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Journal of Non-Crystalline Solids 353 (2007) 1397–1401

JOURNAL OF NON-CRYSTALLINE SOLIDS

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Characterization of Eu^{3+}-doped fluorophosphate glasses for red emission

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Available online 26 March 2007

Abstract

Fluorescence spectra and decay curves of the $^5D_0$ level for different concentrations of Eu^{3+} ($4f^6$) ions in K–Ba–Al fluorophosphate glasses have been measured at room temperature and are analyzed. The Judd–Ofelt intensity parameters Ω_2 and Ω_4 have been determined from the intensity ratios of emission peaks corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 2$ and 4) to $^5D_0 \rightarrow {}^7F_1$ transitions for 1.0 mol% glass. The intensity parameters thus obtained are in turn used to calculate the radiative properties of the fluorescent levels of Eu^{3+} ions. Second and fourth rank crystal-field parameters have been evaluated by assuming a C_{2V} site symmetry for the local environment of Eu^{3+} ions to estimate the crystal-field strength experienced by Eu^{3+} ions in the present host. The decay profiles of the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions in the present glasses are found to be single exponential for all the studied Eu^{3+} ion concentrations. A marginal increase in lifetime of the $^5D_0$ level has been noticed with Eu^{3+} ion concentration up to 2.0 mol% and then the lifetime marginally decreases for higher Eu^{3+} ion concentrations.

PACS: 79.60.Ht; 78.55.−m; 71.70.Ch; 42.70.Ce

Keywords: Optical properties; Luminescence

1. Introduction

Alkali aluminometaphosphate glasses are the promising hosts among oxide glasses for lanthanide (Ln) ions due to their relatively higher refractive indices, lower dispersion, larger stimulated emission cross-sections, higher gain, better chemical durability and lower thermo-optical qualities when compared with many other hosts such as silicates [1]. They are very easy to prepare in various compositions in bulk form and they preserve useful properties upon the introduction of a significant amount of Ln ions. Addition of fluoride contents will further improve the radiative properties by reducing the number of hydroxyl (OH^-) groups in the glass network [2].

Among Ln ions, trivalent europium (Eu^{3+}) ion is the best candidate to be used as a probe to investigate the local structure around Ln ions in condensed matter. This is because, the low lying energy level scheme of Eu^{3+} ions is simple and the transition between $^7F_0$ and $^5D_0$ non-degenerate levels is convenient to apply the fluorescence line narrowing technique to analyze changes from site to site through energy level scheme analysis [3]. Also Eu^{3+}-doped materials are frequently used in photonic applications as red phosphors for field emission technology due to the narrow and monochromatic emitting nature of the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions at 610 nm. The present work reports the fluorescence and local field properties of different concentrations of Eu^{3+} ions in K–Ba–Al fluorophosphate glass.

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doi:10.1016/j.jnoncrysol.2006.10.063

2. Experimental

Eu^{3+}-doped fluorophosphate glasses with composition (in mol%) $(56 - x/2)P_2O_5 + 17.0K_2O + (15 - x/2)BaO + 8.0Al_2O_3 + 4.0AlF_3 + xEu_2O_3$ (referred as PKBAFEu) for $x = 0.01$, 0.1, 1.0, 2.0, 4.0 and 6.0 mol%, were prepared by the conventional melt quenching technique using high purity chemicals of KH_2PO_4, $Ba(PO_3)_2$, $Al(PO_3)_3$, AlF_3 and Eu_2O_3 as starting materials. The batch composition was melted around 1075 °C for 1 h. The samples were then kept for annealing at 350 °C for 10 h and then slowly allowed to cool to room temperature (RT). Refractive index, density, optical absorption, emission and fluorescence decay measurements were carried out following the similar methods mentioned in Refs. [4,5].

3. Results

3.1. Emission spectra – determination of Judd–Ofelt parameters

The optical absorption and emission spectra for the 1.0 mol% Eu^{3+}-doped PKBAFEu fluorophosphate glass (referred as PKBAFEu10) were recorded at RT and are shown in Figs. 1 and 2, respectively. The bands in the absorption spectra correspond to the transitions originating from the $^7F_0$ and $^7F_1$ levels and the peaks in the emission spectra correspond to the well-known $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–6) transitions. The Judd–Ofelt (JO) intensity parameters, Ω_λ ($\lambda = 2$, 4 and 6) have been calculated using the ratio of intensities of $^5D_0 \rightarrow {}^7F_J$ ($J = 2, 4$ and 6) transitions to that of the $^5D_0 \rightarrow {}^7F_1$ transition [5–9].

3.2. Radiative properties

The calculated JO parameters have been used to determine the radiative properties by following the procedure outlined in the earlier reported works [7–10]. The Ω_λ, ($\times 10^{-20}$ cm^2), experimental (τ_{exp}) and calculated (τ_{cal}) lifetimes (ms), quantum efficiencies (η), non-radiative transition probabilities (W_{nr}, s^{-1}) and intensity ratios ($R(J/1) = ({}^5D_0 \rightarrow {}^7F_J)/({}^5D_0 \rightarrow {}^7F_1)$, $J = 2$ and 4) have been determined for the PKBAFEu10 glass and are presented in Table 1. Similar results obtained for other Eu^{3+}:glasses such as $58.5P_2O_5 + 17K_2O + 14.5BaO + 9Al_2O_3 + 1Eu_2O_3$ (PKBAEu10) [5], $55.5P_2O_5 + 17K_2O + 11.5BaO + 6BaF_2 + 9Al_2O_3 + 1Eu_2O_3$ (PKBFAEu10) [5], Eu^{3+}:$Ba(PO_3)_2$ (PBEu) [11], $Al(NO_3)_3 + SiO_2 + Eu_2O_3$ (ASEu) [12] and $57ZrF_4 + 36BaF_2 + 3LaF_3 + 3AlF_3 + 1EuF_3$ (Eu^{3+}:ZBLA) [13]; and $SiO_2 + Al_2O_3 + Eu_2O_3$ xerogels (SAEu) [14] are also presented in Table 1 for comparison. The emission peak wavelengths (λ_p, nm), radiative transition probabilities (A, s^{-1}), experimental and calculated branching ratios (β_R), effective bandwidths ($\Delta\lambda_{eff}$, nm) and peak stimulated emission cross-sections ($\sigma(\lambda_p)$, $\times 10^{-21}$ cm^2) have been determined for different transitions originating from the luminescent $^5D_0$ level of Eu^{3+} ions in PKBAFEu10 glass and are shown in Table 2.

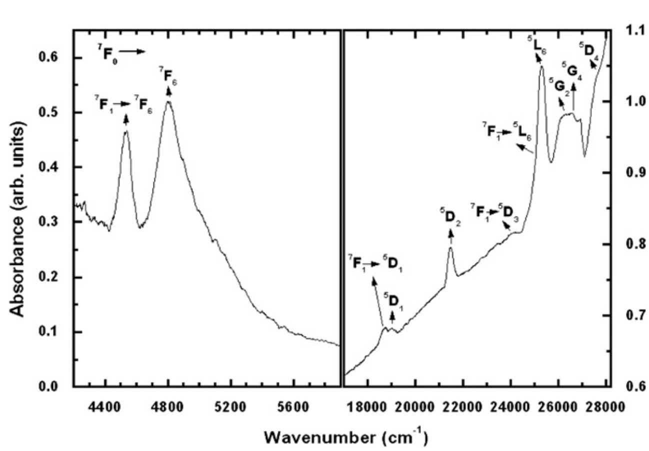

Fig. 1. Optical absorption spectrum of PKBAFEu10 glass at room temperature (all the transitions are originated from the ground $^7F_0$ level, unless otherwise specified).

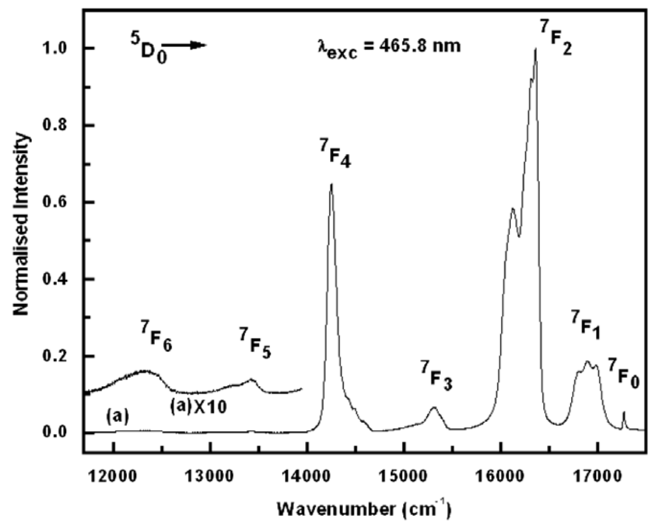

Fig. 2. Emission spectrum of the PKBAFEu10 glass at room temperature (weak intense $^5D_0 \rightarrow {}^7F_{5,6}$ peaks are also shown with tenfold magnification).

3.3. Crystal-field analysis

A careful observation of $^5D_0 \rightarrow {}^7F_J$ ($J = 1$ and 2) peaks in the emission spectrum shown in Fig. 2 yields Stark splittings of these peaks into 3 and 5 components, respectively. The second and fourth rank crystal-field (CF) parameters B_{kq} and the CF strength parameter (S) have been calculated by assuming the C_{2V} site symmetry around Eu^{3+} ions in PKBAFEu10 glass [15–18]. The CF parameters B_{kq} and their ratios B_{22}/B_{20} and B_{44}/B_{40} for the present PKBAFEu10 glass are presented in Table 3 along with similar parameters for the PKBAEu10 and PKBFAEu10 glasses [5] for comparison.