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Intense green luminescence associated with two-fold coordinated Si in silica aerogel doped with Al³⁺

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Abstract. Amorphous silica aerogels doped with Al³⁺ ions (SADAs) were prepared by the sol-gel route and supercritical drying. The visible luminescence of SADAs was measured and compared with that of porous silicon (PS), pure silica aerogels (PSAs) and silica xerogels doped with Al³⁺ ions (SXDA). The effect of annealing on the luminescence intensity of SADAs was investigated. Results show that (1) the luminescent intensity of as-prepared SADAs is much higher than that of as-prepared PSAs and SXDAs after annealing at 300 °C; (2) after annealing at 500 °C, the visible luminescence of SADAs is further substantially enhanced and becomes much higher than that of PS. However, for PSAs and SXDAs after annealing at 500 °C the luminescent intensity is still kept at a very low value in comparison with that of SADAs. The strong visible luminescence appearing in SADAs is ascribed to significant amounts of the twofold coordinated Si (the Si(II)⁰ (neutral) centre) in SADAs.

1. Introduction

The large-scale flat display industry and various optical devices require continuous improvement of the luminescence efficiencies of optical materials. In recent years, many scientists have paid considerable attention to studying and preparing new materials for photoluminescence and electroluminescence with high luminescence efficiencies; especially, synthesis of strong blue- and green-light materials has become a very important project. Since the 1990s, porous Si and porous SiC have attracted much interest because they exhibit blue or green luminescence caused by the quantum confinement effect (QCE) under certain conditions [1–5], and thus they possess very important application prospects as novel optoelectronic materials. Some authors [6] observed that porous Si doped with Sm with SiO₂ layers presents green–yellow luminescence, but the luminescence intensity is very low. Some authors [7] found extraordinary optical properties of fullerene–porous matrix composites. Zhu *et al* [8] reported that visible light emission could be observed from fullerene doped silica aerogel. In the present paper, SiO₂ aerogels with a high porosity of about 60% containing Al³⁺ ions (SADAs) were prepared. The photoluminescence in the wavelength range of 400 to 800 nm was investigated and compared with that of pure

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amorphous SiO₂ aerogels (PSAs), amorphous SiO₂ xerogels doped with Al³⁺ (SXDA) and porous Si (PS). The origin of the strong photoluminescence of SADAs was discussed in detail.

2. Sample preparations and experiment

The amorphous SiO₂ aerogels with doping of Al³⁺ ions were synthesized by the following procedure.

2.1. Wet-gel preparation

Al(NO₃)₃ · 9H₂O was added to ethanol. After being stirred, a solution was formed. Then, tetraethoxysilane (TEOS) was added to this solution and stirred by a magnetic stirrer. After the TEOS had dissolved completely in the solution, a dilute aqueous solution of HNO₃ (0.01N) was added slowly. The molar ratio of the mixture is about SiO₂ : Al³⁺ : EtOH : H₂O = 1 : 0.1 : 5 : 8. After stirring for 30 minutes, a uniform sol was formed. This sol was transferred into test tubes and gelled within 3 days at 50 °C. As a result, transparent gels were obtained in tubes. Then, pure ethanol was added over the gels to exchange water in the pores of the network. After ageing in air at room temperature for 5 days, wet SiO₂ gels were supercritically dried.

2.2. Supercritical drying

Wet SiO₂ gels immersed in ethanol were supercritically dried by extraction with N₂. The supercritical drying process is as follows. The tubes containing wet SiO₂ gels, which were immersed in ethanol, were placed in a glass vessel of the autoclave. After that, the autoclave was closed, flushed by dry nitrogen gas for 10 minutes, and pressurized to 1.65 MPa to rarefy the oxygen concentration. The temperature was then slowly increased above the critical temperature (243 °C) and the critical pressure of ethanol (6.3 MPa) at a heating rate of 2 °C min⁻¹. When the temperature reaches a constant temperature (265 °C), the pressure was about 10.7 MPa. This pressure was maintained for 2 h. Then, the ethanol vapour was slowly released (from 10.7 MPa) until the atmospheric pressure was reached, which took about 4 h. Heating was continued for about 2 h while flushing with nitrogen in order to remove the remaining ethanol vapour. Afterwards, the heater was switched off and the autoclave was cooled to room temperature within 2 days. The as-prepared SiO₂ aerogels were obtained. Some of these specimens were heat treated at 500 and 600 °C for 4 h, respectively, followed by cooling in a furnace.

Pure SiO₂ aerogels were synthesized with the same method, but no Al(NO₃)₃ · 9H₂O was added.

SiO₂ xerogels doped with Al³⁺ were prepared by slowly drying the SiO₂ wet gels at 40 °C for 3 days. Then, they were heat treated at 300 and 500 °C for 4 h, respectively.

Porous Si was prepared as follows. An n-type Si(100) wafer was used as an initial material. PS samples were formed in anodization for 20 minutes with electrolytic solution 1 : 1 mixture of 44 wt% HF and ethanol at current density of 40 mA cm⁻². During the anodization, the wafer was illuminated with a 500 W lamp from a distance of 10 cm.

In order to investigate the strong photoluminescence mechanism of SADAs, aluminium silicate (AS) was synthesized by the following process. An Al₂(SO₄)₃ solution (0.05 M) and an Na₄SiO₄ solution (0.05 M) were mixed and stirred. Then, the precipitate of aluminium silicate was filtered and washed with distilled water three times. After the powder was dried

at 40 °C in air, the disc shaped sample 13 mm in diameter and about 1 mm in thickness was obtained by compacting the powder under an uniaxial pressure of 600 MPa. After that, samples were heat treated at 500 °C for 4 h.

The diameters of particles in aerogels and aluminium silicate were measured by means of a transmission electron microscope (JEM-200CX), operating at 200 kV. The sample preparation for TEM observation was as follows. The sample was pulverized in an agate mortar. The powder was immersed in ethanol and dispersed with ultrasonic vibration for 5 minutes, then floated onto a prefabricated carbon film sprayed on a Cu grid for TEM observation. From TEM photographs (see figure 1), the largest linear dimensions of particles were recorded. Then the average dimension of 100 particles was calculated in terms of the formula

$$d_{average} = \frac{1}{100} \sum n_i d_i.$$

Here, d_i is the dimension of the i th kind of particle and n_i is the number of particles with dimension d_i .

The porosities and the apertures of SADAs and PSAs were measured on a specific surface area and aperture analyser (type Omnisorp100CX).

Photoluminescence (PL) spectra were measured on a Hitachi 850-type visible-ultraviolet spectrophotometer with an Xe lamp as the excitation light source at ambient temperature. The excitation wavelength was 390 nm and a 430 nm filter was used. Infrared (IR) spectra were measured on a Vector-22 FT-IR.

3. Experimental results

3.1. Morphology microstructures and particle diameters

Figures 1(a)–(c) are the bright-field micrographs and electronic diffraction patterns of an SADA, a PSA and AS, respectively. Figures 1(a) and (b) indicate that the particles in SADAs and PSAs are isotropic in shape and their sizes are very small ($d_{average} = 5$ nm). Comparison of $d_{average}$ values of particles in SADAs (figure 1(a)) with that in AS (figure 1(c)) shows that the former are much less than the latter. In each diffraction pattern, only a dispersive and broad diffraction ring is observed. This means that all samples possess an amorphous structure.

The results obtained by means of the specific surface area and aperture analyser demonstrate that the porosity and the aperture in SADAs and PSAs are about 60% and 2–4 nm, respectively.

3.2. Photoluminescence

Photoluminescence spectra of an as-prepared SADA (curve 1), PSA (curve 2) and SXDA after annealing at 300 °C for 4 h (curve 3) are shown in figure 2. It is clear that a broad luminescence band for each sample appears in the wavelength range of 400 to 700 nm. The luminescence intensity of SADAs is much higher than that of PSAs and SXDAs. The peak positions of luminescence bands for SADAs and PSAs are 520 and about 470 nm, respectively.

Figure 3 displays photoluminescence spectra of an SADA, AS, an SXDA and a PSA after annealing at 500 °C for 4 h (curves 1–4) and PS (curve 5). The photoluminescence spectrum of SADAs exhibits two broad peaks, one at 530 nm (P_1) and the other at 560 nm (P_2). This demonstrates that heat treatments at 500 °C cause the luminescent peak positions

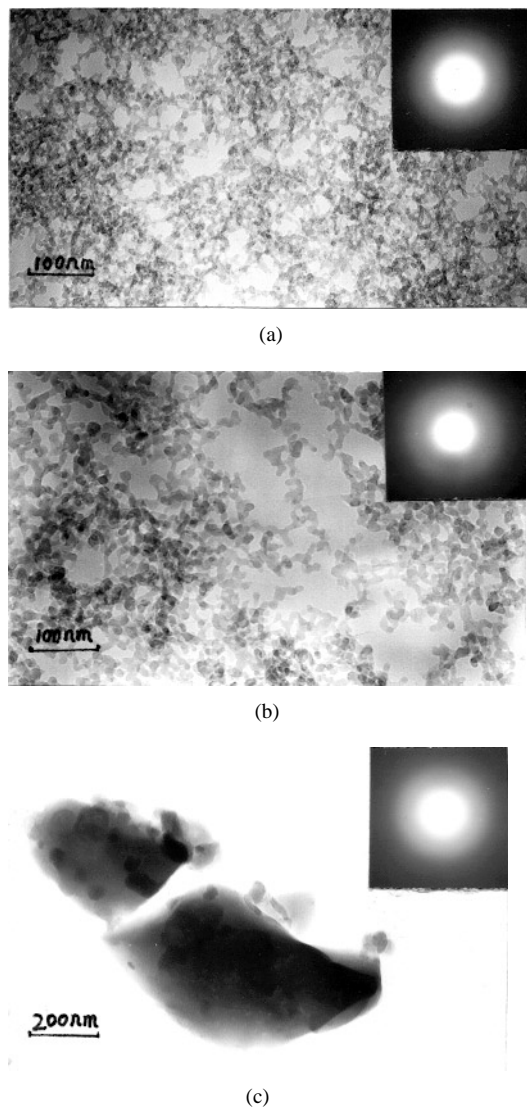


Figure 1. The bright-field micrographs and electronic diffraction patterns of an SADA (a), a PSA (b) and AS (c).

of SADAs to exhibit red shifts in comparison with that of as-prepared SADAs, and the luminescent intensities of P_1 and P_2 to become higher than that of PS (comparing curve 1 with curve 5) and about 40 times higher than that of PSAs (comparing curve 1 with curve 4) and 32 times higher than that of SXDAs (comparing curve 1 with curve 3). Curve 2 shows that aluminium silicate also presents a broad luminescence band in the wavelength range of 430 to 800 nm, whose distribution wavelength range is almost the same as that of SADAs.

The influence of the annealing temperature on luminescence spectra of SADAs is given in figure 4. Curves 1, 2 and 3 correspond to luminescence spectra of SADAs after annealing at room temperature (RT), 500 and 600 °C, respectively. It can be seen that with increasing the annealing temperature from RT to 500 °C, the intensity of the P_1 band increases rapidly.

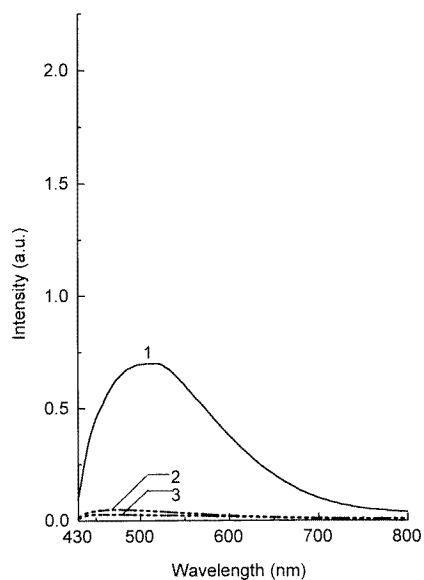


Figure 2. Visible photoluminescence spectra of an as-prepared SADA (curve 1), PSA (curve 2) and SXDA after annealing at 300 °C for 4 h (curve 3).

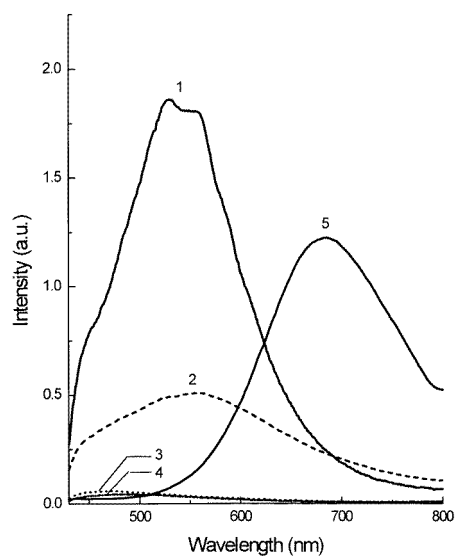


Figure 3. Visible photoluminescence spectra of an SADA (curve 1), AS (curve 2), an SXDA (curve 3), a PSA (curve 4) annealed at 500 °C for 4 h and PS (curve 5).

With further raising the annealing temperature from 500 to 600 °C, the intensity of the P₁ band becomes quite weak.

Figure 5 shows infrared (IR) spectra of an SADA, a PSA and AS. In the wavenumber range of 500 to 1500 cm⁻¹ four absorption bands exist (P₁–P₄) for PSAs and SADAs (curves a and b) and six bands for AS (curve c). For the IR spectrum of PSAs (curve a),

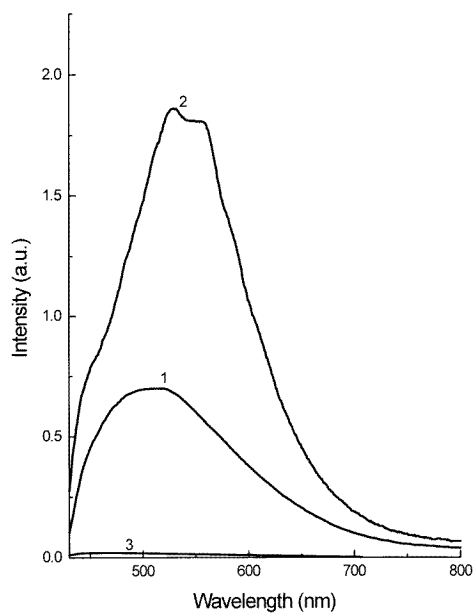


Figure 4. Effect of the annealing temperature on the luminescence of SADAs. Curves 1, 2 and 3 correspond to luminescence spectra of SADAs after annealing at room temperature (RT), 500 and 600 °C, respectively.

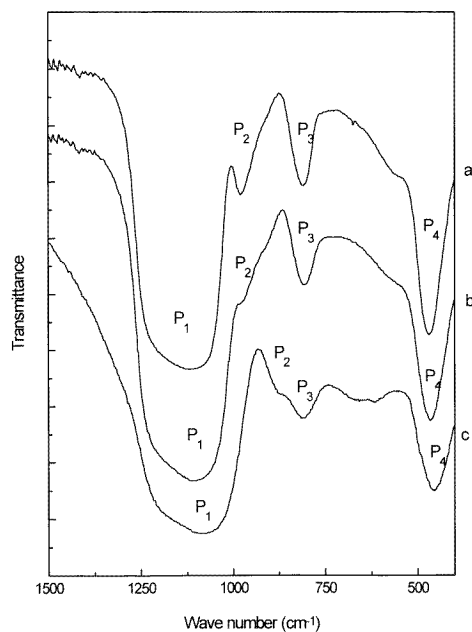


Figure 5. Infrared spectra of a PSA (curve a), an SADA (curve b) and AS (curve c).

bands (P_1 , P_3 , P_4) with peak positions of 1102, 804 and 468 cm^{-1} are caused by the stretching mode, asymmetric bending mode and symmetric bending mode of Si–O–Si,

respectively, and band P₂ with the peak position of 971 cm⁻¹ is attributed to the stretching vibration of the external Si–O group [9]. The IR spectrum of SADAs (curve b) is similar to that of PSAs (curve a), but all the absorption bands of SADAs move slightly to lower wavenumber (1097, ~962, 801 and 466 cm⁻¹) and band P₂ becomes weaker in comparison with that of PSAs. For AS, the peak positions of three strong bands (P₁, P₃ and P₄) (1089, 808 and 455 cm⁻¹) in curve c close to those of SADAs (1097, 801 and 466 cm⁻¹). Here P₁, P₃ and P₄ are related to vibration of Si–O–Si(Al) bands [10].

4. Discussion

4.1. Origin of visible photoluminescent band in SADAs

As we know, many scientists have investigated blue photoluminescence in oxygen-deficient a-SiO₂ [11–15]. They found that the blue luminescent band, which is located at 467–477 nm, is closely related to defects in a-SiO₂. Nishikawa *et al* [11] observed one blue luminescent band with a peak position of 477 nm in a-SiO₂ and indicated that this blue band was ascribed to oxygen vacancies. Many authors [12–14] also found one blue luminescent band with a peak position of 477–460 nm appearing in oxygen-deficient a-SiO₂ and Skuja *et al* [13] attributed this blue band to electronic transition of ³B₁ → ¹A₁ in a two-fold coordinated Si (an Si(II)⁰ (neutral) centre). ¹A₁ and ³B₁ are the ground state level and the triplet state level, respectively. El-Shall *et al* [15] observed a broad band in a-SiO₂, which is composed of two bands, one at 467 nm and the other at 422 nm. He considers that the blue emission band at 467 nm is induced by the Si(II)⁰ centre. From our experimental result (figure 3), it can be seen that the visible luminescent spectrum of SADAs after annealing at 500 °C is very similar to that reported by El-Shall *et al* [15], but the peak positions of P₁ and P₂ for SADAs exhibit quite obvious red shifts. From the similarity of the shapes of the spectra of SADAs after annealing at 500 °C and a-SiO₂ used by El-Shall *et al*, we can suppose that band P₂ at 560 nm of SADAs corresponds to the blue band at 467 nm in a-SiO₂ reported by El-Shall *et al*. The reason for the substantial red shifts of P₂ for SADAs is analysed as follows. Comparison of curve b with curve c in figure 5 indicates that three FTIR absorption bands of AS (P₁, P₃ and P₄), which are caused by vibration of Si–O–Si(Al) bonds, are similar to those of SADAs, and their peak positions are close to those of SADAs. At the same time, the luminescent bands of AS and SADAs are located in the same visible light range (figure 3). Therefore, it can be deduced that Si–O–Al bonds like those in AS exist in SADAs, which are mainly formed during supercritical drying. Namely, during supercritical drying, Al³⁺ ions capture oxygen only from the Al³⁺ doped silica gel, including the interiors of the SiO₂ particles and interfaces between SiO₂ particles, to form Si–O–Al bonds (aluminium silicate forms) because almost no oxygen is in the surrounding alcohol vapour of the Al³⁺ doped silica gel, resulting in an increase of the concentration of oxygen vacancies in SADAs. In addition, some of the oxygen escapes from the Al³⁺ doped silica gel to enter the surrounding alcohol vapour. This also induces oxygen vacancies in SADAs to increase. Therefore, an SADA possesses a very high concentration of oxygen vacancies. Philipp *et al* [16] observed that with increasing oxygen vacancies, the band gap of silica can change from ≥8.0 to 3–4 eV. The energy levels of the Si(II)⁰ centre are located in the band gap of silica. Therefore, with increasing oxygen vacancies, the decrease of the band gap of silica will induce the spacings of the energy levels of Si(II)⁰ to become narrow. As a result, the luminescent band, P₂, of SADAs, which arises from the electronic transition from ³B₁ to ¹A₁, moves to longer wavelength (red shifts). From figures 2 and 4, it can be observed that for as-prepared SADAs only one broad luminescent band with the

peak position at 520 nm occurs in the visible light range and its intensity is about half that of SADAs after annealing at 500 °C. The change from one peak for as-prepared SADAs to two peaks (P_1 and P_2) for SADAs after annealing at 500 °C can be explained as follows. For the former the peak positions of P_1 and P_2 are too close to be distinguished. However, for the latter the amounts of movement of P_1 and P_2 are different, so that the distance between them becomes large. Therefore, P_1 and P_2 are easy to distinguish. As mentioned above, the amounts of oxygen vacancies are lower in as-prepared SADAs than in SADAs after annealing at 500 °C. With decreasing oxygen vacancy concentration, P_1 descends. This suggests that P_1 is associated with oxygen vacancies.

4.2. Reasons for high intensity of visible luminescence in SADAs

Why is the intensity of visible luminescence for SADAs much higher than that for PSAs and SXDAs under as-prepared conditions? As mentioned above, large amounts of oxygen vacancies in as-received SADAs arise mainly from loss of oxygen induced by oxygen combining with Al^{3+} ions in the Al^{3+} doped silica gel during supercritical drying. The as-received pure silica aerogel (PSA) was synthesized by supercritical drying of the silica gel without Al^{3+} ions. Therefore, the amounts of oxygen vacancies are much less in PSAs than in SADAs under as-prepared conditions. The as-prepared SXDA is obtained by drying at 40 °C and then heating at 300 °C in air the Al^{3+} doped silica gel. Then, Al^{3+} ions easily capture oxygen from air to form Si–O–Al bonds in the gel. In other words, here the formation of Si–O–Al bonds almost does not exhaust any oxygen in the gel to form new oxygen vacancies; inversely, oxygen in air enters the gel to combine with oxygen vacancies to decrease the amounts of oxygen vacancies. Therefore, the numbers of oxygen vacancies are much less in SADAs. The $Si(II)^0$ centre arises from the existence of oxygen vacancies in oxygen-deficient a- SiO_2 [13]. El-Shall pointed out that the $Si(II)^0$ centre was present in significant amounts in oxygen-deficient silica. This proposal was also supported by data obtained with time-resolved photoluminescence in a- SiO_2 [12]. This suggests that with the elevation of oxygen vacancies, the concentration of the $Si(II)^0$ centre increases. According to the above analysis, it is clear that the amounts of the $Si(II)^0$ centres in SADAs are much higher than that in both PSAs and SXDAs. Many fewer $Si(II)^0$ centres in PSAs and SXDAs lead bands P_1 and P_2 in both samples to become much weaker than in SADAs. In addition, large amounts of aluminium silicate existing in SADAs also contribute to the enhancement of luminescence. Therefore, the visible luminescence intensity in SADAs is much stronger than that in PSAs and SXDAs.

4.3. Effect of annealing on intensity and luminescence peak position

Figure 4 indicates that with increasing the annealing temperature from room temperature to 500 °C, the luminescence intensity is substantially enhanced for SADAs. The luminescent intensity is about 40 times higher than that of PSAs and 32 times higher than that of SXDAs and the peak position of P_2 shifts from about 520 to 560 nm, as shown in figure 3. The high intensity of P_2 is ascribed to the following factors. For as-prepared SADAs the significant amounts of oxygen vacancies give rise to large lattice distortion in SADAs, resulting in large internal stress being established in SADAs. During annealing at 500 °C, this internal stress accelerates Si–O–Al bond (aluminium silicate) formation. When the formation rate of Si–O–Al bonds becomes bigger than that of oxygen diffusing into the SADAs, oxygen combined with Al^{3+} ions are mainly provided by the SADA itself. This causes the concentration of oxygen vacancies in the SADA to rise dramatically and hence the numbers of $Si(II)^0$

centres increase substantially. This makes P₂ become very strong. The elevation of oxygen vacancies also gives rise to enhancement of P₁. This is why annealing at 500 °C induces the visible luminescent intensity of SADAs to be further enhanced. However, for as-prepared SXDAs the concentration of oxygen vacancies is very low in comparison with that of SADAs. This implies that internal stress induced by lattice distortion is very low in SXDAs. This internal stress may be too low to accelerate formation of Si–O–Al bonds during annealing at 500 °C. At this time, the formation rate of Si–O–Al bonds probably becomes slower than the diffusion rate of oxygen diffusing into SXDAs. Then, oxygen combined with Al³⁺ ions arises mainly from air because enough oxygen diffuses into the SXDAs. In other words, annealing almost does not exhaust any oxygen in SXDAs, so that no more new oxygen vacancies are formed. This causes the amounts of the Si(II)⁰ centres to decrease and thus P₂ drops. Moreover, the smaller amounts of oxygen vacancies in SXDAs makes P₁ become weak. This is the reason for the very low luminescent intensity of SXDAs. For PSAs, during annealing at 500 °C, no Si–O–Al bonds are formed, so that the amounts of oxygen vacancies do not increase. Therefore, the luminescent intensity keeps a low value. Red shifts of the peak position of P₂ caused by annealing at 500 °C are due to the decrease of the energy spacings of Si(II)⁰ with the elevation of oxygen vacancies induced by annealing.

After annealing at 600 °C for 4 h, the luminescent intensity of SADAs becomes suddenly very weak (see figure 4). This phenomenon can be attributed to the following factor: on annealing at 600 °C, the annihilation rate of oxygen vacancies becomes faster than the formation rate of oxygen vacancies, so that only a few oxygen vacancies remain in SADAs. This leads to the luminescent intensity dropping dramatically.

5. Conclusion

(1) The luminescence intensity of amorphous silica aerogels doped with Al³⁺ ions (SADAs) without annealing is higher or much higher than that of as-prepared pure amorphous silica aerogels (PSAs) and amorphous silica xerogels containing Al³⁺ ions annealed at 300 °C for 4 h (SXDAs).

(2) Annealing at 500 °C for 4 h induces the visible luminescence of an SADA to be substantially enhanced, so that its luminescent intensity becomes much higher than that of PSAs, SXDAs and porous silicon (PS). After annealing at 600 °C for 4 h, the luminescence of SADAs becomes suddenly very weak.

(3) The very strong luminescence of SADAs arises mainly from formation of significant amounts of oxygen vacancies and hence the Si(II) centre associated with oxygen vacancies since Al³⁺ ions capture oxygen from SADAs to form Al–O–Si bonds (aluminium silicate).

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