

Nucleation and crystallization behavior of RE – doped tellurite glasses

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Abstract. The microstructure and crystallization of the glasses with composition $(100-x-y)\text{TeO}_2-x\text{PbO}\cdot\text{P}_2\text{O}_5-y\text{PbF}_2:z\text{MF}_3$ ($\text{M}=\text{Er}, \text{Eu}, \text{Nd}$; $x=42.5-30$, $y=5-30$, $z=0.5-3.0$) were investigated by transmission electron microscopy (TEM) and luminescence methods. It was found that the doping with the rare-earth (III) fluorides promoted nucleation in the bulk glasses. The sizes of generated particles are about 2–5 nanometers and their shapes are close to spherical. The growth rate of crystallites depended on the lead fluoride content and glass forming rate. The heat treatment of the samples promotes the glass ceramic formation, where the crystalline phase is $\text{Pb}_2\text{P}_2\text{O}_7$.

1. Introduction

Tellurium dioxide based glasses are of increasing interest due to a possibility of their application as components of the optical data storage devices and telecommunication systems [1, 2]. It is possible to use these glasses in production of lasers because of the high solubility of rare-earth ions and relatively low phonon energy among oxide glass-formers [3]. Doped glass ceramics are the most perspective materials for these applications. Rare-earth fluorides often act as nucleating centers [4].

Preparation of oxyfluoride glasses in the ternary system $\text{TeO}_2\text{-PbF}_2\text{-CdF}_2$ was reported previously [5]. Recently the $\text{Pb}(\text{PO}_3)_2\text{-TeO}_2$ glass system was studied in the whole range of glass composition [6]. Furthermore, a glass formation of the $\text{TeO}_2\text{-PbO}\cdot\text{P}_2\text{O}_5\text{-PbF}_3:\text{MF}_3$ system was investigated [7].

We analyzed in [7] the thermal properties and the ionic mobility in the system $\text{TeO}_2\text{-PbO}\cdot\text{P}_2\text{O}_5\text{-PbF}_3:\text{MF}_3$ ($\text{M}=\text{Er}, \text{Eu}, \text{Nd}$) by the DTA and NMR methods. This paper is a continuation of the work mentioned above. Our purpose was to consider an effect of the rare-earth (III) fluorides on crystallization of the $\text{TeO}_2\text{-PbO}\cdot\text{P}_2\text{O}_5\text{-PbF}_3:\text{MF}_3$ system.

2. Experimental section

Glass samples compositions of $(100-x-y)\text{TeO}_2-x\text{PbO}\cdot\text{P}_2\text{O}_5-y\text{PbF}_2:z\text{MF}_3$ ($\text{M}=\text{Er}, \text{Eu}, \text{Nd}$, $x=42.5-30$ mol. %, $y=5-30$ mol. %, $z=0.5-3.0$ mol. %) were examined. Influence of rare-earth fluorides concentration on glass nucleation was investigated. Samples contained 5 and 20 mol. % of PbF_2 for



52.5TeO₂-42.5PbO·P₂O₅-5PbF₂ and 45TeO₂-35PbO·P₂O₅-20PbF₂, respectively, were doped with 0.5÷3.0 mol. % of ErF₃ (in addition to 100 % of the basic glass). Reagents preparation, glass synthesis, data of differential thermal analysis (DTA) and X-ray diffraction (XRD) discussed in more details in [Ошибка! Залкада не определена.].

2.1. Samples preparation

Thin plates of glasses were prepared by two techniques: 1) slow cooling to the room temperature of the glass melt that was poured on a bulky nickel plate heated to the temperature below then T_g on 10÷15 °C (to 220-300°C against to constitution); 2) fast cooling between two cold nickel plates.

2.2. Luminescence spectra

Luminescence spectra were recorded in the IR region on spectrometer SDL-1 (Russia). Xenon lamp DKsSH-150 with combined filter SZS23+SZS25 was used for illumination of the samples. Luminescence intensity was measured on 1054 and 1550 nm for Nd(III) and Er(III), respectively. Visible spectra of the glasses were recorded on RF-5301 (Shimadzu, Japan) at 300 K.

2.3. TEM

TEM images were obtained using Libra-200 (Carl Zeiss, Germany). Samples preliminarily were dispersed in acetone through the Bandelin Sonopuls HD-2070 (Germany) with wedge-shaped tip MS-73. Ultrasonic dispersing mode was 30 min and 5 cycles. Droplet of this dispersion was placed onto a cooper grid covered with an amorphous polymer formvar and dried at 40 °C.

3. Results

Compositions and thermal properties of the samples (100-x-y)TeO₂-xPbO·P₂O₅-yPbF₂ : zMF₃ (M= Er, Eu, Nd, x=42.5-30 mol. %, y=5-30 mol. %, z=0.5-3.0 mol. %) were considered in [Ошибка! Залкада не определена.]. Their x-ray amorphous structures confirmed the existence of glassy phases. All glass samples with 5 mol. % of rare-earth (III) fluorides were transparent and slightly yellow. The color became slightly pink after erbium fluoride doping, light violet with the addition of neodymium fluoride and slightly green in the case of europium fluoride.

The 52.5TeO₂-42.5PbO·P₂O₅-5PbF₂ glass remained transparent with addition up to 2.0 mol. % of ErF₃. Thickness of these samples was 3 mm. The opaque appeared after introduction of 3.0 mol. % of ErF₃. Compositions with 20 mol. % of PbF₂ showed opalescence after addition of 1 mol. % of erbium fluoride (thickness of the glasses was ~ 4 mm). Further ErF₃ doping up to 2.0 mol. % led to non-transparency of the samples.

The effect of non-transparency indicates indirectly on the formation of crystallites in the bulk of glass. It is interesting to note that it was impossible to recognize crystallization visually. XRD data confirmed amorphous structures of the samples.

According to luminescence data increasing the PbF₂ (figure 1) and rare-earth (III) fluorides (figure 2) concentrations led to rise of both neodymium(III) and erbium(III) luminescence intensity in the IR range. Similar dependence observed for europium(III) luminescence in the visible range (figure 3). Luminescence of erbium(III) at typical wavelength of 550 nm was very weak. But another intensive emission band appeared at 450 nm. The ErF₃ doped glasses didn't show visual luminescence under UV exposure.

Increasing of luminescence intensity evidences that crystallite structures appear in samples and rare-earth ions segregate into crystallite particles. These particles must be nanosized due to the absence of crystal phases on XRD spectrum.

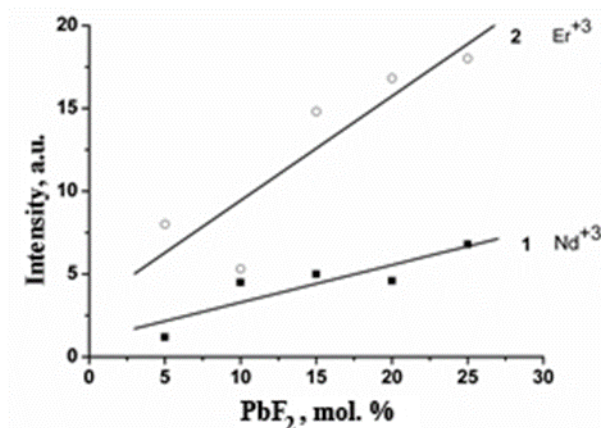


Figure 1. Dependences of the luminescence intensities at wavelengths 1054 (Nd^{3+}) and 1550 (Er^{3+}) nm on PbF_2 concentration in the samples $(100-x-y)\text{TeO}_2-x\text{PbO}\cdot\text{P}_2\text{O}_5-y\text{PbF}_2:0.5\text{MF}_3$ ($\text{M}=\text{Er}, \text{Nd}$, $x=42.5-30$, $y=5-30$ mol. %)

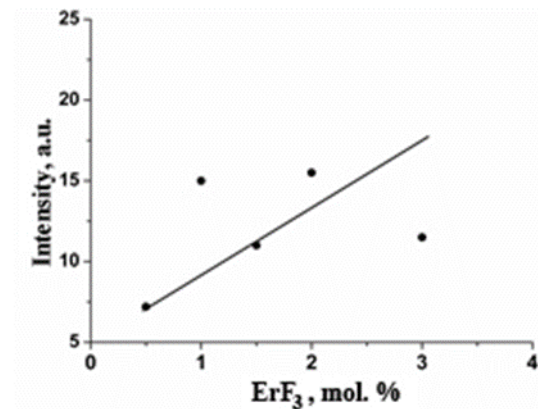


Figure 2. Dependence of the luminescence intensities at wavelength 1550 nm (Er^{3+}) on ErF_3 concentration in the samples $52.5\text{TeO}_2-42.5\text{PbO}\cdot\text{P}_2\text{O}_5-5\text{PbF}_2:x\text{ErF}_3$ ($0.5 < x < 3.0$).

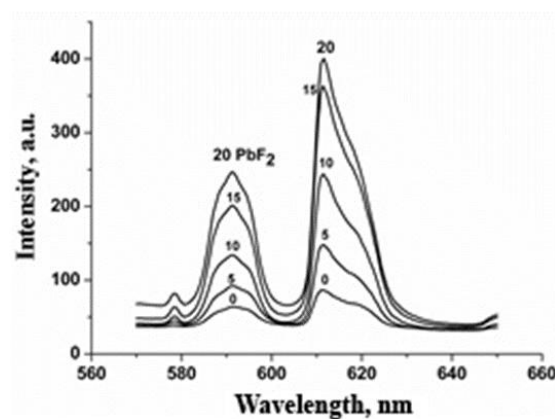


Figure 3. Dependences of the luminescence intensities of Eu^{3+} on PbF_2 concentration in the samples $(100-x-y)\text{TeO}_2-x\text{PbO}\cdot\text{P}_2\text{O}_5-y\text{PbF}_2:0.5\text{EuF}_3$ ($x=42.5-30$, $y=5-30$ mol. %).

TEM images confirm the existence of the structures with approximate dimensions 2–5 nm. It is seen from the photos (figures 4–7) that shape of the particles is closed to spherical. Moreover, their number and dimensions depend on concentration of the rare-earth (III) fluorides, lead fluoride and the rate of glass formation. Increasing of the ErF_3 doping results in growing amount of the nucleation centers. There are a lot of particles with small dimensions (figure 5). Increasing of the PbF_2 concentration in glass compositions with small ErF_3 doping results in growing of particle dimensions (figure 6). Fast cooling on cold plates decreases dramatically the number of particles and the rate of their growing (figures 8, 9). On the other hand, slow cooling results in aggregation of crystallite nanoparticles and in their growing rate.

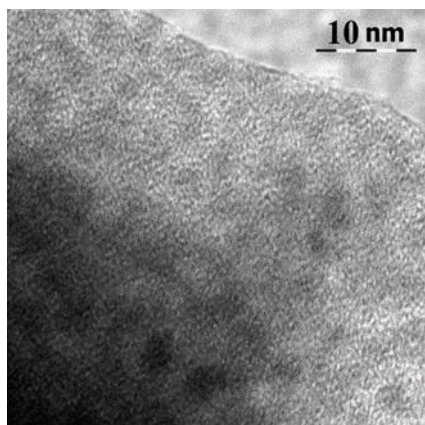


Figure 4. TEM image of the 52.5TeO₂-42.5PbO P₂O₅-5PbF₂ :0.5ErF₃ sample, hot plate.

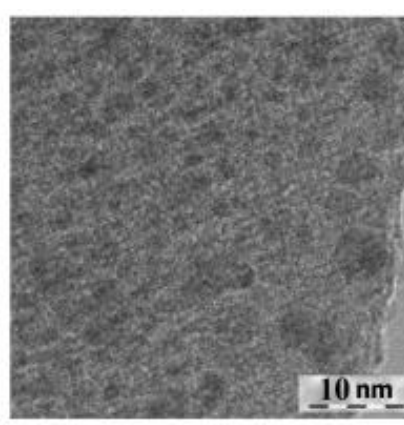


Figure 5. TEM image of the 52.5TeO₂-42.5PbO P₂O₅-5PbF₂ :3.0ErF₃ sample, hot plate.

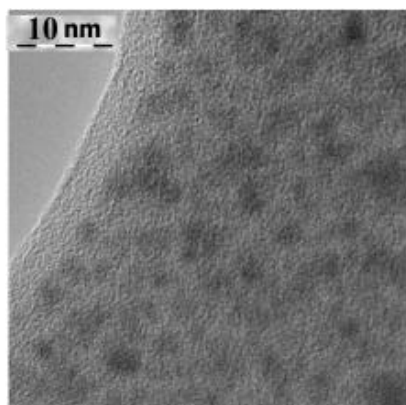


Figure 6. TEM image of the 40TeO₂-30PbO P₂O₅-30PbF₂ :0.5ErF₃ sample, hot plate.

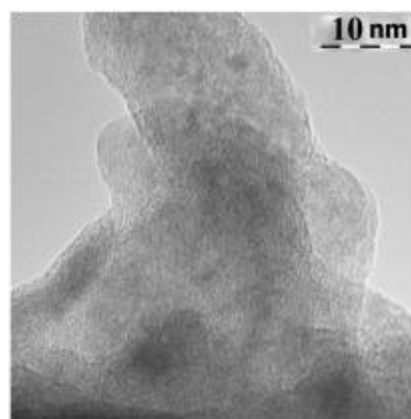


Figure 7. TEM image of the 40TeO₂-30PbO P₂O₅-30PbF₂ :0ErF₃ sample, hot plate.

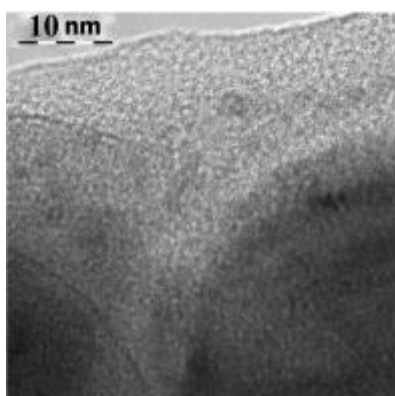


Figure 8. TEM image of the 40TeO₂-30PbO P₂O₅-30PbF₂ :0.5ErF₃ sample, cold plate.

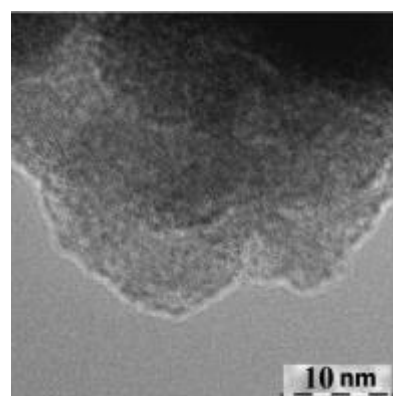


Figure 9. TEM image of the 52.5TeO₂-42.5PbO P₂O₅-5PbF₂ :3.0ErF₃ sample, cold plate.

Thus, erbium fluoride plays the role of nucleation agent. Previously, this fact was noted for other glass systems [8, 9, 10].

Heat treatment of the glasses consisted of 5–10 mol. % of PbF_2 and doped with neodymium or europium fluorides during 1–1.5 hours at 490 °C (the range T_g - T_x) promoted glass ceramics formation. Composition of the crystal phase corresponded to $\text{Pb}_2\text{P}_2\text{O}_7$ that was confirmed by the XRD data. Probably, actual composition of the crystal nanoparticles corresponded to $\text{Pb}_2\text{P}_2\text{O}_7\cdot\text{REF}_3$.

We kept the 52.5 TeO_2 –42.5 $\text{PbO}\cdot\text{P}_2\text{O}_5$ –5 PbF_2 : 0.5 NdF_3 glass at 490 °C during 0.5; 1, 2 and 3 hours to determine the influence of annealing time on glasses stability. After 1 hour of heat treatment, weak reflexes of $\text{Pb}_2\text{P}_2\text{O}_7$ appeared on XRD spectrum. Their intensity rises with the increase of annealing time. Samples remained transparent up to 2 hours of heat treatment. After 3 hours they became opaque.

The crystal phase formation of $\text{Pb}_2\text{P}_2\text{O}_7$ occurred in the case of the $(\text{PbO})_{0.50}(\text{P}_2\text{O}_5)_{0.50-x}(\text{TeO}_2)_x$ system [11]. This phase was produced during the annealing of the glasses with molar ratio $(\text{PbO})/(\text{P}_2\text{O}_5)>1$.

4. Conclusions

Nucleation and crystallization phenomena in the $(100-x-y)\text{TeO}_2$ - $x\text{PbO}\cdot\text{P}_2\text{O}_5$ - $y\text{PbF}_2$: $z\text{MF}_3$ ($\text{M} = \text{Er}, \text{Eu}, \text{Nd}$, $x=42.5$ -30 mol. %, $y=5$ -30 mol. %, $z=0.5$ -3.0 mol. %) glasses were investigated. It was found that the rare-earth (III) fluorides doping results in the formation of spherical nanosized crystallites in the bulk glass and segregation of rare-earth ions from glassy phase to crystallites. ErF_3 plays the role of nucleation agent in glasses. Heat treatment of the investigated glasses at suitable conditions enables to produce transparent glass ceramics.

Acknowledgments

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