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Journal Name

Reducing of Eu^{3+} Due to the Change of Topological Structure of BO$_3$ Unit in Borate Glass

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Adjusting and controlling ions chemical state has always been a focus of researchers attention. Herein, an intense long-lasting phosphorescence of Eu^{2+} is obtained without any sacrificial reductant. The remarkable self-reducing process and the unique luminescent properties stem from the variety of the topological structure of BO$_3$ triangle.

In order to obtain a functional material, methods to purposefully change the valence of ions have always been concerned.[1-5] Due to the pervasive oxygen in air, reducing an ion is always a challenge. Reductant such as H$_2$, CO or metal element, etc. should be presented. Therefore, much energy and cost are required to maintain the chemical reaction, and inevitably more energy and cost to preserve the environment and worker's safety. Recently, the self-reducing process of raw materials during preparation has received a great deal of attention. For example, in iron and steel smelting process a self-reducing pellet can be used to decrease the energy consumption in iron making.[6,7] Besides the smelting of metal, for many advanced functional materials self-reducing phenomena are also attractive. Rosen et al. invented a new ink which can enable the 3D printing of conductive objects utilizing a self-reducing copper precursor.[8] Annadhasan et al. reported an environmentally benign method of preparing gold nanoparticles using N-cholyl-l-valine as a self-reducing and stabilizing agent.[9] However, the reducing process of the ions due to the change of the host topological structure is less reported.

Optical and luminescent material, as a kind of important functional material, their characteristics are generally depending on the doped ions.[10-13] Lanthanide ions have been widely used as the doped ions. Due to the remarkable optical properties of the low valence lanthanide, many commercial and distinguished optical materials are activated by them, Y$_3$Al$_5$O$_{12}$:Ce^{3+}, BaMgAl$_{10}$O$_{17}$:Eu^{2+}, SrAl$_2$O$_4$:Eu^{2+}, Dy^{2+} and so on. Obtaining and stabilizing a low valence lanthanide ion in an oxide host, however, is a significant chemical process, such as the reducing of Eu^{3+} to Eu^{2+} and Ce^{4+} to Ce^{3+}. It is a common knowledge that reducing agent such as H$_2$ or CO is needed in preparing low valence lanthanide ion by high temperature solid-state reaction.

Interestingly, it is found that in some host materials, lanthanide ions can be reduced into its low valence spontaneously in air condition. Reduction of Sm^{3+}, Eu^{3+}, Tm^{3+}, Yb^{3+} and even radioactive transuranium elements Cf^{3+} ions to their divalent counterparts in air at high temperature has been reported.[14-23] Some necessary conditions for reducing trivalent rare earth in air have been proposed.[14, 24] However, it should be noted that these phenomena can only present in some certain crystal structure. In this paper, the reducing phenomenon is essentially different with the results mentioned above. First, a glass material is synthesized, not crystal, where only the BO$_3$ unit is observed. Second, the host crystal is SrAl$_2$O$_4$ in which Eu^{3+} cannot be adequately reduced into Eu^{2+} directly in air condition according to the existing researches. Third, along with the reducing of Eu^{3+}, a long-lasting phosphorescence is observed in the glass-ceramic.

Borate glasses have potential application superiorities in a broad range of areas, including laser, communication, biomaterials, electro-optic materials and so on. The preparation, characterization and structure of borate glasses and ceramics are always the key focus for researchers. In this study we present a Eu^{2+} and Dy^{3+} codoped SrO-Al$_2$O$_3$-B$_2$O$_3$ glass ceramic (named SABED), in which a precipitated crystalline phase of SrAl$_2$O$_4$ is appeared (experimental details can be found in the Supporting Information (SI)). Generally, if we desire divalent Eu^{2+} ions in SrAl$_2$O$_4$ matrix, reducing process is indispensable. Herein, significantly, the divalent Eu^{2+} ions are obtained without any reducing process.

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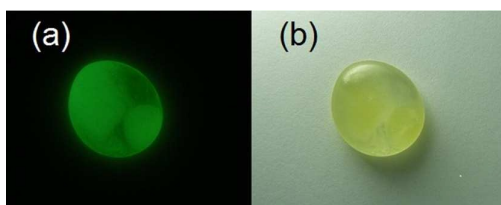
Fig. 1 (a) The photograph of SABED under standard lamp (D65); (b) the photograph of SABED when turn off the lamp.

Figure 1a shows the photograph of SABED under a standard lamp. Superficially, the sample SABED is separated into two phases: a colorless transparent phase and a yellow-green opaque phase. When turn off the lamp, a bright yellow-green light appears (The emission spectrum is shown in Figure 4). This persistent luminescence is called long-lasting phosphorescence (LLP, the emission mechanism and applications about the LLP materials are given in Supporting Information).[25] The colorless transparent part of the sample cannot show any LLP. These phenomena give the first impression that a Eu^{2+} doped $SrAl_2O_4$ crystal is synthesized.

The XRD of SABED is measured after grinding it into powder. Figure 2 shows the XRD pattern. A diffuse peak located around 30° is observed, which is originated from the glass phase. As expected, the needle like diffraction peaks in the pattern is in good agreement with the PDF card, No. 74-0794 for $SrAl_2O_4$.

$SrAl_2O_4$: Eu^{2+}, Dy^{3+} is a famous commercial LLP material. The luminescent properties of it are familiar for many optical and luminescence material researchers. Figure 3 shows the photoluminescence (PL) emission spectrum of SABED under 365 nm excitation (the emission spectrum under 254 nm excitation is shown in Figure S2). An intensive band emission peaked at 515 nm is observed, which can be ascribed to the characteristic emission of Eu^{2+} due to the $4f^65d-4f^7(^8S_{7/2})$ transition. The quantum yield of the 515 nm emission is about 30%. Because the sample is grinded into powder, the spectrum behaves in a mixed emissions consisting of the line-emission of Eu^{3+} and Dy^{3+}. The PL excitation spectrum of SABED is shown in Figure S3. Actually, the emission of Eu^{3+} and Dy^{3+} is originated from the transparent glass phase of the sample. Figure 4 shows the LLP emission spectrum of SABED measured after the irradiation by 254 nm light for 5 min. Only the emission of Eu^{2+}

appears (the photo of the LLP emission is shown in Figure 1a). Insert of Figure 4 shows the time decay curve of LLP intensity (details can be found in supporting information). The persistent emission can be seen by naked eye even after 24 hours after excitation. The excellent LLP property is the best evidence for the existence of Eu^{2+}. Hence, what shocks us is that the Eu^{3+} is reduced into Eu^{2+} in SABED both and the LLP emission, in view of the air atmosphere as the reaction condition.

Four necessary conditions for reducing trivalent rare earth in air have been proposed.[14, 24] One of them is that the host compounds should have rigid three-dimensional tetrahedral topological structure, such as BO_4, SiO_4 or AlO_4. In SABED, the crystal phase of $SrAl_2O_4$ adopts a stuffed tridymite monoclinic structure with space group of P21.[26] The AlO_4 tetrahedra can connected to form a 3-D framework.[27] On account of the 3-D framework of $SrAl_2O_4$, Eu^{2+} ions can be effectively isolated and shielded from the oxidizing atmosphere (the crystal structure is shown in Figure S4). Therefore, the particular structure clarify the stabilization of Eu^{2+} ions in SABED in one aspect, but it still cannot explain how the raw material of Eu^{3+} is reducing into Eu^{2+}, because the bright Eu^{2+} and LLP emission will not obtained in $SrAl_2O_4$ crystal without reducing agent, in spite of the weak reducing atmosphere in chamber electric furnace at high temperature.

Considering at the structure and composition of SABED, we deduce that the existence of boron is a major cause of the reducing of Eu^{3+} in SABED. It is reported that the topological structure of B-O group in host will strongly affect the chemical valence of the doped ions. In the host lattice where B-O coordination polyhedron are triangle, for example in $BaLnB_9O_{16}$: Eu (Ln = La, Gd, Y), $M_3La_2(BO_3)_4$: Eu (M = Ca, Sr, Ba), the reduction of Eu^{3+} cannot be completely realized, or Eu^{2+} is unacquirable even if the preparation is performed in a strong reducing.[17] Machida et al found that the Eu^{2+} ions in the crystalline BaB_8O_{13} host lattice will be oxidized into Eu^{3+} ion in the vitreous form if melting BaB_8O_{13}, in which only the BO_3 units are observed.[18] The latest research indicates that the Eu^{2+}/Eu^{3+} equilibrium in borate glasses is strongly associated with the topological structure and component of B-O groups.[28]
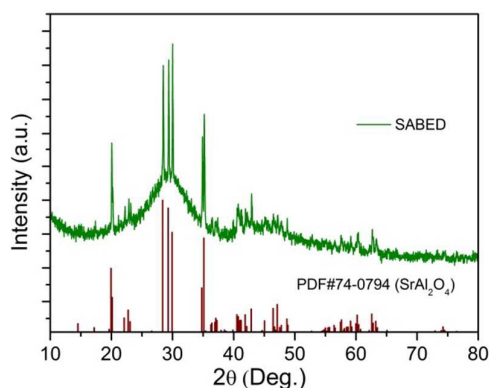

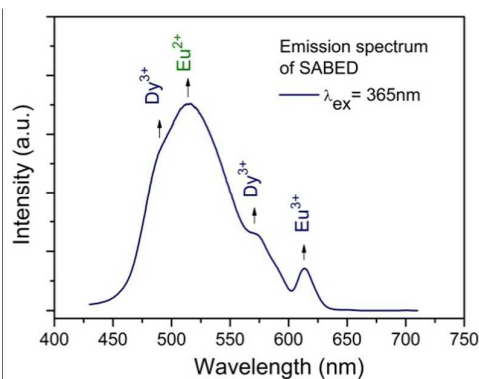**Fig. 2** X-ray diffraction pattern of SABED.

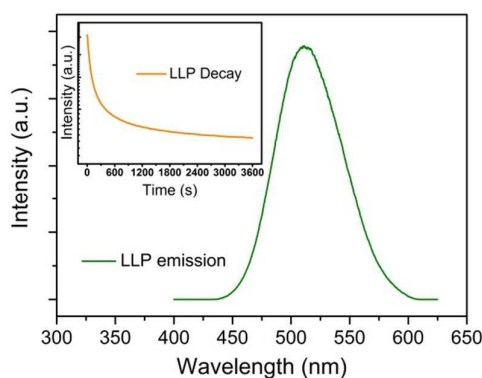**Fig. 3** PL emission spectrum of SBAED excited by 365 nm.

Fig. 4 LLP emission spectrums of SABED measured after the irradiation by 254 nm light for 5 min. Insert: decay curve of the phosphorescence of SABED measured after the irradiation by 254 nm light for 5 min.

Figure 5 is the FTIR spectrum of SABED. Both the patterns of Al-O and B-O units are demonstrated. The band at 419 cm^{-1} and 448 cm^{-1} and the band at 648 cm^{-1} are due to the O-Al-O symmetric and antisymmetric bending vibrations, respectively. Antisymmetric stretching of AlO_4 appears in the region 780 – 850 cm^{-1}.[29] Comparatively, we care more about the IR absorption patterns of the B-O groups. The structure of B-O unit may have two spatial configurations, trigonal $[BO_3]$ and tetrahedral $[BO_4]$. As shown in Figure 5, The absorption band originated from B-O symmetric stretching of trigonal $[BO_3]$ units in the 1100-1500 cm^{-1} range is obvious.[30, 31] Moreover, the characteristic absorption bands of B-O stretching of $[BO_4]$ units in the 850-1100 cm^{-1} region are absent in the spectrum.[30] Therefore, we deduce that in the glass phase of SABED the B-O groups tend to form $[BO_3]$ units rather than $[BO_4]$ units. This finding is contradictory to the results mentioned above that $[BO_4]$ unit is needed to reduce Eu^{3+}.

In preparing the sample SABED, the starting material is vitreous B_2O_3. It is clear that a mixture of simple BO_3 triangles and hexagonal boroxol B_3O_6 rings compose the microscopic structure of vitreous B_2O_3 (Scheme 1), in which the boroxol ring is predominant.[32, 33] When increasing the temperature in melting, the boroxol ring concentration is decreased and the BO_3 triangle is developed in a random network.[34, 35] Namely,
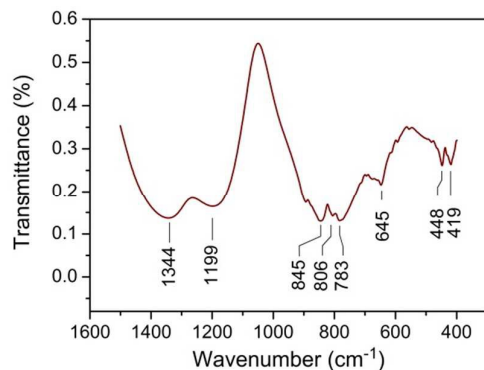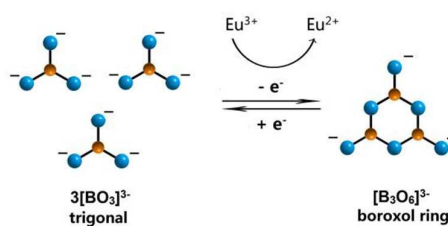

Figure 5 Fourier transform infrared spectrum of SABED measured by using a Bruker IFS66 v/s vacuum-type spectrometer with KBr pellet technique.

Scheme 1. Sketch of the topological structure changing between 3$[BO_3]^{3-}$ trigonal units (left) and $[B_3O_6]^{3-}$ boroxol ring (right).

the bridging B-O-B bond is broken, while terminal (B-O-) bond is formed. When cooling the liquid, B_3O_6 rings are reshaped. It is possible that the extra negative charge due to the change of the topological structure of BO_3 unit results in the reducing of Eu^{3+} to Eu^{2+} (Scheme 1). Similar reducing process is reported in Bi doped borate glass matrix (BO), in which the B_3O_6 and AlO_4 topological structure is observed. The chemical state of Bi can be reduced from +2 to +1 and 0, because Bi ion can extract trapped electrons from dangling bonds, over-coordinated atoms or 'wrong bonds'.[36] The reducing process may also be analogous to the reducing of Eu^{3+} in the crystallization process of BaB_8O_{13}.[18] When the terminal oxygens denoted as O⁻ in the BO_3 units are connected to one another to form BO_4 units in the crystallization process of BaB_8O_{13} host lattice, the Eu^{3+} ions were reduced by evolving the free oxygens.[18]

Along with the reducing of Eu^{3+}, $SrAl_2O_4$ crystal is precipitated. Hence, Eu^{2+} is stabilized by the $SrAl_2O_4$ matrix, resulting in the bright green emission and the distinguished LLP emission (more details can be found in supporting information). The remained Eu^{3+} is stay in B-O vitreous, giving the red emission of the transparent glass phase. Similar phenomenon is also found in Ce^{4+} doped borate glass, where the reducing of Ce^{4+} to Ce^{3+} is remarkably increased with an increase of melting temperature.[18] It is proposed that the reducing process is due to the dissolved Al^{3+} from Al_2O_3 crucible. However, we speculate that the change of the topological structure of B-O unit should also be taken into consideration. Therefore, more and advanced measurements are still needed to deeply investigate the structure change of vitreous (Raman spectroscopy, electron spin resonance, nuclear magnetic resonance, for example), which are worthy of our further concern.

In summary, a Eu^{2+} doped $SrAl_2O_4$ crystal is precipitated in boro-aluminate glass-ceramic without any reducing agent. Due to the rearrangement of connection model of B-O structure unit and the stabilization of the AlO_4 channel, the Eu^{3+} ion is reduced into Eu^{2+} ion. These findings are not only beneficial for synthesizing low valent lanthanide ions doped optical materials, but also the results give a valuable insight of the microstructure of B-O vitreous from the view of luminescence.

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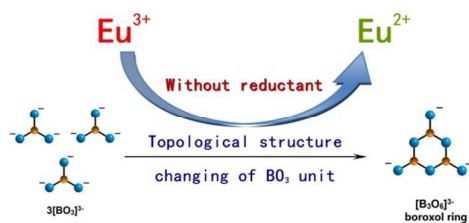
A reducing of Eu^{3+} into Eu^{2+} is observed in borate glass matrix prepared in air condition without any reductant. A bright green long-lasting phosphorescence of Eu^{2+} indicates the existence of Eu^{2+}. The remarkable reducing process is due to the changing of the topological structure of BO_3 triangle.