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SYNTHESIS AND PROPERTIES OF MULTICOMPONENT LEAD FLUOROBORATE GLASSES CONTAINING RARE EARTH IONS

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A new multicomponent oxyfluoride glasses in $PbO – PbF_2 – B_2O_3 – Al_2O_3 – WO_3 – Ln_2O_3$ system (where *Ln* = Pr, Nd, Eu, Tm, Er) were prepared. Lead oxide was partially or totally substituted by lead fluoride in oxide matrices, where the weight ratio of the lead to the boron atom is changed from 1:4 to 4:1. However, only several transparent glass samples with the Pb : B ratio from 1 : 2 to 4 : 1 have been obtained. The $(PbO+PbF_2)/B_2O_3$ compositional dependence on the existence of the borate species was also supported by Raman spectroscopy. The strong peak at about 805 cm^{-1} due to the totally symmetric vibration identified as trigonal deformation of the boroxol ring has been observed for samples with the Pb : B ratio equal to 1 : 2, whereas coexistence of both BO_3 and BO_4 units is evident with increasing of total $(PbO+PbF_2)$ lead concentration.

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Since 1988 lead borates and lead fluoroborates have been known as promising fast ion conductors and easy forming glassy materials over a wide PbO and/or PbF_2 concentrations range. The formation and properties of glasses in the binary $PbF_2 – B_2O_3$ and the ternary $PbO – PbF_2 – B_2O_3$ systems have been extensively studied by Gressler and Shelby [1,2]. Different metal oxides have been added to the system based on $PbO – B_2O_3$ in order to improve thermal stability and modify glass properties. Recently, some structural [3] and optical [4] properties of $PbO – B_2O_3$ based glasses with different value of the PbO/B_2O_3 ratio have been analyzed. Relationship between glass composition and optical parameters has been evaluated in $BaO – PbO – B_2O_3$ system, where the lead atoms behave as a network modifiers or formers.

According to the our previous work [5], rare earth – doped lead borate glasses in multicomponent $PbO – B_2O_3 – Al_2O_3 – WO_3 – Ln_2O_3$ (*Ln* = Pr, Tm) system present interesting spectroscopic properties. Less attention has been given to the multicomponent rare earth – doped lead fluoroborate glasses with various PbF_2 concentrations. Systematic studies indicate that rare earth – doped oxide glasses are interesting as a luminescence material emitting rather in the visible and UV spectral region. In many cases, near – infrared transitions between excited states of rare earth ions are inactive in oxide matrices. Addition of fluoride component to the oxide matrix significantly increases radiative parameters and near – infrared transitions between excited levels of rare earth ions have been observed. Thus, the oxyfluoride glasses containing rare earth ions play an important role for application in the near – infrared optoelectronics. Especially, erbium – doped oxyfluoride glass can be used as potential advanced host material for developing broadband optical amplifiers in the wavelength-division-multiplexing network system [6].

In this short communication, we present our first experimental results related to the synthesis and some properties of multicomponent oxyfluoride glasses in $PbO – PbF_2 – B_2O_3 – Al_2O_3 – WO_3 – Ln_2O_3$ system (*Ln* = Pr, Nd, Eu, Tm, Er), where $PbO : PbF_2 : B_2O_3$ ratio is changed. These compositional changes are observed using Raman spectroscopy.

Glass samples were prepared using anhydrous lead fluoride and metal oxides of 99.99% purity (Aldrich Chemical Co.) as starting materials. The samples were synthesized in a dry box filled

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with Ar gas. To prepare samples, several batches in mass of 5 grams were mixed homogeneously and heated in atmosphere of dry argon. Glasses were melted at 850 – 1250 ^{0}C in platinum crucible, depending on heavy metal (PbO and/or PbF_2) concentration. Next, they were poured into preheated copper moulds and annealed below the glass transition temperature, T_g. After this process, samples were slowly cooled to the room temperature. The samples were prepared in a conventional way similar to that used for fluoride glasses, including the steps of melting, fining, casting and annealing. Fig. 1 demonstrates the glass forming region for the multicomponent oxyfluoride glasses based on $PbO – PbF_2 – B_2O_3$.

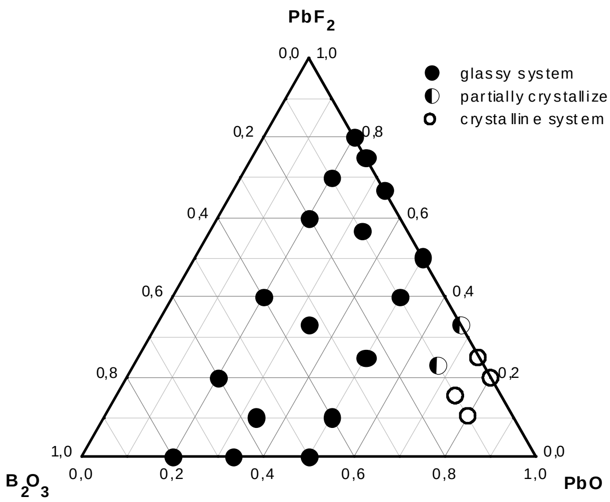

Fig. 1. Glass-forming region for multicomponent glasses based on $PbO – PbF_2 – B_2O_3$.

Transparent samples for four series of glass matrices with nominal compositions (given in wt%) were obtained:

$(72–x)PbO – xPbF_2 – 18B_2O_3 – 6Al_2O_3 – 3WO_3 – 1Ln_2O_3$; x = 0, 9, 18, 36, 54, 72; Pb : B = 4 : 1
Ln = Pr, Nd, Eu, Tm, Er (1)

$(60–x)PbO – xPbF_2 – 30B_2O_3 – 6Al_2O_3 – 3WO_3 – 1Ln_2O_3$; x = 0, 9, 30, 51, 60; Pb : B = 2 : 1 (2)

$(45–x)PbO – xPbF_2 – 45B_2O_3 – 6Al_2O_3 – 3WO_3 – 1Ln_2O_3$; x = 0, 9, 22.5, 36, 45; Pb : B = 1 : 1 (3)

$(30–x)PbO – xPbF_2 – 60B_2O_3 – 6Al_2O_3 – 3WO_3 – 1Ln_2O_3$; x = 0, 9 ; Pb : B = 1 : 2
Ln = Er, Eu (4)

whereas two series with Pb : B ratio equal to 1 : 3 and 1 : 4 were completely crystallized on cooling.

Next, the glassy samples with the lead to the boron atom ratio from 1 : 2 to 4 : 1 were analyzed using Raman spectroscopy. The Raman spectra were measured at room temperature with FTIR Brucker spectrometer using an Ar^+ ion laser at the wavelength of 514.5 nm. The spectra were carried out with resolution of 2 cm^{-1}. Fig. 2 presents the Raman spectra of $PbO – PbF_2 – B_2O_3$ based glasses activated Er ions. For samples with Pb : B = 1 : 2 (a), the strong peak at about 805 cm^{-1} has been observed, which can be attributed to the totally symmetric vibration (trigonal deformation mode) of the boroxol ring [7]. The intensity of this peak decreases with increasing of total (PbO and/or PbF_2) lead concentration (Pb : B = 1 : 1) and additional two broad bands located in 850 – 1050 cm^{-1} and 1200 – 1500 cm^{-1} spectral region have been observed (b). These bands are associated to the BO_4 and BO_3 units, respectively. They are shifted in direction of lower frequency, when Pb : B ratio in the glass is changed from 1 : 1 to 4 : 1 (c). Thus, the strong peak at about 805 cm^{-1} is already invisible. Besides bands associated with borate groups, the peak at about 115 cm^{-1} due to the Pb – O vibration is observed. The intensity of this peak considerably increases with increasing of lead content and the second peak as a shoulder at about 330 cm^{-1} is formed.

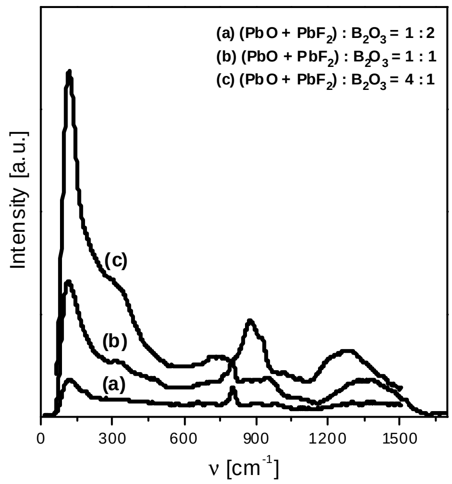

Fig. 2. Raman spectra for multicomponent glasses based on $PbO – PbF_2 – B_2O_3$.

At consequence, addition of heavy metal elements (PbO and/or PbF_2) to the borate matrices change their structural properties. Especially, the surrounding around rare earth ion is changed and thus significantly influences on its radiative parameters. Influence of PbF_2 concentration on photoluminescence properties of Er^{3+} ions in lead fluoroborate glasses with Pb : B ratio equal to 4 : 1 is reported in [8]. Photoluminescence intensity at 1.55 μm due to the main $^4I_{13/2}$ – $^4I_{15/2}$ laser transition and value of $^4I_{13/2}$ lifetime considerably increase with increasing of PbF_2 concentration. The effect of PbO/B_2O_3 and PbF_2/B_2O_3 ratios on excited state relaxation of other rare earth ions will be studied in the oxyfluoride glass, which is particular interest from the fundamental and practical points of views.

In conclusion, a new multicomponent oxyfluoride glasses in $PbO – PbF_2 – B_2O_3 – Al_2O_3 – WO_3$ system containing rare earth ions were synthesized. Several transparent samples have been obtained in glass-forming region for lead fluoroborate glasses, where Pb : B ratio is changed from 1 : 2 to 4 : 1. Structural changes in the glass are evidenced by Raman spectroscopy, where different borate species are formed depending on heavy metal (PbO and/or PbF_2) concentration.

Acknowledgements

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