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Investigation on crystallization kinetics and luminescent properties of Eu^{2+}/Eu^{3+}-coactivated hexacelsian based glass ceramics

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ABSTRACT

The thermal properties and crystallization behavior of $MgO-BaO-SiO_2-B_2O_3-Al_2O_3$ glass have been investigated by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). After crystallization at temperature (800 °C) close to the DSC crystallization peak, dendritic hexacelsian crystals are found to form as the major crystalline phase among glass. The crystallization kinetics was studied by analyzing DSC curves with Chen's and Ozawa's equations. The mean crystallization activation energy and Avrami's parameter are evaluated to be 229 kJ/mol and 1.4, indicating that the crystallization process occurs predominantly by surface crystallization as consistent with experimental data. Concurrent emissions of Eu^{2+} and Eu^{3+} under 304 nm excitation demonstrate that partial reduction of Eu^{3+} to Eu^{2+} occurs, which could be ascribed to the partition of Eu^{3+} into the precipitated hexacelsian crystals during the sintering process of glass ceramics. These results indicate that glass ceramic route may serve as an intriguing way for synthesis of phosphors applicable to lighting and display fields.

1. Introduction

Among the rare earth (RE) species, europium has found applications as an attractive activator in modern lighting and display fields. For instance, trivalent europium ions exhibit parity-forbidden 4f–4f transitions, which yield narrow band emissions independent of ligand field strength. The characteristic dominant emission due to $^5D_0 \rightarrow {}^7F_2$ transition enables the development of commercial red-emitting phosphors with high color purity [1,2]. There also exists the potential for white light-emitting diodes by tailoring full color emissions attributed to $^5D_J \rightarrow {}^7F_J$ transitions [3]. Besides, the strong luminescence dependence of $^5D_0 \rightarrow {}^7F_2$ transition on the site symmetry of Eu^{3+} relative to $^5D_0 \rightarrow {}^7F_1$ transition makes it possible to monitor the site situation around Eu^{3+} ions [4,5]. On the contrary, the parity-allowed 4f-5d transition of divalent europium ions is strongly field-dependent, which results in the adjustment of emission color from ultraviolet to red for WLED application [6,7]. Moreover, the broad and tunable excitation bands of Eu^{2+} make it attractive as sensitizer ions for the potential application in solar cells [8,9].

Since trivalent europium ions are readily available in europium sources, synthesis of Eu^{2+} activated luminescent materials is generally conducted under reducing atmosphere such as H_2, H_2/N_2 or CO [6,10–12]. The reduction of Eu^{3+} to Eu^{2+} in air is highly expected for the sake of reducing cost and increasing safety and simplicity during the synthesis process. For many years, researchers have found that such abnormal reduction of $Eu^{3+} \rightarrow Eu^{2+}$ is feasible in some inorganic crystals, which have rigid three-dimensional enclosed crystal structures linked by tetrahedral anion groups (BO_4, SO_4, SiO_4, AlO_4, or PO_4) [13–15]. Also, Eu reduction is favored in acidic glass systems with low optical basicity, but at the cost of chemical and mechanical performances [16,17].

In recent years, glass ceramics have been frequently investigated as a promising host for rare earth ions due to the combined merits of glasses and polycrystalline materials. The easy formability, low cost, and excellent chemical and mechanical stability of glasses together with desirable optical properties exhibited by crystalline phases make them excellent substitutes for each component phase. Moreover, recent researches have demonstrated that the reduction of Eu^{3+} to Eu^{2+} can be realized in air by inducing the precipitation of crystals for several glass systems [5,18–20]. To the best of our knowledge, most of the reported glass ceramics were developed from robust glass systems containing more silica, thus requiring a much higher temperature to prepare the molten glass [5,19]. However, relatively few investigations have been undertaken to examine the crystallization of the invert glasses based on

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alkaline earth borosilicate system. In the present study, we report the synthesis of hexacelsian based glass ceramics from the MgO−BaO−SiO_2−B_2O_3−Al_2O_3 glass system. Characteristic temperatures and crystallization activation energy of the glass have been determined by a non-isothermal method using DSC. Phases and microstructures of glass ceramics produced by thermally induced crystallization and sintering routes have been identified by XRD and SEM. The luminescence measurements reveal that the reduction of Eu^{3+} to Eu^{2+} is possible in hexacelsian based glass ceramics sintered in air. The influence of sintering condition on the crystallization and luminescence properties of these glass ceramics was examined and discussed.

2. Material and methods

2.1. Sample preparation

The precursor glass denoted as B2 with the nominal molar composition of 29MgO−20BaO−19SiO_2−27B_2O_3−5Al_2O_3 was prepared using a conventional melt quenching method. Analytical reagent-grade Mg$(OH)_2$, $BaCO_3$, H_3BO_3, SiO_2, and Al_2O_3 were used as the raw materials for the glass matrix. High purity (99.99%) Eu_2O_3 was added for the partial substitution of SiO_2 as the dopant. Homogeneous mixtures of batches (30 g) were transferred into corundum crucibles and melt at 1350 °C for 45 min in ambient air. Transparent glasses were obtained by casting the melts into a preheated (200 °C) stainless steel mold. To relinquish the inner stress, the obtained glasses were annealed at 480 °C for 2 h before cooling slowly down to room temperature. Glass of B2 composition doped with 0.5 mol% Eu_2O_3 in the present work were labeled with B2E. For comparison, we attempted to fabricate B2ER glass under CO reducing atmosphere which was maintained in a covered crucible by adding 5 wt% activated carbon on the surface of the batch. By contrast, the counterpart melted in air was denoted as B2EA. To obtain glass ceramics, both thermally induced crystallization and sintering methods were employed. In the former case, the bulk glass was heat-treated at 800 °C for 4 h to fabricate B2-800bk glass ceramics. Sintered glass ceramics were prepared by sinter-crystallization of glass frit having a chosen size of 200–250 mesh. Glass frit of 0.5 g was pressed into a pellet of 14 mm in diameter by a uniaxial stress of 230 MPa. Subsequently, the resultant glass-powder compacts were sintered at 700 °C, 800 °C and 850 °C for 4 h in a muffle furnace at a heating rate of 5 °C/min. For instance, the sintered B2E glass-powder compacts were labeled as B2E-700, B2E-800, and B2E-850, respectively.

2.2. Characterization and measurements

The density of B2 glass was measured to be 3.281 g/cm^3 using Archimedes' liquid immersion method on an analytical balance. Differential scanning calorimetry (DSC) measurement was performed on the glass frit (especially, particle size of 58–75 μm) by using a Netzsch STA 409EP calorimeter at a heating rate of 10–25 °C/min. The characteristic temperatures of the precursor glasses were presented in Table 1. XRD patterns were recorded by a Brucker D8-advance X-ray powder diffractometer (Cu Kα, 40 kV/40 mA) for crystalline phase identification. The glass ceramic samples were polished and etched in 2 wt% HF solution for 15 s for microstructure characterization by a field-emission scanning electron microscope (FEI QUANTA FEG 250, 10kV). The excitation and emission spectra were recorded on an Edinburgh Instruments FLS920 spectrofluorometer equipped with a

Table 1
Measured characteristic temperatures of B2 glass at different heating rates α of DSC.

Heating rates α (K/min)	T_g (°C)	T_p (°C)
10	597	806
15	607	823
20	610	834
25	612	845

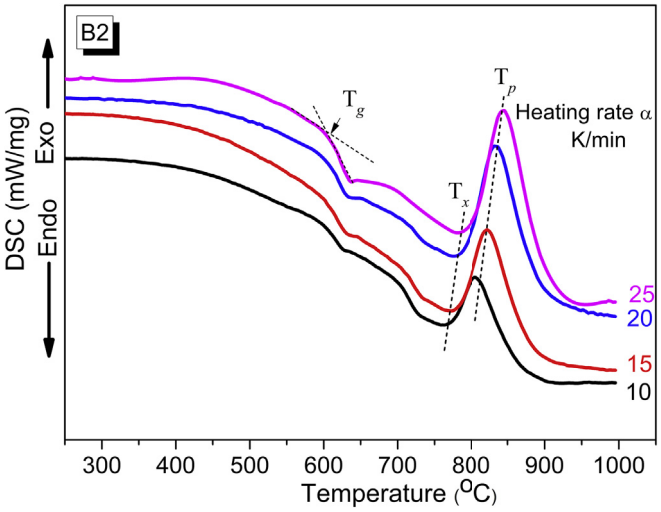

Fig. 1. The DSC curves of B2 glass recorded at different heating rates.

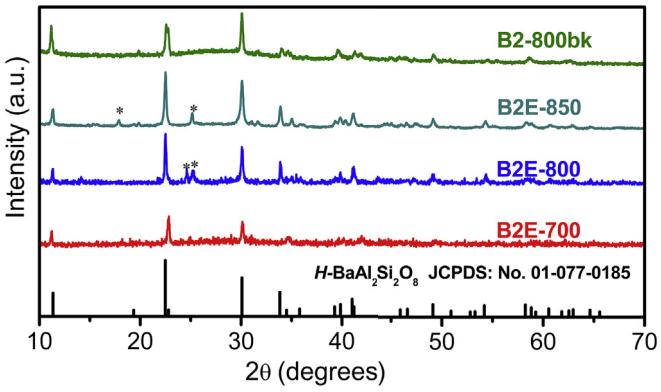

Fig. 2. XRD patterns of B2 bulk glass sample heat-treated at 800 °C for 4 h and B2E glass-powder compacts sintered at different temperatures for 4 h. The precipitated phases are indexed via comparing the standard XRD data of hexagonal $BaAl_2Si_2O_8$ (JCPDS card No. 01-077-0185).

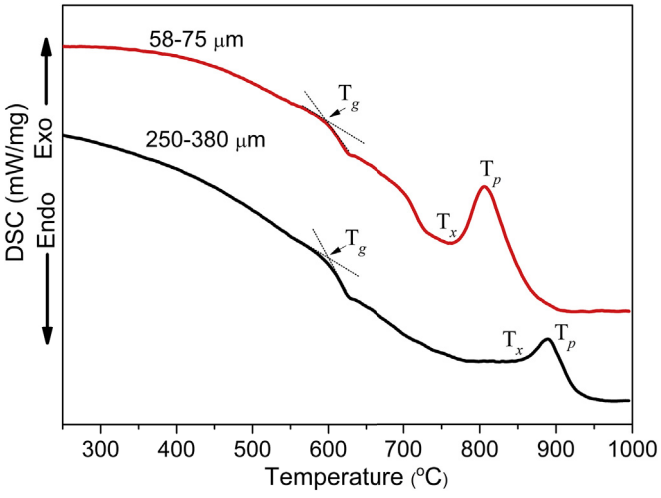

Fig. 3. DSC curves for B2 glass at different particle size (heating rate of 10 K/min).