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Transparency, photoluminescence and X-ray luminescence study of Eu³⁺ doped mayenite glass

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ABSTRACT

Novel Eu³⁺ doped mayenite glass phosphors with Eu element homogeneously doped and high transparency were successfully synthesized by aerodynamic levitation method. The transmittance reached as high as 88% from the visible light up to 6 μm in the mid-infrared wavelength. Under the excitation of 254 nm (charge transfer), 393 nm (Eu³⁺, $^7F_0 \rightarrow {}^5L_6$ transition) and 464 nm (Eu³⁺, $^7F_0 \rightarrow {}^5D_2$ transition), glass phosphors emitted strong red luminescence with 615 nm ($^5D_0 \rightarrow {}^7F_2$ transition) predominant in the emission spectra. Differences of decay lifetime in excitation wavelengths and Eu dopant concentrations could be ascribed to the non-radiation relaxation process and luminescent concentration before the quenching effect. Furthermore, Eu doped mayenite glass could also emit red light at 615 nm ($^5D_0 \rightarrow {}^7F_2$ transition) under the X-ray excitation. Therefore, the high transparent C12A7: Eu glass phosphors could be promising candidates for solid state lighting, X-ray radiation detection, and even transparent displaying in the visible and mid-infrared ranges.

1. Introduction

Rare-earth (RE) doped photonic glasses have played a crucial role in applications of optical communication, solid-state laser medium, infrared detection, and biomedical imaging [1–4]. Unfortunately, the widely used silica based photonic glasses suffered from problems with limited low solubility, great difference of melt density and melting temperature with rare-earth ions. The incorporated ions would be segregated from glass easily, causing serious damage to the optical transparency as photonic glasses [5–8]. Therefore, it was still challenging to develop novel photonic glasses with rare earth ions homogeneously doped and high transparency maintained to meet the needs of wavelength bands near the mid-infrared area. Recently, alumina photonic glasses have aroused great interest for good solubility of active dopants with wide transparency range up to 6 μm [5,9,10].

The compound of $12CaO \cdot 7Al_2O_3$ (C12A7, mayenite) was a member of alumina family. C12A7 single crystals and ceramics had been successfully converted from electrical-insulator into a conductor [11–15] and even superconductor at ~2.4 K by partly/fully extraction of electrons from free oxygen ions accommodated in its charged 3D connected sub-nanometer-sized cages. C12A7 films loaded on ruthenium electrode was even reported as a reversible hydrogen-storage catalyst [16,17] that had shifted the bottleneck for ammonia synthesis. The excellent properties in electricity and catalysis of C12A7 could be attributed to its additional "cage conduction band" (CCB) in the fundamental band gap of C12A7 band structure [18,19], which might supply a unique glass host for photo-optics and photoluminescence. However, rare earth doped C12A7 photonic glasses had not yet been fully developed for difficulties in the glass synthesis without additives of alkali metal oxide or SiO_2 or heavy-metal oxides by conventional glass-making technology.

Aerodynamic levitation (ADL) was a newly developed technology for the exploration of amorphous materials with melts solidified at a levitated state. Deep under-cooled melts could be easily retained without heterogeneous nucleation or crystallization for the free-contact with container walls. With melts under-cooled and convection stabilized, ADL technology had obtained great success in vitrifying some binary systems which was almost impossible by conventional technology, such as La_2O_5-based [20,21], TiO_2-based [22] and Nb_2O_5-based [23,24] glasses.

In this work, the ADL technique was innovatively proposed to prepare Eu³⁺ doped C12A7 photonic glass. The optical

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transparency, photoluminescence and X-ray luminescence were studied. Furthermore, the luminescence mechanism was discussed by luminescent decay kinetics study.

2. Experimental

2.1. Preparation

A series of C12A7:xEu (x=0–0.6) glass samples were prepared by aerodynamic levitation method. The starting chemicals included carbonica calcarea ($CaCO_3 \cdot 8H_2O$, 99.99%), aluminum oxide (Al_2O_3, 99.99%) and europium oxide (Eu_2O_3, 99.99%). Powder was uniformly mixed, pressed into slices, and sintered at 1000 °C for 3 h in a muffle furnace. Slices were then melted and solidified at a levitated state within an aerodynamic furnace (ADF). A 100 W CO_2 laser device was used as heating source and pure oxygen gas was employed as the levitation force. Samples were melt at 1450 °C (measured by a IR thermal-pyrometer over the top of ADF) within 10 s, held stable for 20 s, and cooled down to room temperature in about 5 s by shutting down of the laser output. Samples finally got into a nearly-perfect sphere shape due to the effect of melt surface extension, and the average scale of transparent spheres as-prepared was about 6 mm in diameter.

2.2. Characterization

Transparent sphere samples were grinded into powder for X-ray diffraction (XRD) diffractometer (Bruker D8 ADVANCE, with Cu-Kα X-ray radiation wavelength of 1.5406 Å), and well polished with 2 mm in thickness on both side for the scanning electron microscope (SEM) characterization on a Hitachi S-3400 field emission instrument. Optical transparency were collected from the visible light zone to the mid-infrared zone by a double beam spectrophotometer (Carry 5000) and a Bruker VERTEX 70 instrument, respectively. The photoluminescence spectra and decay curve were performed on a FLS-980 fluorescence spectrophotometer equipped with a uf2 lifetime detector. The X-ray excited luminescence spectra were measured with X-rays generated voltage and currency at 40 kV and 40 μA, respectively. All measurements were performed at room temperature.

3. Results and discussions

Fig. 1a shows the typical XRD patterns of the prepared C12A7 with/without Eu^{3+} doped samples. There was an identical weak and broad diffraction band between 20 and 40° (2θ) and no sharp diffraction peaks were observed, demonstrating that the C12A7 samples with/without Eu^{3+} doped were glass phases. Fig.1b is a FE-SEM micrograph (typically, x=0.6 was selected), which shows the microstructure of C12A7:0.6Eu glass with EDS inserted. No obvious grains, second phases or residual pores were observed in the scale of hundreds of nano-meters, thus a high transparency of Eu ions doped glass could be expected. It could also be further inferred that Eu ions were homogeneously separated by the framework of AlO_4 tetrahedron (typical network former in aluminum glass) in the C12A7 glass matrix.

Fig. 2 shows transmittance spectra of the C12A7:Eu glass in the visible wavelength region (Fig. 2a) and mid-infrared region (Fig. 2b) with 2 mm in thickness. The glass was highly transparent as seen in the inserted Fig. 2a. The transmittance steeply increased up to ~80% at the end of the ultraviolet (UV) range, increased to 88% afterwards, and finally got cut-off up to 6 μm in the mid-infrared region (Fig. 2b). Compared with C12A7 glass, the transmittance of Eu doped glass was nearly the same except several sharp bands at 393 nm, 464 nm, 530 nm and a broad band at 2–3 μm which can be attributed to the light absorption of Eu^{3+} ions. Transparency in the mid-infrared region gradually deceased due to noegligible light scattering as the incident wavelength increased according to Saghir and Chenu [25]. This high transparency of C12A7:Eu glass allowed for promising detection and transparent displaying in the visible and mid-infrared ranges.

Fig. 3a shows the excitation spectra for various concentrations of Eu-doped C12A7 glass monitored at 615 nm emission ($^7F_2 \rightarrow {}^5D_0$ transition of Eu^{3+} ions). The excitation spectrum showed various sharp peaks between 350 and 600 nm, which were attributed to the excitations from the ground $^7F_0$ state to the excited upper state, such as $^5D_{0,1,2,4}$, $^5L_6$ and $^5H_4$. The broad band extending from 230 to 350 nm was assigned to the well-known O^{2-}–Eu^{3+} charge transfer (CT, $2p(O^{2-}) \rightarrow 4f(Eu^{3+})$) band [26–28]. The CT band slightly red shifted with the increase of Eu^{3+} concentration in the C12A7 glass, which implied the increases of the nephelauxetic effect of Eu–O bond in glass host and the decreases of energy required to remove an electron from the ligand O^{2-} to Eu^{3+}.

Fig. 3b, c and d shows the emission spectra of the C12A7: xEu^{3+} glass phosphors under 254 nm (CT band), 393 nm ($^7F_0 \rightarrow {}^5L_6$) and 464 nm ($^7F_0 \rightarrow {}^5D_2$) excitations, respectively. It was shown
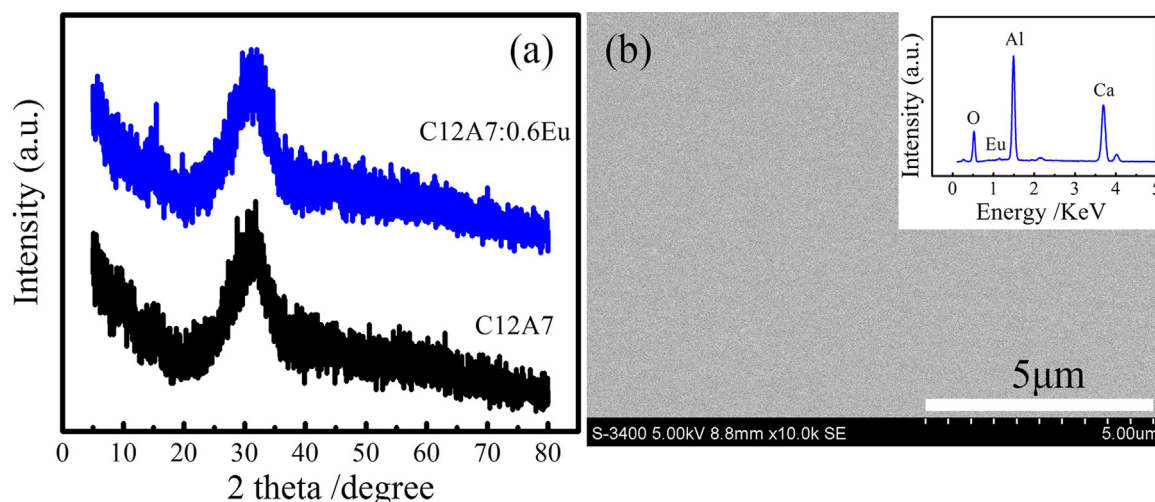

Fig. 1. (a) XRD patterns of C12A7 and C12A7:0.6 sample; (b) FE-SEM micrograph of C12A7:0.6 sample with EDS spectrum inserted.