons in the investigated range. The emission of O⁻ anions and electrons were mainly caused by the decomposition of remaining O²⁻ in the bulk of the material:



where c, s, g stand for the anions in the cage, surface of the material, gas phase, respectively. The TOF result shows that the C12A7-Cl⁻ material has the ability to emit Cl⁻ anion. The anionic distribution emitted from the C12A7-Cl⁻ would indirectly demonstrate that Cl⁻ anions should be the major anions stored in the materials of C12A7-Cl⁻.

Comparing with the common direct synthesis method of C12A7-Cl⁻ which we have reported before^[17], present sol-gel method has successfully decreased the sintering temperature for about 350 °C (from 1350 to 1000 °C). Moreover, the chlorine gas is not needed in sol-gel method, which lowers much danger. So the sol-gel method could be considered as an alternative method for the energy-saving and safety.

3 Conclusions

In this work, we prepared porous crystal functional material of C12A7-Cl⁻ by sol-gel method. The XRD result shows that the C12A7 structure has been successfully synthesized *via* the nano particles of CaO and Al₂O₃ formed from the gel. The transformation temperature from CaO/Al₂O₃ to 12CaO·7Al₂O₃ (C12A7) by present sol-gel method decreased about 350 °C, comparing with common direct synthesis of C12A7 *via* CaO and Al₂O₃ powder. According to IC result, Cl⁻ anions are the dominant anion species stored in the C12A7-Cl⁻ material. TOF observation proves that Cl⁻ anions can be emitted under suitable temperature and electric field conditions. Present sol-gel method has shown as an alternative synthesis method for decreasing sintering tempera-

ture and avoiding chlorine gas. Potentially, present sol-gel method is useful to develop a Cl⁻ anion source, which may be applied to the fields such as etching, film preparation, sterilization, material modification, and anion mass spectrometer, etc.

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