Research Article

Structural Features and Synthesis of CeO$_2$-Doped Boroaluminosilicate Oxyfluoride Transparent Glass Ceramics

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This study investigated the effects of CeO$_2$ on structure and synthesis of boroaluminosilicate transparent glass ceramics containing CaF$_2$ nanocrystals prepared through isothermal crystallization of the melt-quenched glasses with composition 54SiO$_2$–10B$_2$O$_3$–13Al$_2$O$_3$–14Na$_2$O–3ZnO–2Li$_2$O–4CaF$_2$ doped with 0–1.2 mol% CeO$_2$. CeO$_2$ in polyvalent states acting as network modifier leads to disruption of the silicate network and the conversion of [BO$_3$] to [BO$_4$] generating the nonlinear variations in crystallization, and thermodynamic and optical features. Glass transition temperature and the crystallization temperature decrease firstly and then increase with the increase of CeO$_2$ content. Correspondingly, the size of CaF$_2$ nanoscale crystals and the absorption coefficient of the glass ceramics are found to pass through a maximum and then decrease with increasing CeO$_2$ addition. Increasing CeO$_2$ concentration and elevating treating temperature lead to red-shift of absorption edge and transparency deterioration of glass ceramics.

1. Introduction

Glasses used in space, nuclear power devices, and other scientific applications may be exposed to high energy radiation like gamma, electron, proton, and neutron [1, 2]. Ionization caused by photon and particle radiation lead glasses to degeneration in performances raising the concern about nuclear environmental hazards to facility as well as health security therein [3]. Radiation often results in recognizable loss in glass transmittance over the visible spectral range and even glass color change. Most glasses become unusable for optical applications under excessive irradiation.

Radiation resistant glasses are referred to glasses which can maintain their physical properties including optical transmittance even after high dose of nuclear radiations. Optical glasses can be stabilized against transmittance loss caused by ionizing radiation by adding cerium to the composition. Since cerium presents in glasses in polyvalent ions, that is, Ce$^{4+}$ and Ce$^{3+}$ via ceric-cerous redox equilibrium, it gives glasses irradiation protection in the ways that Ce$^{3+}$ capture holes and Ce$^{4+}$ trap electrons yielded by irradiation to avoid their recombination and hence the formation of permanent defect centers [4].

In the past few years, cerium oxide (CeO$_2$) has been used as a stabilizer or sensitizer agent in doping silicate glass to improve irradiation resistance, luminescence properties, and so on [5–7]. As a well known heat resistant glass, borosilicate glass achieved extensive application thanks to its excellent physical and chemical properties [8]. In particular, the superior dissolving capacity of rare earth (RE) makes borosilicate glasses very suitable for developing RE-doped optical glasses and for immobilization of high-level nuclear wastes [9–11]. By doping CeO$_2$, alkali borosilicate glasses gain modification on physical properties and can be widely used in irradiation ambient such as aerospace, nuclear facilities, and photovoltaic devices as well as medical and military fields [12].

Although CeO$_2$ helps borosilicate glass increase resistance to radiation damage, the undesirable yellowing effect arising from high cerium content limits its extensive application with requirement of stable optical properties. The onset
of yellowing in most of alkali borosilicate glasses occurs at 1-2 mol% CeO₂ [13]; thus addition of CeO₂ has to be minimized as much as possible to avoid coloration of host glass at the expense of partial irradiation resistance.

Notwithstanding at the present time borosilicate glass as the generally accepted first generation nuclear waste form, its microstructure change due to high temperature and pressure and watery environment allows easy leach of radionuclide. The high melting point, high thermal conductivity, and radiation stability have been proved to make ceramics the competitive candidate for irradiative waste immobilization [14]. Glass ceramics (GC), a kind of inorganic composite materials with crystalline fillers dispersed in vitreous matrix, may manifest the irradiation resistance in a different mode from the generic glasses as evidenced from the following study cases. A glass ceramic made of 50 vol.% fluorophlogopite mica crystals embedded in a borosilicate glassy matrix exhibits properties stability and even strength gain when exposed to high-fluence neutron irradiation [15]. Glass ceramics based on SiO₂–Al₂O₃–MgO and SiO₂–Al₂O₃–Y₂O₃ used as pressureless low activation joining materials for nuclear applications show much remarkable similarity and unaffected mechanical strength before and after neutron irradiation [16]. Excellent radiation resistance makes scintillating glass ceramic a promising alternative to glass in the field of scintillation detector which always works under scintillating glass ceramic a promising alternative to glass in the field of scintillation detector which always works under scintillation detector which always works under radiation condition that can influence the energy resolution of detectors [17–20].

Transparent glass ceramic (TGC), which achieved wide use in optical materials field, can be formed via controlled crystallization of precursor glass [21] in case of fine precipitated crystals well below the wavelength of the visible light or a negligible refractive index difference between the amorphous and crystalline phases. The latter criteria can be dismissed provided with the smallness of crystal less than dozens of nanometers because the light wave propagating in it cannot feel a modulation of the refractive index in dimensions far shorter than its wavelength [22]. It is of much significance to investigate the irradiation effects of TGC used in radioactive ambient, and the first of all problems is to synthesize preliminarily glass ceramics that meet certain requirements on existing modification of irradiation resistance.

We intentionally selected alkaline boroaluminosilicate system as the precursor glass for the preparation of TGC in consideration of its wide use in irradiative condition ranging from nuclear waste immobilization [23] to aerospace facility components such as solar cell cover [24] and microelectromechanical system due to the mentioned merits. The structural evolutions as well as the property variations of some boroaluminosilicate glasses doped with RE as surrogate of the actinides under irradiation have been investigated [10, 25, 26]. Additionally, molybdenum-added boroaluminosilicate as the model system has been applied to synthesize glass ceramic containing powellite crystals for high-level waste immobilization [27], whereas, to our knowledge, TGC doped with CeO₂ for irradiation sheltering purpose are less documented. In particular CeO₂-doped borosilicate oxyfluoride TGC, which has great potential applications for advanced optical materials such as large telescope mirror blanks, liquid crystal displays, solar cells, and energy conversion materials that may be subject to harsh irradiation, deserves to place an emphasis on investigation. Besides, there have been many inconsistencies on the role of cerium playing in structure and synthesis of glass ceramics; for instance, cerium can act as promoter [28, 29] or inhibitor [30] of crystallization depending on glass composition and crystallized species. Hence, the goal of this study is to investigate the effect of cerium on the structure, synthesis, and properties of limited CeO₂-doped boroaluminosilicate oxyfluoride TGC containing CaF₂ crystal.

2. Experimental

2.1. Glass Preparation. The precursor glasses (G) were synthesized by conventional melt-quenching method using analytical pure reagents SiO₂, Al(OH)₃, B₂O₃, Na₂CO₃, Li₂CO₃, ZnO, CaF₂, and CeO₂ as starting materials. The base glass batch mixture with a fixed glass composition 54SiO₂–10B₂O₃–13Al₂O₃–14Na₂O–3ZnO–2Li₂O–4CaF₂ (mol%) was previously prepared by ball-milling the compounded ingredients for 1 h, and subsequently CeO₂-doped mixtures were fabricated by adding extra 0%, 0.4%, 0.8%, and 1.2% CeO₂ powder (mol%) over the batched mixture of base glass (keeping the ratio of base components constant). The glass batch was heated to 1400°C at a heating rate of 20°C/min holding for 2 h in an open platinum crucible in air. Afterwards the melt was poured onto a preheated graphite plate and was pressed to form a disk followed by being annealed in a muffle furnace at 500°C for 1 h to release the internal stress. The as-prepared glass discs were polished with SiC papers up to 1200 grit, ultrasonically cleaned in acetone and anhydrous ethanol, respectively, and then washed with distilled water for further measurements. Glass samples were referred to by their doped molar percentage of CeO₂ relative to 100 mol base glass, that is, G0, G0.4, G0.8, and G1.2, respectively. The glass ceramics (GC) were prepared by reheating the obtained glasses to crystallize at a certain temperature above its glass transition temperature T_g for 3 h.

2.2. Spectroscopic Analysis. Infrared (IR) spectra measurements for the glasses and glass ceramics from 400 to 4000 cm⁻¹ were carried out at room temperature by a Nicolet 1010 Fourier transform infrared spectrometer (FTIR) using the standard KBr pellet method. The pellets were prepared by tightening a specialized screw mould containing a mixture of 200 mg spectrum pure KBr and 2.0 mg glass powder. The recorded spectrum of the pulverized sample pellet was subtracted by that of the matrix KBr.

2.3. Thermal Analysis. Glass transition temperature and crystallizing temperature were preliminarily determined by differential scanning calorimetry (DSC) as the basis to formulate the heat treatment schedules. The measurement was carried out on about 20 mg glass powder placed in a platinum crucible with lid under Ar ambient at a heating rate of 10 K/min using a NETZSCH STA449F thermal analyzer.

2.4. X-Ray Diffraction (XRD) Measurements. XRD analysis was conducted to detect the crystalline phase precipitated in
the glass matrix of as-prepared glass ceramics in the form of powder ground in an agate mortar with a pestle. The XRD spectra were recorded within Bragg angle $2\theta$ from 20° to 80° by means of a diffractometer (D/MAX-III A) using Cu Kα radiation with a scanning speed of 3°/min.

2.5. Morphology Observation. Morphologies of the studied glass ceramics were observed by using a field emission scanning electronic microscopy (FE-SEM, Hitachi S-4700 Japan). Prior to observation, the surface was soaked in 10% HF solution for several seconds and ultrasonically cleaned in deionized water; then the samples were sputtered with gold on dried surface.

2.6. UV-Vis Spectroscopic Analysis. The transmittance as function of wavelength for each TGC was measured using a UV-Visible spectrophotometer (PERSEE T6) with a dual light source by scanning from 190 to 1100 nm using air as a reference at 4 nm resolution. The as-prepared TGC were successively polished with SiC papers up to 1200 grit and cerium oxide powder slurry, ultrasonically cleaned in acetone and anhydrous ethanol, respectively, and then rinsed with distilled water and dried for measurements.

3. Results and Discussion

3.1. Glass Structure. Figure 1 shows the FTIR spectra of the as-prepared glass and glass ceramics with variations in CeO$_2$ content. A sharp peak at 1627 cm$^{-1}$ identifies the vibrations of residual moisture or OH$^-$ present in the glass structure [31, 32]. The band at about 1420 cm$^{-1}$ is assigned to carbonate groups which results from the interaction between CO$_2$ and silicate melts at high temperature [33, 34]. The band centered at about 1300 cm$^{-1}$ is due to the asymmetric stretching relaxation of the B–O bond of trigonal [BO$_3$] units [2, 35, 36]. The broad band ranging from 850 to 1200 cm$^{-1}$ arises from the overlapping contributions of silicate and borate groups [37]. Within this range, silicon-oxygen tetrahedral with varying numbers of nonbridging oxygen (NBO), which is commonly denoted as Q$^n$ describing Si–O tetrahedral group with $n$ bridging oxygen per structural unit, can be assigned to respective IR band [38, 39]. A shoulder at about 1150 cm$^{-1}$ within the composite peak can be assigned to Q$^3$ stretching. The intense band located at 1020 cm$^{-1}$ can be attributed to the combined asymmetric stretching vibration of Si–O–Si and B–O–B network of tetrahedral structural units including [SiO$_4$] and [BO$_4$] groups [40–42]. As more alkaline is introduced in the base glass than Al$_2$O$_3$, alumina is assumed to enter Si–O tetrahedral network contributing to the vibration of this band, that is to say, all aluminum is 4-fold coordinated and unaffected by doping CeO$_2$. The band at about 705 cm$^{-1}$ is associated with the bending of B–O–B linkage in the borate network [39, 43]. Moreover, a band situated at 450 cm$^{-1}$ is generally attributed to Si–O–Si bending [35, 36, 41].

For both the glasses and glass ceramics, the variations in curve shape exhibit the analogous trends. Specifically, with increasing CeO$_2$ content, absorption band at 1300 cm$^{-1}$ arising from stretching of triangles [BO$_3$] appears to gradually decrease in intensity. Meanwhile within the range of 850–1200 cm$^{-1}$, shoulder at 1150 cm$^{-1}$ tends to weaken and peak centered at 1020 cm$^{-1}$ concomitantly intensifies with the increase of CeO$_2$ concentration. These revelations suggest two opposite modifications in network structure, that is, the depolymerization of Si–O skeleton network and the concomitant conversion of [BO$_3$] triangles to [BO$_4$] tetrahedral in borate network, leading to nonlinear variations in glass connectivity when doping CeO$_2$. It is proposed that cerium oxide acting as network modifier in glass [44, 45] introduces NBOs allowing for the rupture of Si–O network and conversion of [BO$_3$] triangles to [BO$_4$] tetrahedral due to “boron oxide anomaly.” In addition to alkali metal ions, cerium ions can also serve to balance negative charge of the neighboring tetrahedrons [46]. Formation of [BO$_4$] by adding CeO$_2$ has been reported elsewhere in similar study regarding borate glasses [30, 47] as well as lithium aluminum borate glasses [44].

On the other hand, cerium oxides in glass melt [44, 45] can present in polyvalent states via a redox equilibrium written as

$$\text{Ce}^{4+} + \text{O}^- \rightleftharpoons \text{Ce}^{3+} + \text{O}$$  \hspace{1cm} (1)

Raising appropriately CeO$_2$ content yields more Ce$^{3+}$ ion that consequently give rise to number of NBOs [12]. Cerium in lower content presents predominantly in Ce$^{4+}$ state yielding more NBOs, while in higher content more Ce$^{3+}$ will transform into Ce$^{4+}$ suppressing the rising NBOs concentration instead [12, 48]. Then variation in NBOs concentration as function of cerium content will have potential effect upon the nonlinear variation in connectivity of silicate network and borate network. Overall, the opposite effects on network former Si and B may allow for an intersection state corresponding to the minimum network connectivity for the glasses doped with CeO$_2$ in the range of 0–1.2 mol%.

3.2. Thermal Analysis. Figure 2 shows the DSC thermograms of the precursor glasses containing varied concentrations of CeO$_2$. A weak endothermic peak situated at $T_g$ corresponding to glass transition and an intense exothermic peak at $T_p$ associated with the crystallization can be identified in the DSC curves. The glass transition temperatures ($T_g$), the crystallization temperature ($T_p$), and the extrapolated onset temperature ($T_c$) of the exothermal peak are determined by plotting method [49]. $T_g$, $T_p$, as well as the gap between $T_c$ and $T_p$ referred to as $(T_c - T_p)$ as function of CeO$_2$ content are depicted in Figure 3.

As shown in Figure 3, $T_p$ together with $T_g$ decreases gradually to a minimum firstly and then begins to increase as function of CeO$_2$ content due to the glass structural evolution. Correspondingly, as seen from Figure 2, the exothermic peak area which can be used as a measure of the released enthalpy to evaluate the thermodynamic scale of crystallization appears to go up initially followed by suppression with the increase of CeO$_2$. The nonlinear fluctuation of thermal properties is the result of the changing network connectivity while increasing CeO$_2$ concentration. Specifically, the gap
between $T_c$ and $T_g$ in terms of $(T_c - T_g)$, which is usually used to assess the glass stability, namely, the resistance to crystallization upon reheating [50], monotonously decreases and inflects with the rising CeO$_2$ content implying that doping CeO$_2$ nonlinearly increases the glasses’ crystallization tendency. The turning point of thermal properties variation more likely occurs at doping with 0.8 mol% CeO$_2$, which roughly accords with the minimized network connectivity of glass as indicated in IR analysis.

In general, to produce glass ceramics through isothermal heat treatment, a heating temperature is popularly selected amid the range from $T_g$ to $T_c$. In this study, for the purpose of finding the dependence of glass crystallization and transparency on the dopant concentration and treating temperature, heat treatment on the individual experimental group of studied glasses was carried out at 570°C, 600°C, and 650°C for 3 h, respectively. The designation of heat treated sample, for example, GC0.4/600, describes the CeO$_2$ content of 0.4 mol% and the treating temperature of 600°C.

### 3.3. Crystallization Behavior

Figure 4 presents the XRD patterns of the glass ceramics obtained by reheating the precursor glasses at different temperatures for 3 h. Comparatively, diffraction peaks of CeO$_2$ doped glass ceramics are more intense than those free of cerium proving that...
appropriate CeO$_2$ addition promotes the crystallization in glass to varied extent. The detected three peaks are identified as (111), (220), and (311) crystal faces of CaF$_2$ crystalline phase by comparing with standard diffraction data (JCPDS#35–0816). Additionally, elevated treating temperature causes the increase in diffraction intensity for all the four groups indicating that higher temperature favors crystallization of CaF$_2$ in CeO$_2$-doped borosilicate glasses as ever.

It has been proposed that the precipitation of CaF$_2$ crystals from glassy matrix follows a diffusion controlled mechanism [21, 51]. As revealed in IR analysis, doping CeO$_2$ can lead to the depolymerization of Si–O skeleton network, which in turn facilitates the easy diffusion of ions and hence precipitation of CaF$_2$ from vitreous host as evidenced from the DSC analysis. Similar investigation on crystallization kinetics of CeO$_2$-added borosilicate glass BaO–SrO–Nb$_2$O$_5$–B$_2$O$_3$–SiO$_2$ demonstrates appropriate amount of CeO$_2$ improves the crystallization of (Sr$_{0.75}$Ba$_{0.25}$)Nb$_2$O by virtue of reduced crystallization activation energy due to loosened glass structure [28].

The mean grain size of CaF$_2$ crystals in glass matrix can be computed according to Scherrer’s formula expressed by

$$D = \frac{k\lambda}{\beta \cos \theta},$$

(2)

where $D$ is the average particle diameter (nm), $k$ is a constant taking 0.89, $\beta$ represents the full width at half

Figure 4: XRD patterns of glass ceramics doped with various content of CeO$_2$ heated at different temperature.

Figure 5: Calculated crystal size of glass ceramics containing varied CeO$_2$ heat treated at 570°C, 600°C, and 650°C, respectively.
maximum (FWHM) of characteristic peak, $\lambda$ is the X-ray wavelength of Cu Kα radiation ($\lambda = 0.154056$ nm), and $\theta$ is the Bragg diffraction angle. The average size of CaF$_2$ crystal was estimated and plotted versus CeO$_2$ content in Figure 5 by using (2) from FWHM of the stronger diffraction peaks positioned at the smaller Bragg angle considering correction from the instrumental broadening created using silicon reference curve. As shown in Figure 5, the computed grain size of CaF$_2$ is less than 50 nm that can be considered as magnitude of nanoscale. For any group undergoing the same heat treatment, the crystal size increases firstly and then begins to decline as CeO$_2$ concentration exceeds 0.8 mol% for the reason of structural speciation as described above. Additionally, the crystalline grain size is positively correlated to heat treatment temperature.

Since fluorine itself can act as effective nucleating agent [52, 53], the strong field strength of calcium ensures easy bonding with fluorine causing the precipitation of CaF$_2$ crystals. Percolation model has been applied to describe nucleation in the glass forming system which can be considered being constructed of the rigid three-dimensional network with modifier-rich floppy region percolating in it. According to this model, the nucleation will occur in case the size of floppy regions exceeds the critical nucleus size and the nucleus will subsequently grow up while heating. The maximum size of floppy regions and hence the crystal size increase with the decreasing covalent bonds number per the network former on account of increased NBOs [54]. As aforementioned, doping CeO$_2$ results in connectivity of skeletal network gradually lowering to a minimum and then picking up a reversal rise. The evolution of network connectivity signifies the changing size of floppy region that have significant influence on the nucleation and growth of CaF$_2$. It is has been proposed that the crystal size is independent on treating temperature and duration because a diffusion-barrier layer is formed around the precipitated CaF$_2$ crystallite hindering its further growth [54]. However this is not the case for the studied glass system as shown in Figure 5, and it may be attributed to the much less CaF$_2$ content than reported elsewhere that is not enough to cause drastic decrease in viscosity of residual glassy phase around the formed crystallite.

3.4. Morphology. Figure 6 displays the morphology images of glass ceramics containing varied content of CeO$_2$. Numerous precipitated crystals shaped in sphere are observed to embed dispersedly in the glassy matrix. Though the visualized grain size seems bigger than the XRD Scherrer estimate likely due
to the attached glassy residue and particle agglomeration, it is of similar size scale to the XRD estimate. The particle size is observed to increase and then drop down with increasing CeO$_2$ content for samples treated at the same temperature, and the variation trend in grain size as function of CeO$_2$ content is consistent with the XRD result. Furthermore, it is evident from the morphologies of the group treated at 600°C that grain size increases with CeO$_2$ addition until reaching the maximum for GC0.8/600, where the precipitated crystalline grains are observed to get agglomerated to reduce system Gibbs free energy. Furthermore, elevating treating temperature helps with the growth of crystals significantly as evidenced from the larger grain size treated at 650°C than at 600°C for both GC0.8 and GC1.2.

3.5. Transparency. According to Beer-lambert law, glass transmittance $T$, which is defined as the intensity ratio of the transmitted light to the incident light, has logarithmic dependence on the product of the absorption coefficient of the substance, $\alpha$, and the path length, $l$. The numerical relation is normally written as

$$\ln T = -\alpha l. \quad (3)$$

In view of the difference in thickness from each other of the as-prepared samples, for the sake of an easy comparison, we tend to use absorption coefficient instead of transmittance to evaluate the transparency because the sample thickness is taken into account. Higher absorption coefficient means better transparency and vice versa.

**Figure 7:** Curves of absorption coefficient as function of wavelength for (a) the precursor glasses and the glass ceramics heated at (b) 570°C, (c) 600°C, and (d) 650°C.
Figure 7 depicts the absorption coefficient as function of wavelength with the inset photographs for the studied parent glasses and the corresponding glass ceramics. In general, the glass ceramics allow for transmission mostly in visible light range (390–780 nm) but strong absorption of UV light (190–390 nm). The wavelength of absorption edge is red-shifted with the increase of the CeO₂ concentration as well as the grain size. As revealed in Figure 7, the wavelength of absorption edge is the shortest for sample G0 free of cerium but is the longest for GC0.8 containing the biggest grains of each group. Red-shift of absorption edge induced by cerium is jointly attributed to $4f^1 \rightarrow 4f5d^1$ transitions of Ce$^{3+}$ and charge-transfer transitions between Ce$^{4+}$ and Ce$^{3+}$ [45], while red-shift arising from the increase of crystallite size may be correlated to the displacement of the scattering spectrum to longer wavelength.

Addition of CeO₂ in silicate glass results in absorption edge red-shift extending to visible range (~500 nm) [4], absorption coefficient increases gradually with the raised CeO₂ content yellowing the glassy matrix. As displayed in Figure 7, samples GC1.2 doped with the maximum content of CeO₂ exhibit a broad absorption band close to the spectrum of yellow light. Meanwhile absorption coefficient also increases with the elevation of treating temperature, and it can be ascribed to the light scattering loss caused by refractive index gap between crystallite and vitreous host. Transparency, in analogy to other features such as network connectivity, thermodynamic parameters, and crystal size, exhibits nonlinear variation as function of doped CeO₂. Specifically, sample GC0.8 doped with lower cerium as compared to GCl.2 contains the largest crystallites and hence possesses the highest absorption coefficient of each group treated at 600°C and 650°C, respectively. For the studied system, glass ceramic doped with high CeO₂ and treated at high temperature may deteriorate its transparency, and thus content of doped CeO₂ just below 0.8 mol% in the studied composition and treating temperature at about 600°C may be optimal for the synthesis of boroaluminosilicate glass ceramic with satisfying transparency.

4. Conclusion

Glass ceramics containing CaF₂ nanocrystal with composition of 54SiO₂–10B₂O₃–13Al₂O₃–14Na₂O–3ZnO–2Li₂O–4CaF₂ doped with 0–1.2 mol% CeO₂ were prepared through isothermal crystallization. In the studied system, CeO₂ in polyvalent states acting as network modifier leads to disruption of the silicate network and the conversion of [BO₃] to [BO₄]. Glass transition temperature as well as the crystalization temperature decreases firstly and then increases with the increase of CeO₂ content. Correspondingly, the size of precipitated CaF₂ crystals and the absorption coefficient of the glass ceramics are found to pass through a maximum and then decrease with increasing CeO₂ addition. The increase of CeO₂ concentration and elevation of treating temperature can lead to red-shift of absorption edge and transparency deterioration of glass ceramics. It is proposed that the opposite effects of CeO₂ addition on silicate and borate network in boroaluminosilicate glass lead to the nonlinear variations in structure, crystallization, and thermodynamic and optical features.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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