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Processing and Optical Properties of Eu-Doped Chloroborate Glass-Ceramic

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Abstract: An europium doped BaO–B₂O₃–BaCl₂ chloroborate glass-ceramic containing a BaCl₂ nanocrystalline phase was produced by melt-quenching followed by glass crystallization during annealing. Structural and morphological investigations using x-ray diffraction and scanning electron microscopy have shown fβBaCl₂ nanocrystals of about tens of nm size accompanied by a smaller amount of the BaB₂O₄ crystalline phase. Photoluminescence spectra have indicated the reduction of Eu³⁺ to Eu²⁺ during processing in air or a reducing atmosphere. The spectra analysis showed the presence of Eu³⁺ ions in the borate glass matrix, while the Eu²⁺ were incorporated in both the BaCl₂ nanocrystals and glass matrix. Thermoluminescence properties were due to the recombination of F(Cl) centers and Eu²⁺ related hole centers produced by irradiation within the BaCl₂ nanocrystals. The color impression of the samples and the photoluminescence quantum efficiency were influenced by the glass processing.

Keywords: glass ceramic; nanocrystals; rare earth; photoluminescence; thermoluminescence

1. Introduction

Glass-ceramics are composite materials formed by a nano-crystalline phase dispersed within a glass matrix. The precursor glass is converted into a glass-ceramic during a subsequent annealing through a controlled nucleation and crystallization processes. Transparent glass-ceramics offer balanced properties between a glassy material and crystals. By proper doping with luminescent rare-earth (RE) ions, they can combine the fluorescence properties and optical transparency due to lack of scattering. The new optical functionalities added are very important for photonics related applications (optical amplifiers, optical waveguides, white LEDs, etc.) at the industrial scale ([1,2] and references therein).

Most studies have been focused on the preparation and characterization of RE-doped transparent oxyfluoride glass-ceramics containing nanocrystalline fluorides such as PbF₂, CaF₂, BaF₂, LaF₃, NaLaF₄, etc. embedded in an aluminosilicate glass matrix ([3] and references therein). The thermal stability and chemical advantages of oxide glasses combine with those of the fluoride environment of dopant ions that assures a high luminescence efficiency because of low phonon energies and low non-radiative decay rates. Transparent fluorozirconate-based glass-ceramics containing RE³⁺-doped BaCl₂ nanocrystals represent new developments in the field, and their crystallization behavior [4,5] and optical properties have been investigated [6]. Eu²⁺-doped glass-ceramics are of special interest [7–9] because of their remarkable scintillating and x-ray storage phosphor properties as shown by the Eu²⁺-doped BaCl₂ crystal [9–11]. Nevertheless, fluorozirconate glass synthesis is performed at relatively high temperature and controlled atmosphere, and therefore other glass matrix options have been considered such as such as borate glasses. The synthesis and crystallization properties of barium borate glass-ceramics in the BaO–B₂O₃ system have been studied, and their structural and optical properties related to the borate nanocrystals (BaB₂O₄, BaB₄O₇, Li₂B₄O₇) [12–15] and BaCl₂ [16,17] nanocrystals have been investigated.
The aim of the present study was to perform a structural and morphological investigation of the Eu-doped chloroborate glass ceramic in the BaO–B₂O₃–BaCl₂ system and to evaluate the influence of the ceramization process on its optical properties: optical absorption, photoluminescence, and thermoluminescence.

2. Materials and Methods

2.1. Samples Preparation

Glass samples with the composition of (34BaO–30B₂O₃–28BaCl₂–1Eu₂O₃) (mol%) [16] were prepared from high purity BaCO₃, B₂O₃, BaCl₂, and Eu₂O₃ precursors, as detailed in [11]. The constituent chemicals were carefully mixed, dried at 80 °C, and melted in a covered corundum crucible at 1130 °C in air for 1 h, followed by fast pouring onto a brass preheated plate. Then, in order to relinquish the inner stress, the glass samples were annealed for 1 h at 400 °C (i.e., below the glass temperature T_g of 500 °C (see thermal analysis section from below)). Glass ceramization has been obtained during subsequent annealing at different temperatures above T_g for various times in air or reducing atmosphere (5H₂–95Ar gas mixture). The initial glass was clear-transparent, but after annealing, it was converted to milky-white as a consequence of the crystallization processes evidenced by the XRD measurements.

2.2. Characterization Methods

For the thermal analysis by thermogravimetry (TG) and differential scanning calorimetry (DSC), we used a SETARAM Setsys Evolution 18 Thermal Analyzer in synthetic air (80% N₂/20% O₂) and a heating rate of 10 °C/min. Structural characterization by X-ray diffractometry (XRD) was carried out by using a BRUKER D8 ADVANCE type X-ray diffractometer in focusing geometry, equipped with copper target x-ray tube and LynxEye one-dimensional detector. The XRD pattern was recorded in the 20 to 60° range, with 0.04° step and 2 s integration time. For the phase composition analysis and crystallographic characteristic, we used the Powercell dedicated software [18]. The morphological characterizations of the samples were carried out by using a Zeiss MERLIN (Jena, Germany) Compact scanning electron microscope (SEM) with GEMINI column and equipped with an energy dispersive x-ray system (EDX) analyzer. The photoluminescence, excitation spectra, and photoluminescence decay curves were recorded at room temperature by using a FluoroMax 4P spectrophotometer (HORIBA Jobin Yvon, Kyoto, Japan); for the chromaticity and quantum efficiency analysis, we used the Quanta-Phy accessory. For thermoluminescence (TL) measurements, we used a Harshaw 3500 TL reader in the 50–350 °C temperature range with a heating rate of 2 °C/s. The TL measurements were performed after x-ray irradiation at room temperature for 30 min (using a copper anode at 40 kV and 40 mA) and storage for 25 min.

3. Results and Discussion

3.1. Thermal Analysis

The thermogravimetry (TG) curve recorded on the prepared glass sample showed a monotone increase with the temperature, but several peaks were observed on the DSC curve (Figure 1). The weak endothermic decrease at about 500 °C was assigned to the glass transition temperature T_g and the sharp exothermic peak at about 710 °C to the bulk crystallization of the glass (T_crg). Between 525 and 600 °C, we observed a composed exothermic peak T_ce that was assigned to the glass ceramization associated with the precipitation of BaCl₂ and β-BaB₂O₄ phases within the glass matrix [11], as was shown by XRD analysis (see below). The inset of the crystallization observed at 530 °C (Figure 1) agreed with the value of 521 °C recorded on a barium borate glass with a similar composition (i.e., the ratio ΣBa: 2B = 1.7) [19].
3.2. Structural and Morphological Characterization

The XRD pattern of the initial glass showed several broad peaks at 21.5, 31, and 41.5°, consistent with its amorphous structure (Figure 2). The glass ceramization started at 535 °C (i.e., right below the composed exothermic peak $T_{cr}$). The XRD patterns of the glass ceramic samples (Figure 2) showed the diffraction peaks assigned to the precipitation of the orthorhombic BaCl$_2$ phase accompanied by the peaks due to the $\beta$-BaB$_2$O$_4$ crystallites [11]; weaker peaks due to Al$_2$O$_3$ from the crucibles were also observed [11]. The stable phase of BaCl$_2$ has an orthorhombic PbCl$_2$ structure (space group D$_{2h}^{16}$, Pnma) with the lattice parameters $a = 7.865$ Å, $b = 4.731$ Å, and $c = 9.421$ Å (PDF 00-024-094) [20].

According to the results of the XRD pattern analysis (Table 1), the cell parameters of BaCl$_2$:Eu$^{2+}$ nanocrystals in the glass ceramic showed a clear increase compared to the corresponding nanocrystalline...
powder. For Eu$^{2+}$-doped BaCl$_2$ nanocrystals where the Ba$^{2+}$ ions are substituted by the Eu$^{2+}$ dopants [20,21], there is a relatively small distortion of the BaCl$_2$ crystalline structure assigned to the ionic radii difference of 1.47 Å for Ba$^{2+}$ and 1.3 Å for Eu$^{2+}$ [22]. However, for the glass-ceramic, we observed a strong crystalline lattice expansion effect (Table 1). Therefore, we assigned it to the particularities of the nanocrystal growth process in the glass matrix, which is strongly influenced by the ionic environment and ionic impurities incorporated during the growth process [23].

| Sample                  | a (Å) | b (Å) | c (Å) | Cell Volume (Å$^3$) |
|-------------------------|-------|-------|-------|---------------------|
| Annealed in air         | 7.903 | 4.751 | 9.422 | 353.9               |
| Annealed in H$_2$-Ar    | 7.906 | 4.752 | 9.426 | 354.2               |
| BaCl$_2$ [20]           | 7.8813(2) | 4.7369(1) | 9.4360(2) | 352.27             |
| BaCl$_2$:Eu$^{2+}$ [21] | 7.878(5) | 4.735(8) | 9.428(1) | 351.68              |

The scanning electron microscopy (SEM) image analysis indicated volume crystallization of the sample as a relatively uniform, compact, and broad distribution of nanoparticles of about tens of nm size (Figure 3); their aggregation and collapse resulted in bigger particles, of about hundreds of nm in size. Previous studies have indicated a surface crystallization in the glasses containing BaO and B$_2$O$_3$ [24], but in the present case, the SEM image (Figure 3) indicated a ceramization process within the glass sample volume.

**Table 1.** The results of the x-ray diffraction (XRD) pattern analysis of Eu-doped chloroborate glass-ceramic annealed at 570 °C in an air and reducing atmosphere (H$_2$–Ar); the lattice parameters for BaCl$_2$ [20] and BaCl$_2$:Eu$^{2+}$ nanocrystals [21] are included for comparison.

The EDX spectral analysis of the glass-ceramic samples showed the presence of elements from the precursor chemicals: 7 at%(C), 72 at%(O), 9 at%(Ba), 2.5 at%(Al), 9 at%(Cl), and 0.5 at%(Eu). There was a deviation from the batch composition that was assigned to the chloride loss during the melting caused by the chemical interaction of the oxychloride melt with water vapor or oxygen [16].

### 3.3. Optical Absorption UV–Vis

The effect of glass ceramization can be clearly observed in the absorption spectra recorded on the initial and glass ceramic samples (Figure 3). The initial glass showed high transparency in the
whole blue-visible region, but for the glass-ceramic, the spectrum was dominated by the scattering on the nanocrystals; two small peaks at about 394 and 463 nm were due to the $^5F_0 \rightarrow ^5L_6$ and $^5F_0 \rightarrow ^5D_2$ transitions of the Eu$^{3+}$ ions [25]. The absorption spectrum recorded on the glass-ceramic followed a $1/\lambda^n$ wavelength dependence, with $n \approx 4$ (Figure 4, dotted curve) consistent with a Rayleigh scattering on nanocrystals much smaller than the wavelength (i.e., <1/10 of the wavelength) [26]. Superimposed on the Rayleigh scattering curve, we observed a weak “bump” at about 480 nm assigned to the Mie scattering on nanocrystal agglomerates larger than the wavelength.

![Figure 4. Optical absorption spectra of initial Eu-doped chloroborate glass and glass-ceramic after 570 °C annealing; the doted curve represents the $\lambda^{-4}$ Rayleigh scattering dependence curve.](image)

### 3.4. Photoluminescence Properties

The luminescence properties of the europium ion are strongly dependent on its valence state (Eu$^{2+}$ or Eu$^{3+}$) and on the nature of the host lattice; sharp visible luminescence peaks were observed for Eu$^{3+}$ and broad blue luminescence for Eu$^{2+}$. The PL and PL excitation spectra recorded on the Eu-doped chloroborate glass and glass-ceramic samples are presented in Figures 5 and 6, respectively.

![Figure 5. Photoluminescence spectra of the initial Eu-doped chloroborate glass and glass-ceramic annealed at 570 °C in an air and reducing atmosphere (H$_2$–Ar) under a 350 nm excitation wavelength.](image)
When the RE ions are incorporated dominantly in the glass matrix. Moreover, for lower phonon frequencies of the precipitated nanocrystals (i.e., reduced (i.e., during the glass ceramization process), this emission coeﬃcient is removed, and for the Eu3+ ions, Stark splitting of the 7F1 final states [27] is expected, which, however, in the present case, could not be observed (Figure 5). The computed results for the 7F0→5D2 transition is the only MD transition, and therefore we used A0-1 = 50 s⁻¹ [31]. The computed results for the J-O parameters are tabulated in Table 2, where a very good agreement with the Ω2, Ω4 parameters
was reported for the Eu$^{3+}$ doped lead borate glass [32] and a small decrease in the glass ceramic as a consequence of structural transformations during the ceramization process could be observed. We suppose that in the glass ceramic, a very small fraction of the Eu$^{3+}$ ions is incorporated within the crystalline lattice, and hence we observed a decrease in the Eu bonds’ covalency degree and of the $\Omega_2$ parameter.

Table 2. The results of the J-O parameter analysis of the Eu-doped chloroborate glass and glass-ceramic annealed at 570 °C in an air and reducing atmosphere (H$_2$–Ar); the J-O parameters for the (29PbO–70B$_2$O$_3$-0.5Eu$_2$O$_3$) lead borate glass are included [32] for comparison.

| Sample                  | $\Omega_2$ ($\times 10^{-20}$ cm$^2$) | $\Omega_4$ ($\times 10^{-20}$ cm$^2$) | PL Lifetime (ms) |
|-------------------------|---------------------------------------|---------------------------------------|------------------|
| Initial glass           | 5.9                                   | 3.9                                   | 1.86 ± 0.02      |
| Annealed in air         | 5.8                                   | 3.9                                   | 2.20 ± 0.02      |
| Annealed in H$_2$-Ar    | 5.1                                   | 3.9                                   | 2.20 ± 0.02      |
| Lead borate glass [32] | 6.03                                  | 4.29                                  |                  |

In the glass ceramic, the Eu$^{3+}$-related luminescence peaks were accompanied by broad blue luminescence peaks at 407 and 480 nm (Figure 5) assigned to the Eu$^{2+}$ ion luminescence in different environments. The Eu$^{2+}$ luminescence occurs from the lowest crystal-field component of the 4P$^5$d excited configuration to the $^8S_{7/2}$ ground state (parity-allowed). This d-f type emission has a broad band character and is strongly dependent on the host lattice (i.e., the coordination number and symmetry of the site occupied by the Eu$^{2+}$ ions) [33]. The Eu$^{2+}$-related luminescence was not observed in the initial glass, but only after the ceramization process as a consequence of the Eu$^{3+}$→Eu$^{2+}$ reduction processes in the glass matrix [34–36], and was enhanced by the reduction atmosphere (Figure 5). As the Eu$^{2+}$ luminescence in BaB$_2$O$_4$ crystals was observed at 380 nm [37] and given that the 407 nm luminescence was close to that observed in bulk orthorhombic BaCl$_2$:Eu$^{2+}$ crystals at 399 nm [38], we could assign the observed features to the Eu$^{2+}$ luminescence in the BaCl$_2$ nanocrystalline phase from the glass ceramic.

The excitation spectrum of the 407 nm luminescence showed two broad bands at about 275 and 330 nm (Figure 6) assigned to energy splitting between the $t_{2g}$ and $e_g$ one electron states of the 5d orbital. Its shape was different from the spectrum recorded on the BaCl$_2$:Eu$^{2+}$ nanocrystalline powder [39], where a broad band in the 250 to 375 nm range was observed. The energy splitting indicated a lower crystal field symmetry at the Ba$^{2+}$ sites occupied by the Eu$^{2+}$ ions (compared to the nanocrystalline powder), which was assigned to the stress and distortion induced by the growth process (see Section 3.2). Such effects might also be responsible for the spectral shift of the 407 nm luminescence, compared to the Eu$^{2+}$ luminescence observed at 396 nm in the nanocrystalline powder [39]. By comparison, the excitation spectrum of the 470 nm luminescence showed a broad and structureless band, which could be tentatively assigned to the Eu$^{2+}$ ions in the glass matrix.

3.5. Colorimetry Analysis

The color impression of the samples was influenced by the glass processing. Figure 7 shows the Commission Internationale de l’Eclairage (CIE) chromaticity diagram of the initial and glass-ceramized (in an air or reducing atmosphere) Eu-doped chloroborate samples, respectively. Under 345 nm excitation, the coordinates $x = 0.677$ and $y = 0.274$ corresponded to the region of red Eu$^{3+}$ luminescence, but after glass ceramization (in air or reducing atmosphere), these changed to $x = 0.404$ and $y = 0.244$ as a consequence of the Eu$^{2+}$ blue luminescence. The photoluminescence quantum efficiency was about 16% for the glass, but decreased to only 4% for the glass-ceramic due to the scattering losses [13].
3.6. Thermoluminescence Properties

Thermoluminescence (TL) represents the light emission by a solid sample when it is heated after irradiation by ionizing radiation such as UV light, x-rays, gamma-rays, etc. [40]. According to the basic model of TL, charge carriers (electrons and holes) are produced during the irradiation, which are subsequently trapped on local energy levels (such as vacancies, interstitials, or impurities) within the band gap; during heating, their recombination is thermally activated, resulting in the emission of light (i.e., TL) [40,41].

Thermoluminescence curves recorded on undoped and Eu-doped chloroborate glass-ceramics are depicted in Figure 8. The glow curve recorded on undoped glass ceramic and BaB$_2$O$_4$ showed a broad band between 75 and 400 °C [42], which was assigned to the thermal recombination of defects within the BaB$_2$O$_4$ nanocrystalline phase. The glow curve recorded on the Eu-doped glass-ceramic (annealed in air) showed two peaks at 97 and 134 °C with a higher magnitude than in the undoped sample, but much weaker than in the Eu$^{2+}$-doped BaCl$_2$ nanocrystalline powder. The same glow peaks were observed in the glass-ceramic annealed in a reducing atmosphere, where 134 °C was the dominant feature, accompanied by a shoulder at about 180 °C. The high temperature peak at 134 °C has been observed on Eu$^{2+}$-doped BaCl$_2$ nanocrystalline powder, and it has been assigned to the recombination of F(Cl) centers in the BaCl$_2$ crystalline lattice [21]. During the heating, the electrons are thermally released from the F(Cl) trapping centers and recombine with holes trapped as Eu$^{3+}$/Eu$^{2+}$-hole centers giving rise to the excited (Eu$^{2+}$)* ions and radiative emission according to:

$$(Eu^{2+\text{-}hole}) + \dot{\epsilon} - k_B T \rightarrow (Eu^{2+})^* \rightarrow Eu^{2+} + h\nu$$

(2)
Conclusions

An europium doped BaO–B₂O₃–BaCl₂ chloroborate glass-ceramic was produced by melt-quenching followed by glass crystallization at T = 570 °C. X-ray diffraction and scanning electron microscopy measurements revealed the formation of orthorhombic BaCl₂ nanocrystals of about tens of nm size accompanied by a smaller amount of BaB₂O₄ nanocrystals. Structural analysis indicated strong distortions of the BaCl₂ crystalline lattice, which was associated with the ionic impurities and other defects during the nanocrystal growth process in the glass matrix.

The photoluminescence properties analysis showed that in the glass-ceramics, the Eu³⁺ ions are incorporated dominantly in the glass matrix. In addition, a reduction process of Eu³⁺ to Eu²⁺ was revealed by the presence of broad blue luminescence peaks at 407 and 480 nm, assigned to the Eu²⁺ ion luminescence in different environments: perturbed sites in the BaCl₂ nanocrystals and in the glass matrix, respectively.

Thermoluminescence curves recorded on the Eu-doped glass-ceramic showed two glow peaks at 97 and 134 °C. The high temperature peak was due to the F(Cl) center recombination in the BaCl₂ nanocrystals, and the low temperature peak at 97 °C was tentatively assigned to the recombination of perturbed F-centers.

In conclusion, glass-ceramic materials based on stabilized rare-earth doped BaCl₂ nanoparticles embedded in a glass matrix were demonstrated as attractive potential candidates for phosphor related applications. They offer a viable solution to overcome the disadvantages of the BaCl₂ crystal phosphor: raw material purification, clean environment control requirements during crystal growth, and chemical instability to water. Hence, its remarkable performances as a scintillator, x-ray storage phosphor, or thermoluminescence dosimeter can be used for practical applications of radiation detection. In particular, new developed chloroborate glass-ceramics can be processed at lower temperature and in an open atmosphere compared to the fluorozirconate glass-ceramics. However, further improvements of the optical properties and transparency through a better control of the processing parameters are required as a prerequisite condition for future applications.
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