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Non-bridging oxygen dependent redox and spectroscopic properties of Cu species in phosphosilicate glasses

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ABSTRACT

We reported a series of phosphosilicate glasses containing different Cu species (Cu^0, Cu^+ and Cu^{2+}). With X-ray diffraction (XRD), Transmission electron telescope (TEM), and absorption spectra (UV–Vis), Cu^0 NPs and Cu^+ were identified in the glasses with low Cu concentrations (0.02; 0.04; 0.1 mol%), and Cu^+ and Cu^{2+} were identified in the glasses with high Cu concentrations (0.2; 0.4; 0.6 mol%). Raman spectra gave a clue that the quantity of non-bridged oxygens were related with the oxidation of $Cu^+ \rightarrow Cu^{2+}$ at high Cu concentration. With photoluminescence spectra(PL) and time resolved decay spectra, different Cu^+ sites were discovered with octahedral coordination predominantly with different tetragonal distortions, and ETs from Cu^+ to Cu^{2+} were also revealed with proposed mechanisms. The study in understanding the structural effect of Cu-doped glass on luminescence would be an important step towards the rational design of transition metal doped luminescent glasses for various applications.

1. Introduction

Introducing noble metal copper (Cu) into glass is currently of great interesting for applications such as nonlinear optics, solar cell technology, and photonic devices [1–5]. Cooper may exist as Cu^0, Cu^+ and Cu^{2+} in glass matrix, and also possibly forms Cu^0 nanoparticles (NPs), so giving rise to a great variety of optical features [6]. Glasses containing Cu^0 NPs are promising materials for the rapidly developing filed of optical switching devices due to their wide range of resonant absorption frequencies, ultrafast time response, as well as large third-order nonlinear optical coefficients associated with the surface plasmon resonance (SPR) of metal nanoparticles in the visible region [7,8]. Equally important, luminescent glasses containing monovalent Cu, which have been studied in the past years for utilization in tunable lasers, have been recently the subject of investigation as considered for optical fibers and photonic waveguides [9–14]. However, the valent state of Cu is very sensitive to the substrate composition as well as to the doping route, and relatively high Cu doping levels usually lead glasses loss their transparencies and homogeneities, thus disabled in many performances. Then, how to homogenously disperse monovalent Cu in the glass hosts with a heavily doping level has always been an urgent subject to be resolved in related fields.

To avoid elaborate procedures to prepare Cu^+-doped glass under controlled reducing, or inert atmospheres, Cu+ doped glasses could be prepared in air with facile procedures by introducing a suitable amount of tin oxide [15–18]. Consequently, to study Cu species in the glass system without tin oxide under air atmosphere will give significant reference to the glass system including tin oxide. Therefore, we mainly investigate spectroscopic properties of different Cu species in $41Si_2O{-}4P_2O_5{-}6K_2O{-}22MgO{-}22CaO{-}5Al_2O_3{-}xCu$ glasses prepared under air atmosphere. The valent change of $Cu^0 \leftrightharpoons Cu^+ \leftrightharpoons Cu^{2+}$ and the formation of Cu^0 NPs are deeply studied by microstructural and spectral analysis. The relationship between a stable monovalent Cu specie and its coordination environment is also proposed to give constructive ideas for precisely control the valency and distribution of Cu species in the glass prepared under air atmosphere.

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2. Experimental

2.1. Materials and synthesis of the Cu-doped phosphosilicate glasses

A series of phosphosilicate glasses with compositions list in Table 1 were prepared via a melt-quenching method by using high-purity SiO_2, $NH_4H_2PO_4$, K_2CO_3, MgO, $CaCO_3$, Al_2O_3, and Cu_2O as raw materials. The mixture of the raw materials were melt at the temperature of 1450 °C for 1 h in a corundum crucible in air. Then the batch-free glass melt were poured onto a cold brass plate and pressed by another brass plate. All the glass samples as melt were polished to 1 mm thick for the spectroscopic measurements.

2.2. Characterization

The X-ray diffraction (XRD) analysis of the glasses were performed on a PANalytical B.V Empyrean 2008 95 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å) and scan speed of 2.00 deg/min. All the glasses were subjected to differential thermal analysis (DTA) measurements conducted on CDR-1 differential thermal analyzer. Transmission electron microscope (TEM) images were obtained from a FEI Tecnai G2F20 field emission transmission electron microscope operating at an acceleration voltage of 200 kV. Raman spectra were taken on the samples using OMNIC Dispersive Raman (Thermo Fisher Scientific, USA) with a DXR LASER OPERATING at 532 nm with incident power of 10 mW. The optical absorption spectra were recorded on a Hitachi U-4100 UV–Vis–NIR spectrophotometer. Photoluminescence (PL) spectra and time resolved spectra (TRES) were measured on an Edinburgh FLSP920 spectrometer equipped with a Xe-lamp and a μs flash lamp as excitation sources. All spectroscopic measurements were performed at room temperature.

3. Result

DTA curves (Fig. 1(a)) showed the glass transition temperature (T_g) locating around 720 °C and two overlapping exothermic crystallization peaks locating at the temperature range from 900 °C to 1000 °C. The glass transition temperature (T_g) slightly decreased with increasing the copper doping level due to the modification role of copper ions (Cu^+ or Cu^{2+}) to the phosphosilicate glass matrices. X-ray diffraction analysis (Fig. 1(b)) showed that all the glasses with different copper content were completely amorphous. The introduction of low copper content of copper into the glasses (GCu0.02, GCu0.04, GCu0.1), caused the glasses appearing reddish color owing to the formation of Cu^0 NPs. HRTEM images (Fig. 1 (c) and (d)) of glass GCu0.04 reveal some lattice fine structures assigned to crystalline Cu^0 NPs with sizes around 2 nm, where the magnified HRTEM image (Fig. 1 (d)) clearly exhibited the lattice fringes of Cu^0 (111) planes. With Fast Fourier Transform methods, the interplanar spacing of Cu^0 (111) was evaluated as 0.209 nm, matching well with the standard value of JCPDS card #04-0836.

The Raman spectra for the glass with different Cu concentration from 0.02 mol% to 0.6 mol% were depicted in Fig. 2. As can be noted, the whole Raman spectral range between 200 cm^{-1} and 1200 cm^{-1} was composed of three regions, i.e., 800–1200 cm^{-1}, 600–800 cm^{-1} and 200–600 cm^{-1}. In the region of 800–1200 cm^{-1}, a shoulder at ~1000 cm^{-1} and a peak at ~960 cm^{-1} can be observed, which can be attributed to the Q^1 (P) (PO_4 tetrahedron with one bridging oxygen), and Q^0 (P) (PO_4 tetrahedron with zero bridging oxygen) units [19]. There are four possible structural units associated with PO_4 tetrahedron may exist in the melt with different numbers of bridging oxygen per P, namely Q^3 (P_2O_5), Q^2 (PO_3^{2-}), Q^1 ($P_2O_7^{4-}$) and Q^0 (PO_4^{3-}), denoted as Q^i(P) ($i = 0$, 1, 2, 3). In addition, the five structural units related to SiO_4 tetrahedron were denoted as Q^i (Si) ($i = 0, 1, 2, 3, 4$). The 600-800 cm^{-1} band was associated with the presence of Si–O stretching linkages. Besides, the peak around 470 cm^{-1} was assigned to the bending mode P–O–P bending.

Fig. 3(a) showed absorption spectra of phosphosilicate glasses with low Cu concentration (0.02; 0.04; 0.1 mol%), where the absorption bands could be mainly assigned to Cu^+ and Cu^0 nanoparticles (NPs). The absorption band centered at 280 nm was arising from the Cu^+: $^1A_g \rightarrow {}^1E_g'$ transition [12], as shown in Fig. 3(c). The small absorption bands at 570 nm had the typical feature of the surface plasmon resonant (SPR) absorption of Cu^0 NPs, agreeing well with the previous literature [6,20,21], suggesting the formation of Cu^0 NPs via the reduction of Cu^+ and aggregation of Cu^0. With increasing Cu concentration up to 0.1 mol%, the absorption intensity at 570 nm were strengthened, while GCu0.1 had an extra absorption band centered at 310 nm due to the charge transfer of $O^{2-} \rightarrow Cu^{2+}$, indicating the oxidation of $Cu^+ \rightarrow Cu^{2+}$. The formation of Cu^{2+} in GCu0.1 was also approved by another broad absorption band. The similar broad band of Cu^{2+} were also observed on the absorption spectra of the glasses with high Cu concentration (Fig. 3(b)). And such broad band was ascribed to the $^2B_{1g} \rightarrow {}^2B_{2g}$ intraconfiguration (d–d) transition [22], as shown Fig. 3(d). In contrast, the glasses with high Cu concentration (0.2; 0.4; 0.6 mol%) only had absorption bands assigned to Cu^+ and Cu^{2+} without any features of Cu^0 NPs, indicating the absence of the Cu^0 specie at higher Cu concentration conditions. The redox of $Cu^0 \leftrightharpoons Cu^+ \leftrightharpoons Cu^{2+}$ was responsible for the red → blue color change of the glasses with increasing Cu concentration.

Fig. 4 showed the photoluminescence (PL) excitation and emission spectra of the glasses with different Cu concentration. Similar with the absorption spectra, the excitation spectra of all the glasses exhibited bands around 280 nm assigned to Cu^+: $^1A_g \rightarrow {}^1E_g'$ transition. With increasing Cu concentration up to 0.2 mol%, another bands appeared at about 320 nm related to the $O^{2-} \rightarrow Cu^{2+}$ charge transfer bands. On the emission spectra, the broad emission band centered at 490 nm were attributed to the Cu^+: $^3E_g'' \rightarrow {}^1A_g$ transition. As Cu concentration increasing to 0.2 mol%, the emission intensity was weakened remarkably. In particular, the emission of GCu0.1 displays a shoulder to the low-energy side around 580 nm, due to the SPR absorption of Cu NPs which located around 580 nm (Fig. 3(a)). Fig. 5 depicted the emission spectral dependence on the excitation wavelength for the sample GCu0.4. Increasing the excitation wavelengths from 280 nm to 360 nm produced a series of emission association with the maximum of the spectrum varying from 490 nm to 580 nm. The inset normalized spectra illustrated such obvious redshift of the emission peak wavelength.

Fig. 6 showed the PL decay spectra of the glasses by excitating at 280 nm and monitoring Cu^+: $^3E_g'' \rightarrow {}^1A_g$ emission at 490 nm. For non-exponential decays, the mean lifetime could be determined by Eq.

Table 1
Composition of the glass samples (mol%).

Sample	SiO_2	P_2O_5	K_2O	MgO	CaO	Al_2O3	Cu_2O
GCu0.02	41	4	6	22	22	5	0.02
GCu0.04	41	4	6	22	22	5	0.04
GCu0.1	41	4	6	22	22	5	0.1
GCu0.2	41	4	6	22	22	5	0.2
GCu0.4	41	4	6	22	22	5	0.4
GCu0.6	41	4	6	22	22	5	0.6