Abstract: Pressure dependent luminescence spectra and decay curves for the $^4G_{5/2}$ level of Sm$^{3+}$ ions in fluorophosphate glass of composition 55.975 P$_2$O$_5 + 14$ K$_2$O + 6 KF + 14.975 BaO + 9 Al$_2$O$_3 + 0.05$ Sm$_2$O$_3$ (referred as PKFBASm005) have been measured as a function of pressure up to 40.2 GPa. In this pressure range, the red-shift (during increase in pressure), the blue-shift (while releasing pressure) and enhanced crystal-field splitting with increase in pressure are observed for $^4G_{5/2} \rightarrow ^4H_J$ ($J = 9/2, 7/2$ and $5/2$) multiplet transitions of PKFBASm005 glass. These pressure induced shifts as well as crystal-field splittings were explained by the interaction of Sm$^{3+}$ ions with its surrounding ligands under pressure. The decay curves for the $^4G_{5/2}$ level are found to be non-exponential in the entire pressure range. The lifetime for the $^4G_{5/2}$ level decreases from 3.23 to 1.62 ms with increase in pressure from ambient to 40.2 GPa. The generalized Yokota-Tanimoto (YT) model has been used to explain non-exponential behaviour of decay curves.

Keywords: Sm$^{3+}$ ions in glass; High pressure; Luminescence properties; Crystal-field.

1. Introduction
Spectroscopic investigations on rare-earth (RE) doped glasses have considerable interest to design and develop new optical devices [1] due to desirable energy level structure for optical pumping, sharp lines observed in the optical absorption and emission spectra, relatively longer lifetimes of excited energy levels, easier fabrication compared to crystals, etc. The interest in selection of phosphate glass as a host matrix for RE$^{3+}$ ions is due to its unique characteristics such as high gain density that is due to high solubility of RE$^{3+}$ ions, high transparency, low refractive index and dispersion, low melting point and good thermal stability. But, the complexity with the use of phosphate glasses as laser ion host is that they have larger thermal expansion coefficient and lower fracture toughness than silicates [2,3].

The importance of preparing fluorophosphate glasses by introducing suitable metal fluorides into phosphate glass composition is of their smaller fluorescence linewidth, low melting temperature, higher stimulated emission cross-section, longer lifetime and reduction in phonon energy. The presence of fluorides in glass medium strongly reduces OH absorption and shifts the IR cutoff edge towards longer wavelengths making them highly suitable for fiber amplifiers [4,5] in telecommunication systems. In phosphate glasses, K$_2$O reduces the melting point and BaO favors the mechanical properties which are important for fiber production. On the other hand, Al$_2$O$_3$ alters the glass structure that can improve the physical properties and chemical stability of the glass. The trivalent samarium (Sm$^{3+}$) ion is one of the
most interesting RE$^{3+}$ ions to study the luminescence properties because its excited $^4G_{5/2}$ level shows relatively high quantum efficiency and also shows different quenching emission channels. The present work reports luminescence spectral and decay curve properties of 0.05 mol % Sm$_2$O$_3$ –doped fluorophosphate glass as a function of pressure up to 40.2 GPa.

### 2. Experimental

The composition (in mol %) of the glass studied in the present work 55.975 P$_2$O$_5$ + 14 K$_2$O + 6 KF + 14.975 BaO + 9 Al$_2$O$_3$ + 0.05 Sm$_2$O$_3$ (referred as PKFBASm005) was prepared by conventional melt quenching technique [6]. High-pressure photoluminescence spectra were recorded with a double monochromator equipped with a photomultiplier tube. The 476.5 nm line of an Ar$^+$ laser was used as an excitation source. The glass under investigation, together with a small piece of ruby, which acts as a pressure calibrant, was placed in a hole of 100 µm diameter of 200 µm thick stainless-steel gasket, which was located between the parallel faces of specially made miniature diamond anvil cells (DAC) [6–9]. A mixture of methanol-ethanol-water 16:3:1 was used as a hydrostatic pressure-transmitting fluid. Decay curves were obtained using a mechanical chopper with a multichannel scalar interfaced to a personal computer that recorded and averaged the signal. All measurements were carried out at room temperature.

### 3. Results and discussion

The luminescence spectra of the PKFBASm005 glass at ambient conditions for successive increasing and decreasing pressures are shown in figure 1, which were measured at room temperature (RT). As seen from figure 1, the peak positions corresponding to the $^4G_{5/2} \rightarrow ^6H_J$ (J = 9/2, 7/2 and 5/2) transitions are shifted towards lower energy side (red-shift) with increase in pressure (figure 1(a)) whereas it has shifted towards higher energy side (blue-shift) while release of pressure (figure 1(b)).

The energy shifts are found to be -5.19, -5.04, and -5.17 cm$^{-1}$/GPa for the $^4G_{5/2} \rightarrow ^6H_{9/2}$, $^4G_{7/2} \rightarrow ^6H_{7/2}$, and $^4G_{5/2} \rightarrow ^6H_{5/2}$ transitions, respectively, which are more or less similar to the corresponding shifts of -5.3, -4.7, and -5.2 cm$^{-1}$/GPa observed in PKFBASm01 glass [10]. The peak shift of these transitions towards lower energy side with increase in pressure is attributed to the changes in Coulomb and spin-orbit coupling interactions due to changes in the overlap of the ligand orbitals with the $4f$ wave functions of the Sm$^{3+}$ ions [11].

In figure 1, the $^4G_{5/2} \rightarrow ^6H_{J}$ (J = 9/2, 7/2 and 5/2) transitions are split into two components and the magnitude of the crystal-field (CF) splitting increases with increase in pressure as well as decreases while release of pressure (see Table 1) for all these transitions. For instance, the splitting of the $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{7/2}$ transitions increase with a slope of 5.04 and 5.17 cm$^{-1}$/GPa, respectively, for the present glass and also similar changes were observed in other Sm$^{3+}$:glasses [10,12]. These changes are mainly due to decrease in average inter-ionic distance between Sm$^{3+}$ ions and ligands with increase of pressure [13]. However, it is not possible to estimate CF parameters because of complex electronic structure of the Sm$^{3+}$ ion in Sm$^{3+}$-doped systems [14,15].

The luminescence decay curves for the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition of Sm$^{3+}$ ions in PKFBASm005 glass have been measured at various pressures by excitation with 476.5 nm line of Ar$^+$ laser. In general, the decay curves exhibit single exponential behaviour at lower concentrations and turn into non-exponential for higher concentrations [16,17]. In the present work, the decay curves are found to be non-exponential in the entire pressure range. The effective lifetimes ($\tau_{\text{eff}}$) for non-exponential decay curves were evaluated using the following expression [18].

$$\tau_{\text{eff}} = \frac{\int t I(t) \, dt}{\int I(t) \, dt}$$

where $I(t)$ is the fluorescence intensity at time $t$ starting from excitation.
The \( \tau_{\text{eff}} \) for the \( ^4G_{5/2} \) level of Sm\(^{3+}\) ion decreases from 3.23 to 1.62 ms with increase in pressure from ambient to 40.2 GPa and are collected in Table 1. These non-exponential decay curves observed beyond 4.1 GPa are well-fitted to the generalized Yokota-Tanimoto (YT) model [19] for \( S = 6 \). This generalized YT model fit is used to explain non-exponential behaviour of decay curves. The analysis indicate that the dominant interaction mechanism involved in the energy transfer processes through cross-relaxation among Sm\(^{3+}\) ions is of dipole-dipole interaction. The calculated energy transfer (Q), donor-acceptor interaction (C\(_{\text{DA}}\)) and diffusion (D) parameters were shown in Table 1.

The decrease in lifetimes with increase in pressure, associated with increasing non-exponential behaviour of the decay curves, has been attributed to the gradual increase in CF strengths around the Sm\(^{3+}\) ions as well as energy transfer processes through cross-relaxation channels \((^4G_{5/2}, ^6H_{5/2}) \rightarrow (^4F_{5/2}, ^4F_{11/2})\) and \((^4G_{5/2}, ^6H_{9/2}) \rightarrow (^4F_{9/2}, ^4F_{7/2})\) in the Sm\(^{3+}\) ion [13,16]. This cross-relaxation is due to the energy transfer from the Sm\(^{3+}\) ion in an excited \(^4G_{5/2}\) state to a nearby Sm\(^{3+}\) ion in the ground \(^6H_{5/2}\) state. Moreover, while releasing pressure the peak positions corresponding to the \(^4G_{8/2} \rightarrow ^4H_{J} (J = 9/2, 7/2 \text{ and } 5/2)\) transitions are shifted towards higher energy side (blue-shift) with a small hysteresis but not any permanent deformation of structure around Sm\(^{3+}\) ions. Similar results have also been noticed in our earlier studies [10,12].

**Figure 1.** Luminescence spectra of PKFBASm005 glass with (a) increasing and (b) decreasing pressures.
Table 1. Effective lifetimes ($\tau_{\text{eff}}$, ms) of the $^4G_{5/2}$ level, energy transfer parameter (Q), peak positions (cm$^{-1}$) of the $^4G_{5/2} \rightarrow ^6H_{9/2,7/2,5/2}$ emission bands, crystal-field splitting (CFS, cm$^{-1}$) for the $^4G_{5/2} \rightarrow ^6H_{7/2,5/2}$ emission bands, donor-acceptor interaction ($C_{\text{DA}}$, $\times 10^{-41}$ cm$^6$ s$^{-1}$) and diffusion ($D$, $\times 10^{-14}$ cm$^2$ s$^{-1}$) parameters of Sm$^{3+}$ ions in PKFBASm005 glass at (a) increasing and (b) decreasing pressures.

| Pressure (GPa) | $\tau_{\text{eff}}$ | Q  | Peak positions | CFS  | $C_{\text{DA}}$ | D    |
|---------------|---------------------|-----|----------------|------|-----------------|------|
| (a) Increasing pressure |
| 0             | 3.23                | 0   | 15511          | 16732| 17809           | 180  |
| 4.1           | 2.89                | 0.011| 15499          | 16718| 17798           | 199  |
| 9.2           | 2.57                | 0.021| 15488          | 16707| 17787           | 221  |
| 18.4          | 2.26                | 0.032| 15469          | 16685| 17765           | 228  |
| 27.2          | 1.96                | 0.036| 15422          | 16644| 17710           | 236  |
| 34.2          | 1.76                | 0.041| 15378          | 16606| 17666           | 275  |
| 40.2          | 1.62                | 0.043| 15361          | 16588| 17654           | 279  |
| (b) Decreasing pressure |
| 37.5          | 1.67                | 0.049| 15373          | 16592| 17650           | 273  |
| 27.0          | 1.99                | 0.027| 15431          | 16646| 17715           | 235  |
| 10.4          | 2.30                | 0.024| 15491          | 16699| 17780           | 223  |
| 5.4           | 2.58                | 0.022| 15512          | 16718| 17801           | 212  |
| 0.6           | 3.00                | 0.015| 15521          | 16736| 17812           | 188  |

4. Conclusions
The pressure dependent luminescence and decay properties of Sm$^{3+}$ ions in fluorophosphate glass have been studied. A red-shift as well as increase in crystal-field splitting for the $^4G_{5/2} \rightarrow ^6H_j$ ($J = 9/2,7/2$ and 5/2) transitions have been observed with increase in pressure and are attributed to the changes in Coulomb and spin-orbit coupling interactions besides changes in the overlap of the ligand orbitals with the 4$f$-wave functions of the Sm$^{3+}$ ions. The blue-shift has also been noticed for $^4G_{5/2} \rightarrow ^6H_j$ transitions while releasing pressure. The non-exponential behaviour of the decay curves increased with increase in pressure and is well-fitted to the generalized Yokota-Tanimoto model indicating that the energy transfer among Sm$^{3+}$ ions is of dipole-dipole interaction. The decrease in lifetime of the $^6G_{5/2}$ level with increase in pressure is due to enhancement in energy transfer efficiency. It has also been observed that there is no permanent deformation of structure around Sm$^{3+}$ ions when pressure is released.

Acknowledgements
This work has been supported through a Major Research Project funded by DAE-BRNS (No.2009/34/36/BRNS/3174, dt.12-02-2010), Government of India. One of the authors (CKJ) is grateful to Department Physik, Universität Paderborn, Germany for his stay as a Guest Scientist.
References

[1] 1993 Rare Earth Doped Fibre Lasers and Amplifiers ed M J Digonnet Dekker, New York
[2] Suratwala T I, Steele R A, Wike G D, Campbell J H and Takeuchi K 2000 J. Non-Cryst. Solids 263-264 213
[3] Jahn W 1961 Glasstechn. Bar 34 107
[4] Naftaly M and Jha A 2000 J. Appl. Phys. 87 2098
[5] Marion J E and Weber M J 1991 Eur. J. Solid. State. Inorg. Chem. 28 271
[6] Jayasankar C K, Venkatramu V, Babu P, Tröster Th, Sievers W, Wortmann G and Holzapfel W B 2005 J. Appl. Phys. 97 093523-1
[7] Von der Ahe W, Diploma thesis 1989 Universitat Paderborn
[8] Piermarini G J, Block S, Barnett J D and Forman R A 1975 J. Appl. Phys. 46 2774
[9] Holzapfel W B 2003 J. Appl. Phys. 93 1813
[10] Jayasankar C K, Jyothi L, Basavapoornima Ch, Tröster Th, Sievers W and Wortmann G 2010 High Press. Res. 30 424
[11] Chen G, Stump N A, Haire R G, Burns J B and Peterson J R 1994 High Press. Res. 12 83
[12] Jayasankar C K, Upendra Kumar K, Venkatramu V, Babu P, Tröster Th, Sievers W and Wortmann G 2008 J. Lumin. 128 718
[13] Qiuping W, Lijun L, DingZheng Z, Yuanbin C and Lihong W 1992 J. Phys. Condens. Matter 4 6491
[14] Renuka Devi A, Jayasankar C K and Reid M F 1994 Phys. Rev. B 49 12551
[15] Garcia D and Faucher M 1998 Handbook on the Physics and Chemistry of Rare Earths vol 21, ed K A Gschneidner Jr. and L Eyring (Elsevier Science, New York) Chapter 144
[16] Venkatramu V, Babu P, Jayasankar C K, Tröster Th, Sievers W and Wortmann G 2007 Opt. Mater. 29 1429
[17] Praveena R, Venkatramu V, Babu P and Jayasankar C K 2008 Physica B 403 3527
[18] Nakazawa E 1999 Phosphor Handbook ed Shionoya S and Yen W M (Boca Raton, FL:CRC Press) p. 104.
[19] Yokota M and Tanimoto O 1967 J. Phys. Soc. Jpn. 22 779.