Fluorescence study of Eu³⁺ doped phosphate glass under pressure

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Summary

The pressure dependence of the luminescence from ${}^{5}D_{0} \rightarrow {}^{7}F_{0, 1, 2}$ transitions of Eu³⁺ ions in 58.5P₂O₅-9Al₂O₃-14.5BaO-17K₂O-1Eu₂O₃ (PKBAEu) glass has been investigated as a function of pressure up to 38.3 GPa at room temperature. Under pressure ${}^{5}D_{0} \rightarrow {}^{7}F_{0, 1, 2}$ transitions exhibit a red shift with different magnitudes, which suggests a decrease in Slater parameters (F^{k}) and the spin-orbit coupling parameter (ξ_{4f}) for the Eu³⁺ ions. Stark components of the ${}^{7}F_{1}$ level have been used to evaluate crystal-field (CF) parameters (B_{0}^{2} and B_{2}^{2}) which are in turn used to estimate the CF strength experienced by the Eu³⁺ ions in the glass. The increase in CF strength parameter is found to have almost cubic dependence on pressure. Luminescence decay curves for the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition are found to be single exponential over the entire pressure range studied. The lifetime is found to be invariant under pressure up to 5 GPa, however a change in the CF strength is noticed in this pressure range. Quenching of lifetime is observed at pressures above 5 GPa which could be partially due to an enhancement in the pressure induced defect centers.

Introduction

Lanthanide (Ln) doped phosphate based glasses have been the subject of recent investigations as potential materials for luminescent applications. Typically, phosphate based multioxide glasses possess high stimulated emission cross-sections, weak up-conversion luminescence and low probability of energy back transfer. In addition, these glasses exhibit high transparency, low refractive index, low melting temperature, high gain, good thermo-optical performance, low rupture strength and good chemical durability [Suratwala, 2000; Jiang, 1998; Wang, 2003; Lin, 2003]. When a Ln ion is incorporated into any host matrix, it experiences an inhomogeneous electrostatic field produced by the surrounding charge distribution and results in two effects which are the centroid shifts of all the free-ion multiplets to the red and the Stark splitting of the energy levels. The centroid shifts are ascribed as the Nephelauxetic effect that explains the reduction of Slater parameters (F^k) and the spin-orbit coupling parameter (ξ_{4f}) for the Ln ion in the host with respect to their free-ion values of F_k^0 and ξ_{4f}^0 . The Stark splitting of the multiplets is ascribed to the change in the sum of various interactions such as covalence, overlap and coulomb interactions between the 4f electrons of the Ln ions and their surrounding

ligands. These two effects significantly influence the luminescence properties of Ln ions in the solids.

The development of luminescence materials for practical applications such as solid state lasers, optical data storage devices, optical sensors, phosphorus and etc. requires a systematic understanding of bonding environment of Ln ions and their luminescence properties. Application of high pressure continuously reduces the interatomic distance and therefore increases the overlap among the adjacent electronic orbitals and the crystal-field (CF) strength, without changing the other physical properties like the point group symmetry of the Ln ion site or the chemical composition. The decrease in the effective volume of the Ln ion containing matrix with high pressure has different effects on different luminescence centers. Thus, pressure dependent luminescence study provides valuable information on the electronic states, CF strength, energy transfers and the interaction between luminescence centers and their hosts [Tröster, 2003].

Glasses doped with trivalent europium (Eu³⁺) ions have been used in optical devices as red emitting materials for field emission technology, phosphors and LEDs which exhibits longer luminescence efficiency [Campbell, 2000; Kityk, 2002; Obaton, 1999; Zhang, 2002]. Apart from these potential luminescent applications, Eu³⁺ (4f⁶) ions have been often used as a probe to estimate the local environment around the Ln³⁺ ions in different materials. The information about the local structure around Eu³⁺ ion can be obtained guite easily from its f-f transition spectra. The luminescence of Eu³⁺ ions also facilitates to estimate the precise information about the non-uniformity of Eu³⁺ ion sites and the strength of Eu–O bonding. The ground state ⁷F₀ and the first excited ⁵D₀ states of Eu³⁺ are non-degenerate under any symmetry and some of the transitions between these levels are sensitive to the local environment. Hence, information regarding the local environment around the Eu³⁺ ion is contained in the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ emission transitions and their splitting. Depending on the number of Stark components into which the ⁵D₀ \rightarrow ⁷F_J emission transitions split, the symmetry at the Eu³⁺ site can be derived by crystal-field parameterization. The crystal field parameters $(B_0^2 \text{ and } B_2^2)$ and their ratio have been used to describe the coordination of the Eu³⁺ ions [Gorller-Walrand, 1996; Capobianco, 1989; Zambelli, 2004]. Thus, Eu³⁺ ion luminescence spectroscopy can be used as a technique to study the effect of pressure on the structure of an amorphous material. The present work reports the results of luminescence spectra of ${}^{5}D_{0} \rightarrow {}^{7}F_{0,1,2}$ transitions and lifetime measurements of the ${}^{5}D_{0}$ level of Eu³⁺ ion in a phosphate glass under high pressure up to 38.3 GPa at room temperature. The effect of a pressure release on these properties is also studied.

Experimental

 Eu^{3+} -doped phosphate-based multi-oxide glass with composition (in mol %) of $58.5P_2O_5$ - $17K_2O_14.5BaO-9Al_2O_3$ - $1Eu_2O_3$ (PKBAEu) was prepared by conventional melt quenching technique. About 5 g of the batch composition was thoroughly crushed in an agate mortar and the homogeneous mixture was heated in a platinum crucible inside an electric furnace for 45 min at a temperature of 1075^oC. The melt was poured onto a preheated brass mold at a temperature of 350^oC and annealed at this temperature for about 5 h to remove thermal strains. Then the sample was allowed to cool to room temperature (RT) and polished for the purpose of optical measurements.

The 465.8 nm line of an Ar⁺ laser was used as an excitation source. The fluorescence spectra were recorded with a double monochromator equipped with a photomultiplier tube. The resolution of the double monochromator depends on the wavelength and the slit width and was typically set to 2.0 cm⁻¹. A special miniature diamond anvil cell (DAC) was used to generate pressures up to 38.3 GPa at RT. A piece of PKBAEu glass was placed together with a ruby pressure sensor in an 80 μ m diameter hole of a stainless steel (INCONEL X750) gasket of 200 μ m thickness. A mixture of methanol:ethanol:water (16:3:1) was used as pressure transmitting medium. This gasket with the sample and pressure transmitting fluid was then compressed by the two opposed anvils of the DAC. The pressure and the hydrostatic conditions experienced by the sample were determined by the shift and broadening of the ruby R₁ lines [Holzapfel, 2003]. A mechanical chopper in connection with a multi-channel scalar allowed for lifetime measurement in the range from 2 μ s to 2s.

Crystal-Field Analysis

When a free-ion is introduced into a solid, it experiences an inhomogeneous electrostatic field produced by the surrounding charge distribution. The Hamiltonian that represents the crystal-field (CF) potential acting on the Ln ion can be expressed in the Wybourne's notation [Wybourne, 1965; Lavin, 2001; Jayasankar, 2004] as

$$H_{CF} = \sum_{k,q,i} B_{q}^{k} C_{q}^{(k)}(i)$$
 (1)

Where $B_q^k = (-1)^q (B_q^k - iS_q^k)$ are the coefficients of the CF expansion that are the functions of the radial distances that can be varied. The $C_q^{(k)}$ are tensor operators of rank 'k' is related closely to the spherical harmonics, which can be calculated exactly [Lavin, 2001]. The number of parameters for H_{CF} in Eq.(1) is greatly reduced by the symmetry selection rules for the point symmetry at the Ln site in the crystal. Although the term "crystal" has been used here, these effects are not confined to crystals only. Any surrounding that breaks the spherical symmetry of the free-ion can lead to a shift and splitting of the energy levels. Thus, the above considerations also apply to materials such as glasses where a long-range order does not exist.

If the J-mixing effects are neglected, then the CF splitting of the ${}^{7}F_{1}$ level of Eu³⁺ ion will depend only on the even CF parameters of second rank (k = 2). It is a general and convenient practice to assume the C_{2v} symmetry for Eu³⁺, when the degeneracy of the ${}^{7}F_{1}$ multiplet is removed completely. For C_{2v} symmetry the "second-rank crystal-field" experienced by Eu³⁺ ions is described by the Hamiltonian as [Wybourne, 1965],

$$H_{CF} = B_{20} C_0^{(2)} + B_{22} \left(C_{-2}^{(2)} + C_2^{(2)} \right)$$
(2)

where B_{20} and B_{22} are the real parts of CF parameters in Eq. (1).

A CF strength parameter N_v has been introduced to simplify the description of the CF parameters due to its independence from the specific crystal structure. Considering only the second-rank CF parameters, N_v has been determined using the following relation [Auzel, 1979]:

$$N_{v} = \sqrt{\frac{4\pi}{5}} \left((B_{20})^{2} + 2 (B_{22})^{2} \right)$$
(3)

Results

A detailed characterization of PKBAEu glasses through optical absorption, photoluminescence and decay times using energy-level model Hamiltonian and Judd-Ofelt theory has been reported in our previous paper [Surendra Babu, 2005]. Figure 1 shows the room temperature photoluminescence spectra of PKBAEu glass for different pressures of ambient(0.0), 12.0, 25.0 and 38.3 GPa, obtained by the excitation of 465.8 nm, along with the band assignments. The spectra correspond to the emission from the ${}^{5}D_{0}$ excited state to ${}^{7}F_{0,1,2}$ ground multiplets of Eu³⁺ ions in PKBAEu glass.



Figure 1: Luminescence spectra of PKBAEu glass at different increasing pressures. The spectra are normalized to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition

Figure 2 shows the pressure dependence of the shift of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0,2}$ emission band positions of the Eu³⁺ ions along with a linear fit to the data obtained with increasing pressure. The energy position of these emission bands are taken at the peak maximum of the bands.



Figure 2: Peak positions of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions of the Eu³⁺ ions in PKBAEu glass as a function of pressure. The solid (open) symbols corresponds to data taken at increasing (decreasing) pressure. The solid line is the fit of a linear equation of the data obtained at increasing pressure.



Figure 3: Energy positions of the three Stark components for ${}^{7}F_{1}$ level of Eu³⁺ ions in PKBAEu glass as a function of pressure (data for decreasing pressure are not shown). The solid squares are the experimental data and the open circles indicate the barycenter. The solid line is the fit of the barycenter to a linear equation.

Figure 3 shows the three Stark splitting obtained for the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition of Eu³⁺ ions in the PKBAEu glass under pressure. These Stark energy levels have been obtained by deconvoluting the ${}^{7}F_{1}$ level into three Gaussian line shape functions. In Figure 3, the solid squres shows the Stark energy positions and the open circles are the barycenter of ${}^{7}F_{1}$ levels along with the linear fit to the data.



Figure 4: Formal negative charge on the oxygen in Eu^{3+} :PKBAEu glass as a function of pressure. The solid (open) squares correspond to data obtained at increasing (decreasing) pressure.



Figure 5: Variation of crystal-field strength parameter (N_v) and lifetime of the 5D_0 level of Eu $^{3+}$ ions in PKBAEu glass with pressure. The solid (open) symbols correspond to data obtained at increasing (decreasing) pressure.

Figure 4 shows the variation of the formal negative charge on the oxygen in Eu^{3+} :PKBAEu glass as a function of pressure. The effect of pressure on the CF strength parameter N_v (Eq.(3)) is shown in Figure 5 for the PKBAEu glass. The derived lifetimes are plotted in Figure 5. As seen from the Figure 5, the lifetimes shows a non-linear dependence on pressure.



Figure 6: Decay profiles of the ${}^{5}D_{0}$ level of Eu³⁺ in PKBAEu glass at various pressures. A single exponential fit is included for the decay curve at 38.3 GPa.

Also the fluorescence decay of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition in PKBAEu glass has been measured up to 38.3 GPa. The decay profiles are found to be single exponential in the entire pressure range studied. Figure 6 shows the decay profiles at different pressures along with single exponential fit to the decay profile at 38.3 GPa.

Discussion

The spectra of Figure 1 correspond to the emission from the ${}^{5}D_{0}$ excited state to ${}^{7}F_{0,1,2}$ ground multiplets of Eu³⁺ ions in PKBAEu glass. Since the transitions corresponding to J = 3 to 6 are of very weak intensity and therefore are not observed under high pressure. The ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{7}F_{1}$ and ${}^{7}F_{2}$ are forbidden, magnetic-dipole allowed and enforced electric-dipole allowed transitions, respectively. As can be seen from Figures 2 and 3, the pressure dependent energy level shift can be expressed as linear function [Souza Filho, 2000; Jovanic, 2001],

$$E_i(p) = E_i(0) + \alpha_i p$$
 (with p in GPa),

where i labels the three different transitions. The $E_i(0)$ values correspond to the values at 0.0 GPa and the coefficients α_i are determined from the fits as

 α (⁷F₀) = -1.4 cm⁻¹ /GPa α (⁷F₁) = -3.6 cm⁻¹ /GPa α (⁷F₂) = -2.6 cm⁻¹ /GPa.

The shift of each J-manifold with pressure results from the reduction of Slater parameters and the spin-orbit coupling parameter due to changes in the overlap of the ligand orbitals with the 4f wave functions of the Eu³⁺ ion [Chen, 1994]. The shift of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0,1,2}$ transitions to lower energy and the broadening of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition, indicating an increase in the CF strength to be discussed later. This behaviour can be attributed to the higher formal negative charges on the ligands (see Figure 4). The sum of the formal negative charges (q) on the ligands directly bonded to the Eu³⁺ ions can be related to the energy (v) of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition by [Chen, 1992],

$$v(cm^{-1}) = 17273 + 2.29q - 0.76q^2$$
 (at T = 296 K)

With this relation and the measured transition energies, the changes in the formal negative charges on the oxygen sites can be evaluated. The above quadratic equation was solved by using the values of v observed at the various pressures. The negative root of the solution of equation was taken as the negative formal charge. As shown in Figure 4, the increase in the value of the formal negative charge on the neighboring oxygens can be related to the expansion of the 4f-orbitals of Eu^{3+} (Nephelauxetic effect). This expansion decreases the electronegativity of the Eu^{3+} ion and causes an increase in the covalency of the Eu-O bonds, as evidenced by the red shift of the ${}^{5}D_{0} \rightarrow {}^{7}F_{0,1,2}$ transitions under pressure (shown in Figures 2 and 3).

Crystal-field analysis has been carried out to evaluate the CF strength experienced by the Eu³⁺ ion in the host. This is because the CF strength experienced by the Eu³⁺ ions is a measure of their electrostatic interaction with the surrounding ligands and an increase of the CF strength indicates an increase in the charge distribution and/or a lower Eu–O distance. As can be seen from Figure 3, the observed increase in the energy separation between the two extreme Stark components qualitatively reflects the increase in the CF strength at the Eu³⁺ ion site with pressure. A more gualitative estimation of the CF strength experienced by the Eu³⁺ ions can be made by the crystal-field parameterization. The complete removal of degeneracy for the ${}^{5}D_{0} \rightarrow$ ⁷F₁ transition at all pressures suggests that the local symmetry of the Eu³⁺ ions in PKBAEu glass is low, corresponding to orthorhombic, monoclinic or triclinic symmetry in a crystal [Lavin, 2001]. From the Stark splitting for ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition it is possible to estimate the CF strength acting on the Eu^{3+} ions in glasses by assuming C_{2v} site symmetry for local environment of the Eu^{3+} ions [Lavin, 2001; Jayasankar, 2004; Surendra Babu, 2005; Chen, 1995; Brecher, 1976]. This is because C_{2v} symmetry is a subgroup of almost all higher-order point groups allowing optical activity from the ⁵D₀ level to practically all ⁷F_J Stark levels. Further, C_{2v} is the highest order noncentrosymmetric point group that lifts completely the degeneracy of the ⁷F_J levels and has the lowest symmetry for which simple crystal-field calculations can be performed. The corresponding CF parameters, B₂₀ and B₂₂, have been calculated by diagonalizing the complete Hamiltonian (free Eu³⁺ ion and the second rank crystal-field described in Eq.(1)) using C_{2v}

symmetry and taking into account the J-mixing as carried out in the earlier work [Lavin, 2001]. The fitting process minimizes the root mean square deviation between the experimental and calculated ${}^{7}F_{1}$ Stark energy levels. As seen from the Figure 5, the CF strength shows a linear dependence on pressure.

Figure 5 also shows the variation of lifetime of the ${}^{5}D_{0}$ level of Eu³⁺ ions in PKBAEu glass under pressure. It is obvious that the lifetime remains almost constant up to 5.1 GPa, though the CF strength increases in this pressure range, and then the lifetime decreases with increasing pressure. These lifetimes were evaluated from the simple exponential behaviour of the decay curves [Jayasankar, 2004; Adam, 1998]. The lifetime at ambient condition is found to be 2520 μs. As can be seen from the Figure 5, the change in the lifetime with pressure is opposite to that of the CF strength. The decay of the ${}^{5}D_{0}$ level is purely radiative as there is a large energy gap of around 12 200 cm⁻¹ between ${}^{5}D_{0}$ and the next lower level ${}^{7}F_{6}$, indicating that the quantum efficiency for the ⁵D₀ level is almost unity. The shortening of lifetime with increasing pressure is attributed to the gradual increase in energy transfer processes, probably enhanced by pressure induced defect centers. A detailed review of such processes is given in [Tröster, 2003]. In general, either an increase of the multiphonon de-excitation probability or an increase of the electronic transition probability can explain the observed decrease of lifetimes under pressure. While the first process can be excluded here because of the large energy gap between the ⁵D₀ and ⁷F₁ levels, the latter effect is easily explained by the increase in CF strengths around the Eu³⁺ ions with pressure. This results in an enhanced mixing of opposite parity configurations with the 4f⁶ configuration, due to the odd-parity CF Hamiltonians, leading to an increase in the transition probabilities. This type of behavior has also been noticed in the case of Sm³⁺ and other Ln³⁺ ions in crystalline solids [Lavin, 2002].

As seen from the Figure 5, the release of pressure has a significant hysteresis effect on the lifetime, even though the crystal-field strength is having reversible nature with pressure. For example, the lifetime at 3.1 GPa (release of pressure) is 2130 μ s, whereas at 16.5 GPa (increasing of pressure), it is 2117 μ s. This observation along with Figure 3, suggests that a permanent deformation of the Eu³⁺ ion site densification of the glass matrix is taking place with the application of high pressure.

Conclusions

Luminescence studies of Eu^{3+} -doped phosphate glass have been performed under pressures up to 38.3 GPa at room temperature. The red shift observed for the emission band positions with increasing pressure is attributed to the variations of the spin-orbit coupling constant. The continuous increase in the magnitude of splittings observed for the ${}^{7}F_{1}$ and ${}^{7}F_{2}$ levels with pressure arises from the variations in the strength and symmetry of the crystal-field around the Eu^{3+} ion. The decay curve of the ${}^{5}D_{0}$ level at ambient pressure is perfectly single exponential which remains same over the entire pressure range studied. Under pressure higher than 5.1 GPa, the reduction of lifetime of the ${}^{5}D_{0}$ level with increase in pressure can be explained by an increase in the electronic transition probabilities arising from the gradual increase in the CF strengths around the Eu³⁺ ions with pressure. The analysis of luminescence properties measured while releasing the pressures suggests that there is a significant structural hysteresis around the Eu³⁺ ion in the glass matrix. The decrease in the lifetime with increasing pressure could also be partially due to enhancement of pressure induced defect centers.

Acknowledgements

One of the authors (CKJ) is grateful to the University Grants Commission, New Delhi, India for the award of the Research Project (F.10-9/2002 (SR-1)) and to the Department Physik, Universität Paderborn, Germany, for the stay as a Guest Scientist.

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