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Effects of doping CeO_2/TiO_2 on structure and properties of silicate glass

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ABSTRACT

In order to elucidate the effects of doping CeO_2/TiO_2 on the structure and physical properties of silicate glass, glasses with composition $72SiO_2–3Al_2O_3–10Na_2O–10K_2O–5CaO$ doped with varied ratios of CeO_2/TiO_2 were synthesized by melt-quenching method and were characterized by X-ray diffraction, infrared and Raman spectrometry, UV–Visible spectrophotometry and micro-indentations. X-ray diffraction conforms the amorphous state of doped glasses. The spectroscopic analysis reveals that doping CeO_2 alone results in depolymerization of glass network and narrowed distribution of Q^n (Si–O tetrahedral with n bridging oxygen atoms), while doping TiO_2 singly or combined with CeO_2 favors the enhanced polymerization of network and regains a broader Q^n distribution relative to doping CeO_2 alone. It is proposed that doped cerium and titanium in glass exists in multivalent state and the former in presence of trivalent state preferentially acts as modifier inducing network depolymerization, whilst the latter in form of tetrahedral tends to interconnect network units as intermediate. Doped cerium in trivalent state contributes mainly to the red-shift of absorption edge while titanium suppresses such change of absorption band. Either adding cerium alone or co-doping with titanium will result in decreased optical band gap due to the structural modifications. The relatively loosened structure due to depolymerization induced by cerium is responsible for the decline in hardness and E-modulus but rising in fracture toughness, whereas network compactness by virtue of interconnectivity of titanium and structural densification may account for the increase of hardness and E-modulus at the cost of slight loss of fracture toughness. For silicate glasses co-doped cerium and titanium, the mechanical properties should be the synergy of the two opposite mechanism.

1. Introduction

It is well established that irradiation results in damage in glass materials used in harsh irradiative environment and consequently their performance deteriorations [1,2]. Optical apparatus in aerospace, nuclear industry as well as military or medical applications require stable optical properties when subjected to various particle irradiations [3]. Irradiation resistant glass is one of the specialized optical glasses distinguished by steady performances especially the minimized decline in transmittance in visible range when undergoing irradiation of high energy particle or rays. Appropriate stabilizers such as transition metal and rare earth oxides are conventionally introduced into glass matrix to improve the irradiation resistance of glass [4,5], among which CeO_2 is the most common one. Cerium presents in glasses two different valence states, namely Ce^{4+} and Ce^{3+}, because there exist a ceric–cerous redox equilibrium in the glass structure. The possible role of irradiation protection that CeO_2 plays in glass shows up as follows: Ce^{3+} capture holes and Ce^{4+} trap electrons produced by irradiation individually to avoid their recombination, hence obstruct the formation of permanent defect centers [6].

In spite of the modification of irradiation resistance in glass, the added CeO_2 can make change to the intrinsic color of glass by enhancive yellowing with increasing addition amount. To avoid this negative effects, the amount of added CeO_2 should be minimized to the greatest extend [7]. It had been proposed co-doping of CeO_2 and TiO_2 provides glass more effective radiation resistance with respective to single doping of CeO_2 and is adjustable in glass coloration [8], however CeO_2/TiO_2 co-doped glass with excessive incorporation of TiO_2 will aggravate the coloration of glass ascribe to the fact that TiO_2 can reduce ceric to cerous and that cerium ions is apt to form color center in glass. So far, explanations for the effects of doping TiO_2, CeO_2 on glass coloration as well as therein reaction features remain sharp controversial. It has also been hypothesized that TiO_2, as a modifier, can suppress reduction of

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Ce^{4+} to Ce^{3+}. However, some objections suggested that CeO_2 as a strong oxidant can easily reduce Ti^{4+} to Ti^{3+} in favor of reduction of Ce^{4+} to Ce^{3+} [9]. Moreover, one view suggested that, in combined incorporation of cerium and titanium oxides, only a limited part of the titanium in the form of $[TiO_4]$ tetrahedrons can be incorporated in the silicon–oxygen structural network, instead complex oxide $Ce_xTi_yO_z$ clusters formed in glass by cerium and titanium ions [10], nevertheless, another hypothesis demonstrated that in silicate glasses because of the random network model of $[SiO_4]$ tetrahedral, Ti^{4+} ion even having greater ionic radii could form tetrahedra and enter into the network resulting in a random packing of tetrahedral [11].

The objective of this study is in attempt to elucidate the effects of doping CeO_2 combined with TiO_2 on the physical properties of silicate glass and to illustrate the correlations between dopant induced structural change and the physical performances.

2. Experimental

2.1. Glass preparation

The glass samples were synthesized by conventional melt-quenching method using analytical pure reagents SiO_2, $Al(OH)_3$, Na_2CO_3, K_2CO_3, $CaCO_3$, CeO_2 and TiO_2 as starting materials to avoid introducing impurities that affect results analysis, base glass with a fixed composition $72SiO_2–3Al_2O_3–10Na_2O–10K_2O–5CaO$ (molar ratio) system was previously prepared by ball-milling the compounded ingredients for 1 h, subsequently doped mixtures were fabricated by adding varied ratio of CeO_2 and/or TiO_2 powder to appropriate amount of base glass. For each composition, 240 g batch in a platinum crucible was heated to 800 °C with a 30 min dwell followed by raising the temperature to 1500 °C and holding at this temperature for 5 h, afterwards the melt was poured into a preheated steel mold and further annealed in a muffle furnace at 550 °C for 1 h prior to cooling down to room temperature slowly. The as-prepared glass discs were polished with SiC papers up to 1200 grit, ultrasonically cleaned in acetone and anhydrous ethanol respectively, then washed with distilled water for further measurements. Nomenclature of individual glass sample was given by a notation as Ce(a)Ti(b), where a, b describes the batched extra dopant molar fraction of CeO_2 and TiO_2 over the base glass (keeping the ratio of base components constant), respectively.

2.2. XRD measurements

X-ray diffraction (XRD) analysis was used to confirm the amorphous state of as-prepared glasses. The XRD spectra was recorded within Bragg angle 2θ from 5° to 80° in a diffractometer (D/MAX-IIIA) using Cu Ka radiation with a scanning speed of 0.05° per second.

2.3. Spectroscopic analysis

Infrared (IR) spectra measurements of the glasses from 400 to 4000 cm^{-1} were performed at room temperature by a Nicolet1s10 Fourier transform infrared spectrometer (FTIR) using the standard KBr pellet method. The pellets were previously prepared by tightening a specialized screw mould containing a mixture of 200 mg anhydrous KBr and 1.5 mg glass powder sieved through a 200 mesh screen, then the screw mould with the prepared clear homogeneous disk was placed in the light path immediately for measurements.

Raman spectra in the range of 200–2000 cm^{-1} were recorded at room temperature on a Labram HR800 micro-spectrometer using the 514.5 nm line of an Ar^+ laser. The focused laser beam was incident on the glass surface perpendicularly, the measured power was 5 mW and the resolution of the system is less than 1 cm^{-1}.

2.4. Physical properties characterization

The transmittance versus wavelength of each glass 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. In accordance with the Beer–Lambert law, the linear absorption coefficient (α) was calculated from transmittance data for each glass using Eq. (1), where α is linear absorption coefficient (cm^{-1}), t is the thickness(cm), and T is transmittance (%):

$$\alpha = \frac{-\ln T}{t} \tag{1}$$

A microindenter system (MT nanotest, MML.UK) was employed to conduct indentation tests with a Berkovich (three-sided pyramidal) diamond indenter, the loading and unloading rate were set equal with a dwell duration of 30 s at maximum load, depth vs. load were recorded throughout the test, and the hardness and elastic modulus of the glass were respectively determined by Eqs. (2) and (3) based on Oliver and Pharr method [12], where P is the maximum load, A is the projected contact area, dP/dh represents the slope of the initial portion of the unloading curve. Since specimens were finely polished using SiC paper, any residual surface compression effects due to surface grinding were minimized by annealing the glasses again in a muffle furnace at 550 °C for 30 min, followed by slow cooling [13].

Separate miniload indentation tests (maximum load set to 500 mN and loading/unloading rate 5 mN/s) with impressions free of cracks were previously carried out to measure the hardness H and elastic modulus E. Subsequently high load indentation with cracking in the impression was made for individual glass samples to determine K_{IC}, the load was set to 5 N and the loading/unloading rate 50 mN/s. Once the residual indentation impression was made, the in situ optical measurement of crack size was simultaneously performed and K_{IC} was calculated using Eq. (4) [14], where x_v is 0.015, a is length measured from the center of the indentation to the crack tip, l is the radial length of crack, c is length measured from the center of contact to the end of the corner radial crack. Above tests were repeated five times at various positions for each sample and the results were averaged to an end result with standard deviation value.

$$H = \frac{P}{A} \tag{2}$$

$$E = \frac{dP}{dh}\frac{1}{2}\frac{\sqrt{\pi}}{\sqrt{A}} \tag{3}$$

$$K_{IC} = 1.073x_v(a/l)^{1/2}\left(\frac{E}{H}\right)^{2/3}\frac{P}{c^{3/2}} \tag{4}$$

3. Results

3.1. Phase structure analysis

The XRD patterns of the studied glasses displayed in Fig. 1 reveal no obvious peaks or lines associated with any crystalline phase confirming the amorphous states for the formed glasses, it has been considered that the introduced dopants cerium, titanium that are characteristic of strong clustering behavior due to their large ionic radii and electron densities tend to induce crystallization in glass melts, however this effect did not evidently affect amorphous glass forming in this study. In addition, a broadened dissemination peak for each pattern reflects commonly the nature of glassy substance, it weakened in intensity with 2θ centered at range of 26–28° corresponding to the (1 0 1) crystal plane of alpha quartz (JCPDS01-0649) stemming from the crystalline silicon raw materials, this phenomenon is consistent with the classical random network theory on glass structure proposed by Zachariasen. According to this theory, the glass builds its structure by highly

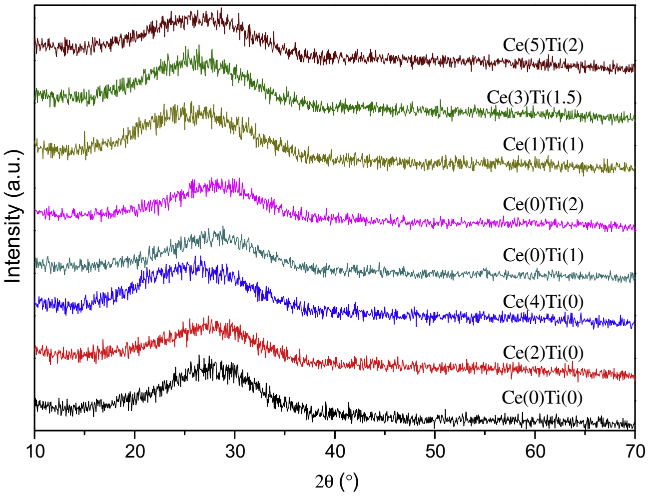

Fig. 1. XRD patterns of pristine and doped glasses with various content of CeO_2/TiO_2.