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Contribution of Eu ions on the precipitation of silver nanoparticles in Ag-Eu co-doped borate glasses

Qing Jiao [a], Jianbei Qiu [a,b,*], Dacheng Zhou [a], Xuhui Xu [a]

[a] School of Materials Science and Engineering, Kunming University of Science and Technology, 253 Xuefu Road, Kunming 650093, China
[b] Key Laboratory of Advanced Materials of Yunnan Province, 304 Xuefu Road, Kunming 650093, China

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ABSTRACT

Ag^+ doped sodium borate glasses with different Eu ions concentration were prepared by the melt-quenching method. The absorption at about 410 nm which was caused by the surface plasmon resonance (SPR) of Ag nanoparticles (NPs) is promoted with increasing of Eu ions concentration. Meanwhile, the luminescent spectra showed that the emission intensity of Ag^+ decreased while that of the Ag aggregates increased simultaneously. The results indicated that the Ag ions intend to form the high-polymeric state such as Ag aggregates and nanoparticles with increasing of europium ions. Owing to the self-reduction of Eu^{3+} to Eu^{2+} in our glass system, it revealed that Ag^+ has been reduced by the neighboring Eu^{2+} which leads to the formation of Ag aggregates and the precipitation of Ag NPs in the matrix. In addition, energy transfer (ET) process from Ag^+/Ag aggregates to the Eu^{3+} was investigated for the enhancement of Eu^{3+} luminescence.

1. Introduction

Rare earth ions doped luminescent materials have been concerned for recent decades due to their prospective utilization in photonic fields and nanotech areas [1–8]. Owing to the parity forbidden character of 4*f*–4*f* transition, they cannot be efficiently excited by ultraviolet or visible light. As a valuable approach, Ag particles are widely used to improve their luminescence by co-doing with rare earth ions (REI) [9–12]. It is first reported that the enhancement of Eu^{3+} ions emission was observed by Malta et al., demonstrating the famous local-field enhancement (LFE) effect induced by SPR of Ag NPs [13]. Subsequently, many researchers investigated the LFE effect on the luminescence of REI such as Eu^{3+}, Pr^{3+} and Er^{3+} [14–17]. However, several theoretical views are trying to explain the influence of the metallic particles on the emission rates of the REI [15,16,18], which unfortunately being a controversial problem until the time.

In order to clarity the influence of Ag particles on the REI luminescence, it is necessary to definite the origin and constitution of Ag particles in glasses. It is reported that Anne Simo explained the formation mechanism of silver nanoparticles stabilized in the glass matrices [19]. At first, the glass contains predominantly silver ions and then the relevant Ag clusters like silver dimers ($d < 1$ nm) forms during the annealing process. With temperature further increased, the clusters as nuclei grow to the final nanoparticles via a monomer (silver atom) addition. Owing to the presence of other Ag species, many reports ascribed the REI enhancement effect to the energy transfer from the intermediate Ag species such as small Ag aggregates (or called Ag clusters, molecule-like Ag) or isolated Ag^+ to REI, and rarely involved to the effect of SPR or Ag NPs [20–22]. Therefore, the investigations of the interaction mechanism between REI and Ag NPs or Ag aggregates are required. However, given the difficulties in controlling the selective fabrication of different Ag species, it is hard to distinguish which kind of the Ag particles do impress on the emission centers.

Recently, Hu et al. observed the increasing of Eu ions concentration suppressed the formation of silver aggregates in γ-ray irradiated glasses [23], which provides another way to investigate the interplay between the metal particles and REI. It is interested that, in our recent work, self-reduction from Eu^{3+} to Eu^{2+} can be controlled by their ligand structure in sodium borate glasses [24]. Therefore, it is reasonable to believe that different Ag species would be regulated in Ag-Eu^{3+} co-doped such glasses with no need of any heat-treatment or γ-ray irradiation. In this work, compared with Hu's report, the contribution effect of europium ions on the precipitation of Ag NPs is demonstrated which is little reported in other literatures. Meanwhile, the luminescence of Ag aggregates is also encouraged by the increase of Eu ions contents which is

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[*] Corresponding author at: School of Materials Science and Engineering, Kunming University of Science and Technology, 253 Xuefu Road, Kunming 650093, China. Tel.: +86 0871 5188856; fax: +86 0871 65188856.
E-mail address: qiu@kmust.edu.cn (J. Qiu).

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opposed to the results of above research. Also, the relevant interaction mechanism between Ag species and RE ions is proposed.

2. Experimental

2.1. Materials and synthesis

Ag and RE ions co-doped glasses were prepared by melt-quenching method with composition of $65B_2O_3$-$27Na_2O$-$8Al_2O_3$-$0.5Ag_2O$-xEu_2O_3 ($x = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5$) (mol%). High purity B_2O_3, Na_2CO_3, Al_2O_3, Ag_2O and Eu_2O_3 were used as raw materials. For comparison, Ag_2O (0.5 mol%), Eu_2O_3 (0.4 mol%) single doped glasses and the glass host were also prepared. First, raw chemicals used were homogeneously mixed and melted at 1300 °C in an alumina crucible for 30 min. Then the glass melt were quenched in a preheated stainless steel mold to form glasses. Finally, samples with thickness about 2 mm were cut and polished for optical experiments.

2.2. Characterization

The optical absorption spectra of samples were measured by HITACHI U-4100 ultraviolet–visible (UV–vis) spectrophotometer. The photoluminescence and excitation spectra for glass samples were recorded on a HITACHI F-7000 fluorescence spectrophotometer using a static 150 W Xe lamp as the excitation source. Size and structural identification of silver nanoparticles were performed by transmission electron microscopy (TEM 2100JEOL) with an acceleration voltage of 200 kV. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Optical absorption and TEM analysis

As mentioned in Ref. [24], it is suggested that the existence of Eu^{2+} ions may play an important role in the formation of different Ag types. The relationship between Eu ions and Ag particles, therefore, needs to be studied more intensively. As mentioned above, a spontaneous reduction phenomenon of Eu^{3+} to Eu^{2+} was demonstrated in the sodium borate glasses under air condition [24]. We hope this result will help us to find out the facts of interaction between REI and the generation of Ag species. In the present work, the influence of Eu ions concentration on the Ag species was studied firstly. Fig. 1 shows the absorption spectra of the Eu-Ag co-doped glasses dependent of Eu ions concentration. It is obvious that the absorption band of Ag NPs appeared at wavelength of about 410 nm when 0.5 mol% Ag_2O is fixed in the above samples, and notably, the absorption intensity is increased by addition of Eu ions in the matrix. While in other reports, Ag NPs cannot be precipitated unless glass samples are annealed under high temperature or external electron filed [25,26]. The results indicated that the precipitation of Ag NPs could be promoted by the Eu^{2+} ions in glass with no need of any heat treatment process.

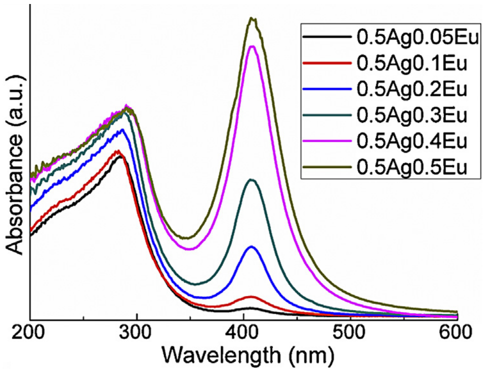

Fig. 1. Optical absorption spectra of Ag/Eu co-doped borate glasses dependent of Eu ions concentration.

As can be seen in Fig. 2(a), the precipitated silver nanoparticles are observed in 0.5 mol% Eu/Ag co-doped glass by TEM measurements. The nearly spherical Ag NPs are randomly distributed in the glass matrix with size of about 4–6 nm diameters. By the high resolution TEM technology in Fig. 2(b), the crystal lattice can be clearly observed in different arrangements, and the cubic structure of silver single crystal pattern is indicated by the electron diffraction picture in the inset.

3.2. Luminescence properties

For the doubt of the increased Ag NPs in glasses, fluorescence spectra of the samples are necessary to be investigated. In Fig. 3(a), the excitation spectra of 0.5 mol% Eu single doped and 0.5 mol% Eu

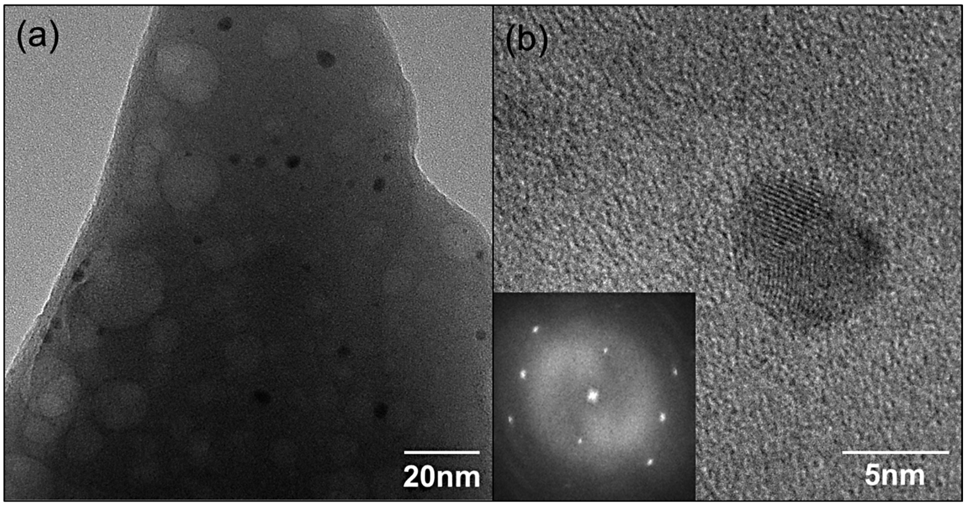

Fig. 2. (a) Typical transmission electron micrographs of the 0.5 mol% Eu/Ag co-doped sample. (b) The HRTEM image of a single Ag nanoparticle and the inset of the selected area electron diffraction pattern (SAED) of the borate glass containing silver NPs.