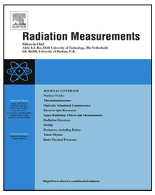
Radiation Measurements xxx (2017) 1–5

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas



X-ray induced luminescence of Sn^{2+}-centers in zinc phosphate glasses

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HIGHLIGHTS

- We prepared Sn-doped ZnO-P_2O_5 glasses by a melt-quenching method in Ar atmosphere.
- X-ray induced scintillation and storage luminescence of the glasses were investigated.
- The ZnO-P_2O_5 glass with the smaller Zn/P ratio shows better emission properties.

ARTICLE INFO

Article history:
Received 14 September 2016
Received in revised form
19 January 2017
Accepted 27 January 2017
Available online xxx

Keywords:
Sn^{2+} center
Phosphate glasses
Emission properties

ABSTRACT

Photo- and X-ray induced luminescence properties of Sn^{2+}-doped zinc phosphate glasses with different chemical compositions were investigated. Decay constants of the glasses decrease with increasing the ZnO amount, which are independent of excitation light sources. By comparison of emission properties, we have found that the glass structure affects both luminescence properties. The broader emission band in the P_2O_5-rich glasses suggests that the site variation of Sn^{2+} centers is mainly due to the P_2O_5 sub-networks. It is expected that the P_2O_5 sub-networks are effective for not only photoluminescence but also the X-ray induced radio-luminescence and storage luminescence.

1. Introduction

Phosphate glasses are interesting amorphous materials because of their large glass formation region, the low glass transition temperature, T_g, the excellent transparent window from UV to near IR region, and the good dissolubility of activators compared with conventional SiO_2 glasses (Seshadri et al., 2014; Abdelghany and Hammad, 2015). Since the pure phosphate (P_2O_5) glass possesses the low-chemical durability, *i.e.* water-resistance, an addition of various metal oxides, such as ZnO, Al_2O_3 and MgO, has been employed to bring changes of the network structure, resulting in the improvement of the chemical durability (Azmi et al., 2015).

ZnO-P_2O_5 glasses are thought to be candidates for Pb-free low-melting glass because they generally possess the low T_g (Tischendorf et al., 2001; Morena, 2000). On the other hand, it has been reported that the main glass network of ZnO-P_2O_5 binary glasses constituted by the PO_4 sub-networks is changed into the ZnO sub-networks around the zinc pyrophosphate chemical composition. It is because not only P_2O_5 units but also ZnO units can form covalent random network, although the network forming ability of the former is better than that of the latter. (Masai et al., submitted).

Similarly to other binary phosphate glasses, ZnO-P_2O_5 glasses are good amorphous hosts for activators. For example, ZnO-P_2O_5 glasses containing dopants are applied as optical waveguides and solid-state laser sources (Tischendorf et al., 2001). From the viewpoint of non-rare earth activators, the ns^2-type ($n \geqq 4$) emission centers can be listed as practical activators possessing high emission efficiencies. The ns^2-type cations exhibit the s-p parity allowed transition (Masai et al., 2013). Because an electron exists in the outermost shell in both the ground state (ns^2) and the excited state (ns^1np^1), their emission properties are strongly affected by the local coordination states of ns^2-type cations (Masai et al., 2012b). We have focused on the Sn^{2+} center belonging to the ns^2-type cations as an activator in glass matrixes due to the low toxicity and the most ubiquitous ions among the ns^2-type ions. Surprisingly, the quantum efficiency (QE) of Sn^{2+}-doped ZnO-P_2O_5 glasses is comparable to that of rare-earth cation-doped glasses or crystal phosphor, such as $MgWO_4$ (Masai et al., 2010). Considering the electron in the outermost shell, we regard Sn^{2+} center as a probe for

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http://dx.doi.org/10.1016/j.radmeas.2017.01.017
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Please cite this article in press as: Torimoto, A., et al., X-ray induced luminescence of Sn^{2+}-centers in zinc phosphate glasses, Radiation Measurements (2017), http://dx.doi.org/10.1016/j.radmeas.2017.01.017

revealing the correlation between the emission properties and the glass structure, including network structures of a host matrix and local structures of Sn^{2+} centers.

Recently, we have examined photoluminescence (PL) properties of 1.0Sn-xZnO-(100-x)P_2O_5 (x = 58, 60, 65, and 70 mol%) and revealed that not only the coordination states but also the site variation of Sn^{2+} centers depend on the network structure of the host matrix (Torimoto et al., 2016). Unlike PL properties which are only correlated with the local states of Sn^{2+} centers, X-ray induced luminescence properties are influenced by both the local states of Sn^{2+} centers and the host structure because the energy transfer from the host matrix to Sn^{2+} centers constitutes the emission process. Since the energy transfer process from the host matrix is affected by the network structure, it is worth investigating X-ray induced luminescence properties, for examples, X-ray induced radio-luminescence (RL), pulse X-ray induced RL emission decay profiles, and storage luminescence of Sn^{2+}-doped zinc phosphate glasses with different chemical compositions.

2. Experimental

2.1. Sample preparation

The chemical composition of the prepared glass was 1.0SnO-xZnO-(100-x)P_2O_5 (x = 58, 60, 65 and 70, in mol%). Herein, this glass system is described as Sn:xZP. According to the previous method (Masai et al., 2012a, 2016b), a mixture of ZnO (99.99%) and $(NH_4)_2HPO_4$ (99.0%) was initially calcined in an electric furnace at 800 °C for 3 h in air. The calcined solid was then mixed with SnO (99.5%) at room temperature (r.t.), and the mixture was melted at 1100 °C for 30 min in Ar (99.999%) atmosphere using a tubular electric furnace (Motoyama). The heating program has been represented in the previous paper (Masai et al., 2014). The glass melt was quenched on a stainless steel plate at 200 °C followed by annealing at the T_g for 1 h, which was measured by differential thermal analysis (DTA). After annealing, the samples were cut (10 mm × 10 mm × 1 mm) and mechanically polished to obtain a mirror surface.

2.2. Analysis

The values of T_g were determined with a TG8120 DTA system (Rigaku) operating at a heating rate of 10 °C/min. Densities were determined by the Archimedes method, using distilled water as the immersion liquid. Molar volumes were calculated by dividing the densities by each molecular weight. PL and PL excitation (PLE) spectra were recorded at r.t. using a F7000 fluorescence spectrophotometer (Hitachi High-Tech.). Slits for achieving an optical resolution of 2.5 nm were used for the excitation and emission measurements. The PL emission decay profiles at r.t. were measured using Quantaurus-Tau (Hamamatsu Photonics) with a 280 nm LED source.

X-ray induced RL spectra at r.t. were obtained with a monochromator equipped with a charge-coupled device (CCD, Andor DU-420-BU2). The supplied bias voltage and tube current were 40 kV and 0.052–5.2 mA, respectively. The irradiated dose was calibrated using an ionization chamber. Pulse X-ray induced RL emission decay profiles were investigated by afterglow characterization system (Yanagida et al., 2014). Thermally stimulated luminescence (TSL) glow curves were recorded using TL-2000 (Nano Gray) with a heating rate of 1 °C/s. The photomultiplier tube used in the instrument was Hamamatsu H7827-001. Photons longer than 500 nm were cut by a thermal radiation cut filter, and the photomultiple tube has the detection sensitivity as low as around 300 nm. Therefore, the recorded spectral range during the TSL measurement was 300-500 nm. All samples were measured immediately after irradiated 10 Gy (40 kV, 5.2 mA, for 10 min). The irradiation was done in the same way as for the measurement of X-ray induced RL spectra.

3. Result and discussion

3.1. PL properties

The all obtained glasses were transparent and homogeneous. Fig. 1 shows the value of T_g (left axis) and the molar volume (right axis) of Sn:xZP glass and Sn-free xZP glass (x = 58, 60, 65 and 70) as a function of the ZnO amount. The value of T_g becomes higher and the molar volume becomes smaller with an increase in the ZnO amount independent of the addition of Sn species. In addition, it has been proposed that the SnO-doped glass exhibits lower T_g compared with the non-doped one (Masai et al., 2016a). These tendencies support the previous result that the network structure changes within the chemical composition range (Masai et al., submitted). The decrease in the molar volume, *i.e.* the densification of the glass network, by the addition of SnO also confirms that some of Sn^{2+} cations make the glass network to be denser packing compared with the non-doped glass (Torimoto et al., 2016).

Fig. 2 shows the normalized PL-PLE spectra of Sn:xZP glass (x = 58, 60, 65 and 70). We can find that the PL peak energy is blue-shifted with narrowing the emission band, and that the PLE peak energy is red-shifted with increasing the ZnO amount. It has been previously indicated that both PL and PLE peak energies changes depending on the ZnO/P_2O_5 ratio (Masai et al., 2010). On the other hand, it has been also demonstrated that the substitution of RO (R = Mg, Ca, Sr and Ba) for ZnO does not decrease the Stokes shift (Masai et al., 2013). Thus, as long as the main phosphate network structure remains intact, the Stokes shift seems to be unaffected. Considering the dependence of PL peak width on the ZnO/P_2O_5 ratio, we assume that the site variation of Sn^{2+} becomes narrower as the ZnO ratio becomes higher. It is expected that the narrowing of PL peak of Sn^{2+} is due to the formation of the ZnO sub-networks and the concurrent shortening of the phosphate sub-networks (Masai et al., submitted) because the phosphate domains have an affinity to cationic Sn^{2+} emission centers.

The PL emission decay profiles of the Sn:xZP glass (x = 58, 60, 65 and 70) are shown in Fig. 3(a). The monitored energies correspond to the peak energy shown in Fig. 2, and the excitation energy (280 nm, 4.4 eV) is almost the same as the observed PLE peak of Sn^{2+} centers. The decay constants in the order of microseconds correspond to the relaxation from T_1 to S_0 state of the conventional Sn^{2+} centers (Jimenez and Zhao, 2014; Leskelä et al., 1985; Reisfeld et al., 1975; Ropp and Mooney, 1960). However, these decay constants are different, although these decay profiles exhibit the

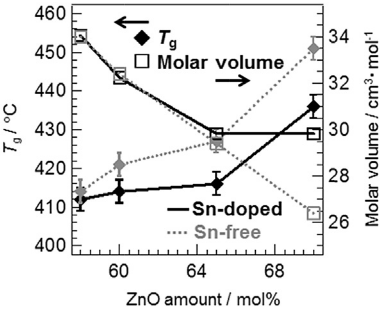

Fig. 1. T_g (left axis) and molar volume (right axis) of Sn:xZP glass and Sn-free xZP glass (x = 58, 60, 65 and 70) as a function of ZnO amount.

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