掺杂 Cs 元素的微孔晶体材料 C12A7 的表征及负离子发射特性

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摘要: 利用浸渍 CsI 的方法在微孔晶体材料 $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C12A7) 表面掺杂 Cs 元素并对其进行场发射扫描电镜、透射电子显微镜、X 射线衍射以及电子顺磁共振的表征。场发射扫描电镜以及透射电子显微镜的结果均证实 CsI 沉积在 C12A7 的表面; X 射线衍射证明 C12A7 的结构并没有被破坏; 电子顺磁共振谱说明了浸渍后 C12A7 中的 O^- 和 O_2^- 浓度也无明显变化。将浸渍后的同原始的 C12A7 进行比较发现, 掺杂样品在结构和存储特性上均无明显变化。此外, 对该材料的发射性能与温度和引出场的关系也进行了研究与分析。结果表明: 浸渍 CsI 至 C12A7 表面不仅降低了氧负离子的发射温度, 还大幅增强了发射强度; 氧负离子发射增强的主要原因归结于浸渍 CsI 后其表观活化能的降低。

关键词: 氧负离子; 掺杂 Cs 元素的 C12A7; 发射特性; 存储特性; 表观活化能

中图分类号: O647

Characterization and Anion Emission Characteristics of the Microporous Crystal Cs-C12A7

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Abstract: Cesium- $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (Cs-C12A7) was fabricated by adding CsI to the C12A7 surface using incipient wetness impregnation. The X-ray diffraction (XRD) structure determined for the Cs-C12A7 material is the same as that of the $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C12A7) crystal, which belongs to the $\bar{I}43d$ space group. The concentrations of O^- and O_2^- in Cs-C12A7 were about $(1.3 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$ and $(1.2 \pm 0.2) \times 10^{20} \text{ cm}^{-3}$, respectively, according to a simulation of the measured electron paramagnetic resonance (EPR) spectrum. This is similar to the data obtained for fresh C12A7 ($[\text{O}^-] = (1.4 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$ and $[\text{O}_2^-] = (1.4 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$). The CsI particles from the C12A7 surface were observed using field emission scanning electron microscope (FESEM) and conventional transmission electron microscopy (TEM). The emission features of Cs-C12A7, including the emission distribution, field effect and apparent activation energy were investigated in detail and compared with those of C12A7. The advanced emission behavior was attributed to a reduction in the apparent activation energy.

Key Words: Atomic oxygen anion; Cs-C12A7; Emission characteristics; Storage characteristics; Apparent activation energy

1 Introduction

Atomic oxygen anion (O^-) is a monovalent negative ion

through the attachment of an electron to atomic oxygen, which is one of the most active oxygen species. As one of the impor-

Received: November 26, 2010; Revised: January 17, 2011; Published on Web: March 2, 2011.

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The project was supported by the National Natural Science Foundation of China (50772107), National Key Basic Research Program of China (973) (2007CB210206) and National High-Tech Research and Development Program of China (863) (2009AA05Z435).

国家自然科学基金(50772107), 国家重点基础研究发展规划(973)(2007CB210206)及国家高技术研究发展计划(863)(2009AA05Z435)资助项目

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tant chemical intermediates, atomic oxygen anion is potentially useful in many fields such as chemical synthesis, air cleaning, and surface sterilization.^{1,2} It has been found that anion implantation or deposition into insulated material surfaces is more suitable than the use of positive implantation because anions have negative polarity and low electron affinity, and besides, there are negligible "surface charging-up" in the former.³⁻⁵ Anions have also been used as an alternative to positive ions for ion fusion drivers in inertial confinement fusion because electron accumulation would be prevented.⁶

The conventional method to form anions is through the attachment of a free low-energy electron to atom or through anion-molecule reactions, appearing in the processes such as plasma, electron impact, or laser irradiation. Anions generated in above processes, in general, are complicated and always accompanied by the formation of manifold species. Alternately, we have developed an approach to selectively generate anions of O^- ,⁷⁻¹⁰ OH^- ,^{11,12} H^- ,^{13,14} F^- ,^{15,16} and Cl^- ^{17,18} via the synthesized anionic storage-emission materials. For example, the microporous material of $C12A7-O^-$ can store and emit O^- , prepared by the solid-state reaction of $CaCO_3$ and $\gamma-Al_2O_3$ in the dry oxygen environment.^{7-10,19} The structure of $C12A7-O^-$ is characterized by a positive charged lattice framework $[Ca_{24}Al_{28}O_{64}]^{4+}$ including 12 sub-nanometer sized cages with a free space of about 0.4 nm in diameter.^{19,20} The storage features of O^- in the cage of $C12A7-O^-$ have been investigated by the electron paramagnetic resonance (EPR) method.¹⁹ On the other hand, the O^- anions stored in $C12A7-O^-$ can be emitted into the gas phase by heating the material.⁷⁻¹⁰ The emitted species from the $C12A7-O^-$ surface are dominated by O^- . More recently, we have also synthesized various derivatives 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 a fast microorganisms inactivation,²³⁻²⁵ the dissociation and oxidation of oxygenated organic compounds.^{24,26,27}

Although there have been previous studies on $12CaO \cdot 7Al_2O_3$ ($C12A7$) and its various derivatives, higher operation temperature remains a main challenge when these materials are used in the anions emission source, catalytic reactions, filming modifications, and anionic sterilization processes. The present study provides a novel approach to generate low-temperature atomic oxygen anions (O^-) emission by using the $Cs-12CaO \cdot 7Al_2O_3$ ($Cs-C12A7$). The emission and structure features of the $Cs-C12A7$ have been investigated in detail. Lower operation temperature, potentially, will promote the practical application of the anion storage-emission material in the O^- source, chemical synthesis, air cleaning, and surface sterilization.

2 Experimental

2.1 Sample preparation

The fresh $C12A7$ was synthesized by the solid-state reaction of $CaCO_3$ and $\gamma-Al_2O_3$ under flowing dry oxygen atmosphere. The powders of $CaCO_3$ and $\gamma-Al_2O_3$ with an average particle di-

ameter of 20–30 μm were mixed and grained at a molar ratio of 12:7. The powder mixture was pressed to a slice of 15 mm in diameter and 2 mm in thickness under a pressure of 1470–1960 $N \cdot cm^{-2}$, and then put into a ceramic tube (length: 1 m, inner diameter: 20 mm). The slice samples were temperature-programmed to 1200 $^{\circ}C$ at heating rate of 10 $^{\circ}C \cdot min^{-1}$, sintered at 1200 $^{\circ}C$ for 10 h, and cooled to room temperature under flowing oxygen atmosphere. We used incipient wetness impregnation technique to add CsI to $C12A7$. The solvent was composed of ethanol and water, and the volume ratio of ethanol to water was 3:1. The concentration of CsI in the solution was about 0.09 $g \cdot mL^{-1}$. Then, the $C12A7$ slices were impregnated into the CsI -mixed solution and dried at 120 $^{\circ}C$ for 24 h. The appropriate CsI content (mass fraction) added to $C12A7$ was about 10% and the molar ratio of each content was $n_{Cs}:n_{Ca}:n_{Al}=0.57:12:14$.

2.2 Characterization of samples

The CsI content of the $Cs-C12A7$ was measured by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atom scan Advantage of Thermo Jarrell Ash Corporation, USA). X-ray diffraction (XRD) measurements were carried out to investigate the structure of the prepared samples. The synthesized samples were crushed into particles of the average diameter of 20–30 μm . The powder X-ray diffraction patterns were recorded on an X'pert Pro Philips diffractometer with a $Cu-K_{\alpha 1}$ source ($\lambda=0.1540598$ nm). The measurement was in the 2θ range of 10 $^{\circ}$ –80 $^{\circ}$, step counting time of 5 s, and step size of 0.017 $^{\circ}$ at 298 K. The measurement of the lattice constant was made from diffractometer traces using Si as the internal standard. Electron paramagnetic resonance (EPR) measurements were performed to investigate the anionic species (O^- and O_2^-) in the resulting material. 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 $CuSO_4 \cdot 5H_2O$ as a standard with an error of about 20%. To investigate the morphology, the samples were first coated with gold layer about 10 nm (SCD 050 Sputter Coater, BAL-TEC) and then observed by field emission scanning electron microscopy (FESEM; Sirion-200, FEI, American). The microstructure of the sample was examined with conventional transmission electron microscopy (TEM, Japan H-800), which has a primary electron energy of 200 keV and a point resolution of 0.45 nm in TEM mode. The powder sample, which was from the surface of $Cs-C12A7$, was dispersed in ethanol and kept in an ultrasonic bath for 3 h, then the sample was deposited onto a carbon-covered Cu supporting grid and dried at 25 $^{\circ}C$ for TEM analysis.

2.3 TOF measurements

The anions emission feature from the $Cs-C12A7$ surface was investigated by a time-of-flight (TOF) mass spectroscopy. The experimental apparatus and measurement method were previously described in detail elsewhere.^{9,10} Briefly, the experimental system consists essentially of a sampling chamber and

an ion detection chamber equipped with a time of flight mass spectrometry (TOF-MS). The sample (diameter: 1.5 cm, thickness: 2 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 with a diameter of 2.5 mm in the center of the flat. The quartz tube was installed in the sample chamber, ensuring that the sample located in the center of the sample chamber. The effective emission area was about 1.75 cm². Total emission current of the anions and electrons emitted from the frontal surface were extracted by an extraction electrode, collected by a Faraday plate and detected by a Keithley model 6485 amperometer. A trace amount of the leak current was measured by the quartz sample instead of the tested material. Part of the emitted species passed through a pinhole of 1 mm in the Faraday plate, which allowed the simultaneous analyses by a TOF mass spectrometry. The background pressure of the chamber was maintained to be less than 3×10^{-4} Pa for all experiments. To guarantee the precision of measurements, the samples were changed when an observable decrease of the emission intensity was observed and the calibration of the intensity was also performed. All experiments were repeated three times. The reported results are the averaged data from three measurements. The differences among the data of the apparent activation energies from each repeating, in general, range from zero to 20%.

3 Results and discussion

3.1 Characterization of Cs-C12A7

Fig.1 shows the XRD patterns from the fresh C12A7 and Cs-C12A7. Through the comparison of the measured peak positions and intensities of the XRD patterns with the standard data in the PDF-09-0413 card, the X-ray diffraction structure for present Cs-C12A7 material completely accords with that of the crystal $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C12A7), belonging to $\bar{I}43d$ space group.²⁸ No other phases such as $\text{Ca}_5\text{Al}_6\text{O}_{14}$ (C5A3), $\text{Ca}_3\text{Al}_2\text{O}_6$ (C3A), and CaAl_2O_4 (CA) were observed. Thus, the impregnation process did not destroy the crystal structure of C12A7. The unit cell value derived from twenty stronger diffraction peaks of the Cs-C12A7 was about (1.196 ± 0.003) nm, which

agreed very well with the data of the fresh C12A7 ((1.199 ± 0.001) nm). All of the diffraction peaks observed from the used Cs-C12A7 sample agreed very well with those from the original ones. In addition, the mean particle sizes (d) were calculated by the Scherrer equation. The mean sizes of the crystallites were about (80 ± 10) nm and (75 ± 5) nm for the fresh C12A7 and Cs-C12A7, respectively. This indicates that there is no obvious congregation of the particles occurring in the impregnation process.

The EPR measurements were performed to investigate the oxygen-containing species such as O^- and O_2^- in the resulting material. Fig.2 shows the EPR spectra from the samples. The EPR spectra can be decomposed into two components, which are attributed to the anionic oxygen species of O^- ($g_{xx}=g_{yy}=2.036$ and $g_{zz}=1.994$) and O_2^- ($g_{xx}=2.001$, $g_{yy}=2.008$, and $g_{zz}=2.074$).^{11,17} The spectral intensity for the Cs-C12A7 was almost the same as that for the fresh C12A7. By the simulation of the EPR spectra and using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a spin concentration standard, the oxygen species concentrations in the resulting material could be estimated. The concentrations of O^- and O_2^- in the Cs-C12A7, according to simulating the measured EPR spectra, were both about $(1.3 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$ and $(1.2 \pm 0.2) \times 10^{20} \text{ cm}^{-3}$, respectively, which were close to the data in the fresh C12A7 ($[\text{O}^-] = (1.4 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$ and $[\text{O}_2^-] = (1.4 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$). On the other hand, the remained species of O^{2-} were estimated by the charge balance, total positive charge concentration ($2.3 \times 10^{21} \text{ cm}^{-3}$) as well as the EPR results.¹⁷ So, accordingly, the chemical formula of the Cs-C12A7 was approximately described as $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot (\text{O}^-)_{0.2}(\text{O}_2^-)_{0.2}(\text{O}^{2-})_{1.8}$.

The morphological alterations after the impregnation of CsI were also observed by the FESEM images (Fig.3). Large numbers of misty gray granules appeared on the surface of Cs-C12A7, which indicated that the CsI particles were uniformly deposited on the surface of C12A7. The average size of the granules was about 1.2 μm for the Cs-C12A7, which was smaller than that for the fresh C12A7 (2.3 μm). Meanwhile, the CsI particle was also observed in the TEM image (Fig.4). The particle of CsI (the black area in the TEM photos) was surrounded by C12A7 particles.

Fig.1 XRD patterns of fresh C12A7 (a) and Cs-C12A7 (b)

Fig.2 EPR spectra of fresh C12A7 (a) and Cs-C12A7 (b)

Fig.3 FESEM images of fresh C12A7 (a) and Cs-C12A7 (b)

3.2 TOF measurements on anion emission from Cs-C12A7

The anions emitted from the Cs-C12A7 surface were identified by a TOF mass spectroscopy. Fig.5 shows typical anionic TOF mass spectra from the Cs-C12A7 at an extraction field of $800 \text{ V} \cdot \text{cm}^{-1}$. At the temperature of 630°C , two peaks at m/z of 0 and 16 appeared synchronously, which corresponded to the emission of the electrons and O^- anions, respectively. This indicated that the anionic species emitted from the Cs-C12A7 surface consisted of the O^- anions and some amount of electrons. It was also noticed that the emission intensity of O^- from Cs-C12A7 was close to that from the fresh C12A7 at 750°C , indicating that the required emission temperature of O^- from C12A7 was greatly reduced by adding Cs.

3.3 Field effects on anions emission from Cs-C12A7

Fig.6 shows that the emission intensities of O^- and e^- from the Cs-C12A7 and fresh C12A7 as a function of temperature under different applied extraction fields ($200\text{--}800 \text{ V} \cdot \text{cm}^{-1}$). Firstly, we noticed that the melting point of CsI is 621°C . High temperature may cause an increasing vapor pressure of CsI and also the emission properties may be affected by the CsI evaporation. In order to avoid such problem, a low experiment temperature range ($450\text{--}650^\circ\text{C}$) was chosen for Cs-C12A7. It was found that the O^- anions emitted both from the Cs-C12A7 and fresh C12A7 surfaces strongly depended on the

applied extraction field (E). In the case of $E=0 \text{ V} \cdot \text{cm}^{-1}$, no detectable emission signal was observed within the experimental detection limit. For the Cs-C12A7 (Fig.6(a)), the emission intensity of O^- significantly increased from $0.41 \mu\text{A} \cdot \text{cm}^{-2}$ to $1.38 \mu\text{A} \cdot \text{cm}^{-2}$ at 650°C when the extraction field rose from 200 to $800 \text{ V} \cdot \text{cm}^{-1}$, which was much higher than that from fresh C12A7 even at 750°C (from $0.18 \mu\text{A} \cdot \text{cm}^{-2}$ to $0.79 \mu\text{A} \cdot \text{cm}^{-2}$). The intensities of the electrons from the Cs-C12A7 were also enhanced by the increasing applied extraction field (Fig.6(b)). Similar field effects on the emission of O^- and e^- from the fresh C12A7 were also observed (Fig.6(c, d)). Otherwise, it was also found that the intensities of the electrons from the Cs-C12A7 were also much higher than those from fresh C12A7.

To reveal further thermal and field effects on the O^- emission from the material surface, Fig.6 was re-plotted with a logarithm scale in the Arrhenius fashion. As shown in Fig.7, all Arrhenius plots exhibit a good linear behavior. Table 1 summarizes the apparent activation energies (E_a) of the O^- and e^- emission measured for the Cs-C12A7 and fresh C12A7 at different fields. The apparent activation energies for the O^- emission from the Cs-C12A7 gradually decreased with increasing the applied extraction field. With increasing the extraction field from 200 to $800 \text{ V} \cdot \text{cm}^{-1}$, for example, the apparent activation energies of O^- (i.e., $E_a(\text{O}^-)$) dropped from about (225 ± 5) to $(178 \pm 3) \text{ kJ} \cdot \text{mol}^{-1}$. The apparent activation energies of electrons (i.e.,

Fig.4 Typical TEM image of Cs-C12A7

Fig.5 Typical TOF mass spectra of the Cs-C12A7 material surface measured at an extraction field of $800 \text{ V} \cdot \text{cm}^{-1}$

Fig.6 Effects of the extraction field on the emission intensities of the O^- anions and electrons

(a, b) Cs-C12A7, (c, d) fresh C12A7

$E_a(\text{e}^-)$ simultaneously reduced from about (280 ± 3) to (234 ± 7) $\text{kJ}\cdot\text{mol}^{-1}$. The decrease of the apparent activation energies indicated that the applied electric field could lower the surface barrier height, as discussed in detail below. It was also noticed

that the apparent activation energies of the O^- emission from the Cs-C12A7 were quite different from those from the fresh C12A7. Under the same extraction field of $800\text{ V}\cdot\text{cm}^{-1}$, for example, the apparent activation energies $E_a(\text{O}^-)$ for the Cs-

Fig.7 Arrhenius plots for the O^- and e^- emissions at a series of fixed extraction field

(a, b) Cs-C12A7, (c, d) fresh C12A7

Table 1 Apparent activation energies (E_a) of the O^- and e^- emissions from the Cs-C12A7 and fresh C12A7 at different extraction fields

$E/(V \cdot cm^{-1})$	Cs-C12A7		fresh C12A7	
	$E_a(O^-)$ (kJ·mol ⁻¹)	$E_a(e^-)$ (kJ·mol ⁻¹)	$E_a(O^-)$ (kJ·mol ⁻¹)	$E_a(e^-)$ (kJ·mol ⁻¹)
200	225±5	280±3	267±7	310±6
400	209±4	262±7	249±6	295±6
600	196±3	253±6	236±7	283±7
800	178±3	234±7	219±6	262±7

C12A7 and fresh C12A7 were about (178±3) and (219±6) kJ·mol⁻¹, respectively. This indicated that adding Cs to C12A7 would reduce the apparent activation energies of $E_a(O^-)$ and $E_a(e^-)$ (Table 1).

Furthermore, the field effects on the O^- emission would be qualitatively understood as follows. When an O^- anion left the material surface, the anion must possess translational energy in excess of the potential which bound it to the surface. The surface barrier height may reduce with increasing the extraction field, leading to the increase of the O^- emission from the material surface at higher extraction field. According to the Arrhenius curves measured under various fields, the apparent activation energy $E_a(O^-)$ indeed decreased with increasing the field (Table 1).

3.4 Emission mechanism of anions for Cs-C12A7

As discussed above, the Cs-C12A7 had the same positively charged lattice framework structure and possessed a similar anion storage character to that of the fresh C12A7, but the behaviors of the anion emission from the Cs-C12A7 were rather different from those from the fresh C12A7. The present results showed that adding a small amount of Cs to C12A7 could significantly promote the emission of O^- and lower the initiative emission temperature from the material surface (Fig.6). The cesium element has a low ionization potential of 3.8 eV and its work function is about 1.8 eV.²⁹ The Cs-containing compounds, are usually used as photoelectric material for the micro channel plate (MCP) and photo multiplier tube (PMT) etc.,^{30–32} because such Cs-containing materials possess very high quantum efficiency and effective secondary-electrons emission.^{33–35} The reduction of the apparent activation energy of the O^- emission and the decrease of binding energy of the surface would be attributed to the promotion effect of Cs on the emission of O^- (Fig.6). The enhancement of the electron emission from the Cs-C12A7 may originate from the thermal electrons emission of CsI. Moreover, it was observed that the emission intensity of O^- was significantly enhanced by the surface temperature and extraction field. The O^- emission from the material surface would mainly be controlled by two kinetic processes, i.e., the diffusion of the O^- anions from the bulk onto the material surface ($(O^- \text{ (cages)} \rightarrow O^- \text{ (surface)})$), and desorption step from the surface into the gas-phase ($O^- \text{ (surface)} \rightarrow O^- \text{ (gas-phase)}$). Accordingly, the increase of the O^- emission intensity with increasing temperature could be attributed to the increase of the

O^- coverage, and to the increase of the desorption rate of O^- in high temperature region. When an O^- anion left the C12A7 surface, the anion must possess translational energy in excess of the potential which bound it to the surface. The surface barrier height may reduce with increasing the extraction field, leading to the increase of the O^- emission from the surface at higher extraction field.

4 Conclusions

By using the cesium-12CaO·7Al₂O₃ (Cs-C12A7), a novel approach to generate low-temperature atomic oxygen anions (O^-) emission in the gas-phase has been developed. The chemical formula of the synthesized Cs-C12A7 could be described as $[Ca_{24}Al_{28}O_{64}]^{4+} \cdot (O^-)_{0.2}(O_2^-)_{0.2}(O^{2-})_{1.8}$, which was almost the same as fresh C12A7. The apparent activation energy of the anions emission was significantly reduced by adding Cs. According to the comparison of characteristics between the Cs-C12A7 and fresh C12A7, adding Cs to C12A7 could significantly promote the emission of O^- which was attributed to the reduction of the apparent activation energy of the O^- emission. Lowering operation temperature, potentially, will promote the practical application of the anion storage-emission material in many fields, like the O^- source, chemical synthesis, air cleaning, and surface sterilization.

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