The fluorescence and thermoluminescence characteristics of α-Al_2O_3:C ceramics*

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This paper reports that polycrystalline α-Al_2O_3:C ceramics are fabricated by conventional ceramics process. The excitation, emission spectra, thermoluminescence (TL) and optical stimulated luminescence (OSL) of α-Al_2O_3:C polycrystalline ceramics are investigated. There exists 410nm maximum emission peak which is caused by recombination of an electron with F^+ centre to produce an excited F centre. The samples show three clear TL glow peaks at 405, 493 and 610 K. The attenuation constant of exponentially decaying fast component (τ_1) and slow component(τ_2) of OSL curve are 8.43s and 41.73s, respectively. Those fluorescence and thermoluminescence characteristics are similar with α-Al_2O_3:C crystal.

Keywords: α-Al_2O_3:C, ceramics, thermoluminescence, optical stimulated luminescence
PACC: 7860K, 7630M, 8120L

1. Introduction

The thermoluminescence(TL) means that emission from an irradiated sample arises upon stimulation with heat. During thermal stimulation the trapped charges are released from metastable trap levels and subsequently recombine with charges of opposite polarity, then light emits. This phenomenon has been known for a long time. The first application of this phenomenon for dosimetric purposes was from Daniels *et al.*[1] Since then much research has been carried out for a better understanding and improvement of the material characteristics as well as developing new TL materials, such as LiF:Mg, Ti,[2] CaSO4:Mn,[3] LiF:Mg,Cu,P[4] and so on. Nowadays, TL dosimetry (TLD) is a well established dosimetric technique with applications in areas such as personnel, environmental and clinical dosimetry.

The minimum measurable dose and dynamic dose range of TL phosphor material depend considerably on the sensitivity of the measuring system. The development of sensitive TL reader systems for the study of phosphor materials is therefore equally important.[5] The α-Al_2O_3 was one of the earlier materials studied for its possible application as a radiation dosemeter, owing to its superior thermal, chemical stability and low effective atomic number.[6] Since then, a sustained effort has been directed towards the improvement of its sensitivity via introduction of various dopants like Si, Ti,[7] Mg and Y,[8] Cr and Ni.[9] However, the substantial improvement in the sensitivity became possible only with the synthesis of α-Al_2O_3 crystal doped with carbon.[10] As a TLD crystal, α-Al_2O_3:C exhibits excellent properties,[11] such as: 1) high TL sensitivity, approximately 40–60 times greater than LiF:Mg, Ti (at a heating rate of 4 K/s); 2) a simple glow curve with TL peaks at 463 K; 3) low background and dose threshold (0.1 mGy with nitrogen flow); 4) low fading during storage in the dark (less than 5% per year); 5) good reproducibility ($< 2\%$) and re-usability without annealing; 6) simple emission spectrum with a maximum at 420 nm which corresponds to the sensitivity of low noise high-sensitivity photomultiplier tubes; 7) wide dose range from 10-7 to 10 Gy; 8) relatively low effective atomic number (10.2).

However, all the reports above were about α-Al_2O_3 crystals. Usually, single crystal growth requires sophisticated laboratories, high temperature (2050°) and highly reducing atmosphere. Processes in the ceramics do not need these conditions of specialties. Compared with single crystal, ceramic materials have

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many advantages: they are easy to fabricate under melting point for a short period and low cost, and they can be mass-produced. Ceramics not only can be produced in large volumes but also can be heavily and homogeneously doped with active ions. They can also be made a multilayer or multifunctional structure. In this paper, the TL and optical stimulated luminescence (OSL) properties of α-Al_2O_3:C polycrystalline ceramics were investigated.

2. Experimental procedure

The α-Al_2O_3:C ceramics were fabricated by conventional ceramics process. High-purity α-Al_2O_3 (99.95 %) and graphite powders were used as starting materials. Specimens were fabricated by weighing the starting powders to achieve the C content of 1 at.% in the α-Al_2O_3 ceramic. The mixed powders were weighed to the desired composition, ball milled together with distilled water and ZrO_2 ball for 24 h. The milled slurry was dried at 150 °C. Disks with 25 mm in diameter and 10–20 mm in thickness were isostatically pressed at 200 MPa and sintered at 1700–1750 °C for 1–15 h in H_2 atmosphere.

Microstructures were observed with S-570 scanning electron microscope (RILI, Japan). The fluorescence spectra of the ceramics excited with 970 nm light detector (LD) were measured with a spectrofluorimeter (Fluorolog-3, Jobin Yvon Spex, France) at room temperature. The TL measurements were performed on RisØTL/OSL-DA-15 automatic reader (RisØ National Laboratory, Denmark) with an integrated $^{90}Sr/^{90}Y$ beta source. The LD was an Electron Tubes 9235QB photomultiplier tube. The measurement was taken from room temperature to 773 K at a heating rate of 2 K/s. The OSL measurement were carried out in continuous wave (CW)OSL mode at room temperature. The excitation light is a high –intensity blue light emitting diode(LED) cluster belonged with RisØTL/OSL-DA-15 automatic reader, and excitation wavelengh is 470±30 nm. The radiation dose is 10 Gy(radiation from $^{90}Sr\beta$).

3. Results and discussion

Figure 1 shows the microstructures of α-Al_2O_3 transparent ceramics and α-Al_2O_3:C ceramics. It reveals that the α-Al_2O_3 transparent ceramics almost have no pores and the grain boundaries are clearer than α-Al_2O_3:C ceramics, because the carbon has effect on ceramic sintering. The grain size of α-Al_2O_3 transparent ceramics is also a little larger than α-Al_2O_3:C ceramics.

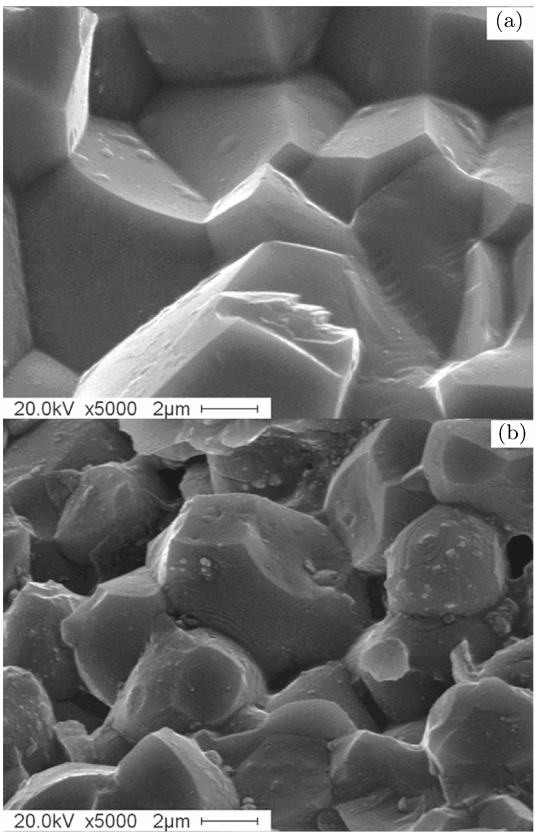


Fig. 1. The microstructures of α-Al_2O_3 transparent ceramics (a) and α-Al_2O_3:C ceramics (b).

Dosimetric properties of α-Al_2O_3:C can be considerably improved by generating oxygen vacancies into its structure. It was suggested that two-valent carbon ions replace the three-valent cations of Al, which leads to introduce oxygen vacancies during the crystals growth process.[10,12] Oxygen vacancies combine with one or two electron formed F or F^+ centres.

For the measurement of optical absorption spectra needs certain optical transmittance, our α-Al_2O_3:C ceramics have not enough transparency now, so we choose α-Al_2O_3 transparent ceramics instead of α-Al_2O_3:C ceramics. The α-Al_2O_3 has similar optical absorption spectra which are caused by F^+ centre and F^+ centre.[13,14] Figure 2 shows the optical absorption spectra of the α-Al_2O_3 transparent ceramics. The sample shows strong absorption band at 192 nm due to electron transition from the 1S level to the 1P level in the F centres,[15] and weaker absorption band at 225 to 250 nm due to electron transitions from the 1A to the 1B and 2A levels in the F^+ centres,[16] which

is similar to α-Al_2O_3:C crystal.[17] After doped with C, the content of F^+ centre and F^+ centre remarkably increased, so the peaks supposed to be clearer.

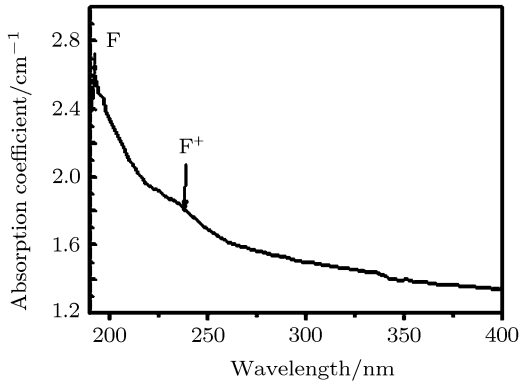


Fig. 2. The optical absorption spectra of the α-Al_2O_3 transparent ceramics.

Figure 3 shows the emission spectrum of α-Al_2O_3:C ceramics. The observed emission peak at 410nm in α-Al_2O_3:C is caused by recombination of an electron with F^+ centre to produce an excited F centre (F^*) which subsequently relaxes to ground state via emission of photon at 410–420 nm according to $F^+ + e^- \rightarrow F^* \rightarrow F + h\nu_{420\ nm}$. The α-Al_2O_3:C crystal has similar maximum emission peak at 420 nm.[10,12,18]

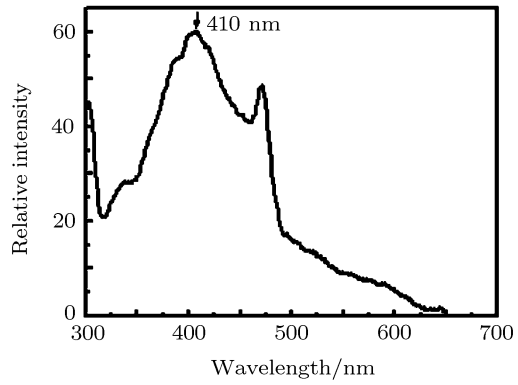


Fig. 3. The emission spectrum of α-Al_2O_3:C ceramics.

Figure 4 shows the excitation spectrum of α-Al_2O_3:C ceramics stimulated at 410 nm at room temperature. There exist three peaks at 300, 340 nm and 376 nm. We can suppose that the 300 nm luminescence peak corresponds to the 250 nm absorption peak. The luminescence peak has a little excursion. That is because the light-emitting ion from the excited state to the ground state transition exists non-radiative transition. The mechanism of production of the 340 and 376 nm is not clear, and further studies are still needed.

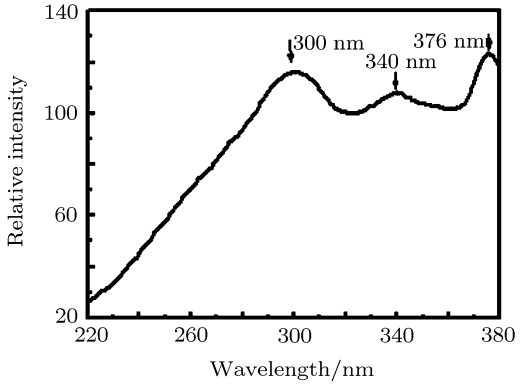


Fig. 4. The excitation spectrum of α-Al_2O_3:C ceramics.

Figure 5 shows the TL curves of α-Al_2O_3 transparent ceramics and α-Al_2O_3:C ceramics. The measurement was taken at the heating rate of 2 K/s in the temperature range of 298–773 K. The α-Al_2O_3 transparent ceramics show three TL glow peaks at 368, 456 and 614 K. The low temperature (368 K) TL peak is much higher than others. The 456 K peak is improved by generating oxygen vacancies which is similar to α-Al_2O_3:C crystal at 462 K.[10] The mechanism of production of the 368 and 614 K peaks is not clear, and further studies are still needed.

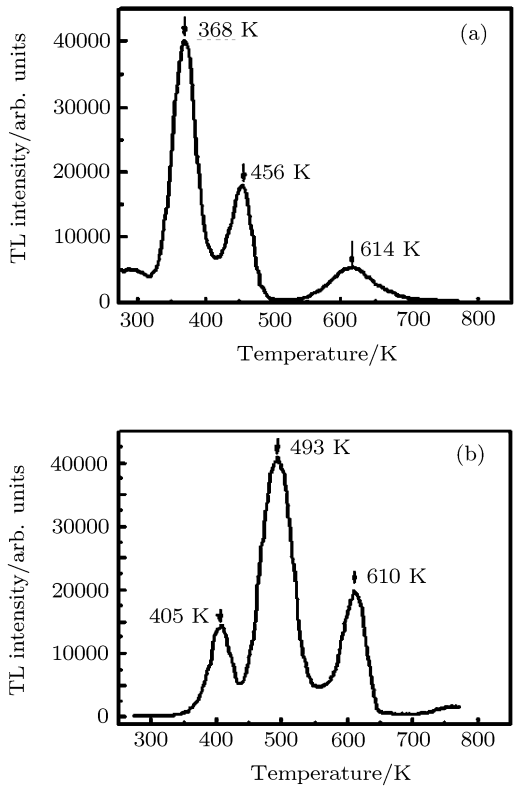


Fig. 5. The TL curve of α-Al_2O_3 transparent ceramics (a) and α-Al_2O_3:C ceramics (b).

The α-Al_2O_3:C ceramics also show three TL glow peaks at 405, 493 and 610 K, which are a little bigger than α-Al_2O_3 transparent ceramics, respectively. However, the sensitivity of 493 K TL glow peak is much higher than others, so we can suppose that the addition of carbon can infectively increase the concentration of oxygen vacancies in α-Al_2O_3 ceramics. The two-valent carbon ions replace the three-valent cations of Al, which lead to introduction oxygen vacancies during the ceramic produce process. The addition of carbon also leads to the TL peaks moving to higher temperatures.

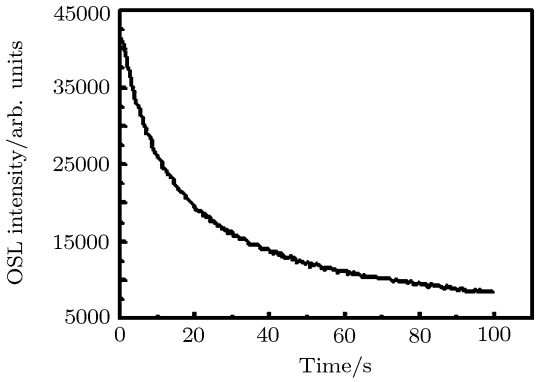


Fig. 6. The CW-OSL response of α-Al_2O_3:C ceramics.

Figure 6 shows the CW-OSL response of α-Al_2O_3:C ceramics. The OSL response could be fitted with two photoionization cross-sections for fast and slow decay components by using the following equation:

$$I_{\rm OSL} = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2), \qquad (1)$$

where $I_{\rm OSL}$ is the total intensity and I_1, I_2 are the initial intensities of exponentially decaying fast and slow components of OSL curve, respectively. The τ_1 and τ_2 are attenuation constant of exponentially decaying fast and slow components of OSL curve, respectively. Using the equation to simulate, we obtain $\tau_1 = 8.43$ s, $\tau_2 = 41.73$ s.

4. Conclusion

The α-Al_2O_3:C ceramics were fabricated by conventional ceramics process. Its excitation, emission spectra, TL and OSL were investigated. It has 410 nm maximum emission peak which is caused by recombination of an electron with F^+ centre to produce an excited F center. The samples show three clear TL glow peaks at 405, 493 and 610 K. The attenuation constant of exponentially decaying fast component(τ_1) and slow component(τ_2) of OSL curve are 8.43s and 41.73 s, respectively. All those fluorescence and TL characteristics are similar with α-Al_2O_3:C crystal which is widely used as a well TLD materials now. The TL intensity of ceramics is weaker than crystal at the same conditions, beacause ceramics are not transparent and α-Al_2O_3 polycrystalline ceramics belong to a trigonal system (usually described as a hexagonal structure with $a = b \neq c$) and is optically uniaxial and birefringent. But α-Al_2O_3:C ceramic powders can be counted as a potential TLD material instead of crystal, which has lower manufacturing cost.

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