

High-pressure luminescence study of Eu^{3+} in lithium borate glass

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The effect of hydrostatic pressure on the emission spectra and fluorescence lifetimes of Eu^{3+} :lithium borate glass has been measured up to 32.6 GPa at room temperature (RT) and up to 25.2 GPa at 15 K. Crystal-field parameters obtained for the Stark splitting of the 7F_1 level reveal that the crystal-field perturbations experienced by the $4f^6(\text{Eu}^{3+})$ electrons change significantly with pressure. Decays of the emission from the 5D_0 level measured under pressure fit a single exponential both at room temperature and 15 K. Both at RT and 15 K, the lifetimes decrease with increasing pressure. However, the lifetime changes up to ~ 5 GPa only marginally, then decreases strongly from ~ 5 to ~ 15 GPa and from ~ 15 GPa only very slowly. This nonuniform pressure-induced variation of the lifetime is unexpected and can be attributed to pressure-induced structural changes.

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I. INTRODUCTION

Lanthanide-doped glasses are the subject of intense current research because of the advantage of using them as optical devices in glass lasers, fiber lasers, up-conversion lasers, optical amplifiers, and other applications.¹ In these devices, excitations and the emissions are due to transitions among $4f$ electronic states of trivalent lanthanide ions, which are highly sensitive to the symmetry and structure of the local environment. Therefore, the luminescence properties, such as spectral shapes and quantum efficiencies of electronic states, are host dependent, and their understanding requires first hand information on relations between luminescence properties and glass structure.

Among lanthanides, the $\text{Eu}^{3+}(4f^6)$ ion is one of the best choices with which to analyze the interaction of the ion with the local field because of its simple electronic structure with a nondegenerate 7F_0 ground state and intense luminescence from the excited 5D_0 state to lower 7F multiplets.²⁻⁸ Furthermore, the 7F ground-state multiplet is well separated (about $12\,000\text{ cm}^{-1}$) from the next 5D_0 excited multiplet which simplifies local (crystal) field analysis⁸ within the Stark level splittings of the 7F multiplet states by assuming pure Russell-Saunders coupling ($>95\%$). The transition intensity ratios of ${}^5D_0 \rightarrow {}^7F_2$ to ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_4$ to ${}^5D_0 \rightarrow {}^7F_1$ determine the Judd-Ofelt parameters,⁹⁻¹¹ Ω_2 and Ω_4 , respectively. These Ω parameters are related to short-range (covalent) and long-range (bulk) properties of the local field.^{2,3,12} Energy level analysis through crystal-field theory, combined with an intensity analysis through Judd-Ofelt formalism,^{2,10,11} are used to determine the symmetry and strength of the local field and to estimate its interactions with the f electrons. This information is essential for correlating the luminescence properties with glass composition, and plays a significant role in the design of glass compositions for specific applications.

Therefore, most of the recent research was devoted to preparing a variety of glass compositions doped with Eu^{3+}

ions to derive detailed information on the local field, as well as on ion-ion and ion-host interaction processes.²⁻⁹ On the other hand, high pressure techniques have been used to vary the local bonding environment, whereby the application of high pressure changes the interatomic bond lengths and bond angles, and therefore also the local field at the Eu^{3+} ion sites.¹²⁻¹⁴ In contrast to the common practice of preparing a variety of new glass compositions to alter the local field, a single selected composition is sufficient to tune the local field through the application of pressure.

Though the pressure tuning of local fields in a selected Eu^{3+} -doped glass has some advantage over preparing a large number of samples with different local fields, so far only a limited number of high pressure studies have been reported on Eu^{3+} glasses.^{12,14} This seems to be due mainly to experimental difficulties involved in the use of pressure cells (diamond anvil systems) and appropriate pressure medium, pressure sensors, gaskets, etc., and in general also by the size of the sample, which should be in the range of only $30\ \mu\text{m}$. All these constraints limit the collection of sufficient luminescence data for further analysis.

In the present work, a detailed study of the luminescence properties of Eu^{3+} -doped lithium borate glasses under pressures up to ~ 32.6 GPa at room temperature and up to ~ 25.2 GPa at 15 K has been undertaken. Crystal-field analysis was used to evaluate the changes in the local structure around the Eu^{3+} ions under pressure.

II. EXPERIMENT

The Eu^{3+} -doped lithium borate glass with a composition of $49.5\ \text{Li}_2\text{CO}_3 + 49.5\ \text{H}_3\text{BO}_3 + 1.0\ \text{Eu}_2\text{O}_3$ (in mol%) (hereafter referred to as LBEu1) was prepared by a melt quenching technique. The starting materials were reagent grade. The mixed material, after thoroughly crushing in an agate mortar, was placed into a porcelain crucible and melted in an electric furnace at 950°C for about 30 min. The melt was poured onto a stainless steel plate at RT and pressed with another

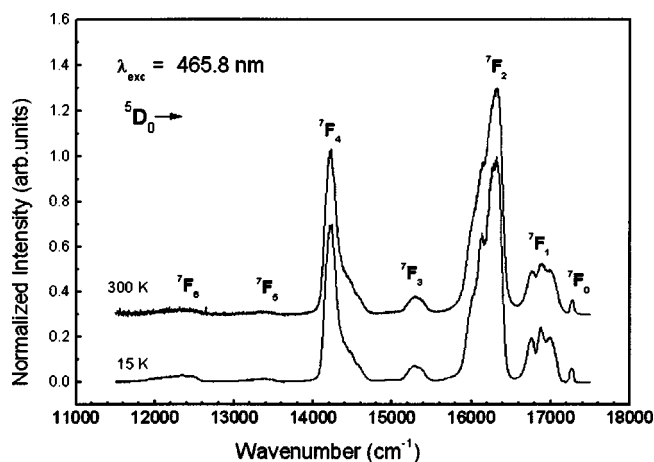


FIG. 1. Normalized emission spectra of LBEu1 glass at 300 K and 15 K at ambient pressure.

similar stainless steel plate. This sample was then annealed at 350°C for 5 h and this procedure resulted in good transparent glasses.

The 465.8 nm line of an Ar⁺ laser was used as excitation source. The emission spectra were recorded with a double monochromator equipped with a photomultiplier. The resolution of the double monochromator depends on the wavelength and the slit widths. In the present study, the typical resolution was between 5 cm⁻¹ and 10 cm⁻¹. A special miniature diamond anvil cell¹⁵ (DAC) was used to generate pressures up to 35 GPa also at low temperatures. A piece of LBEu1 glass was placed together with a ruby pressure sensor into a 80 μm diameter hole of a stainless steel (INCONEL X750) gasket of 200 μm thickness. A mixture of methanol:ethanol:water (16:3:1) was used as a pressure transmitting medium. This gasket with the sample and pressure transmitting fluid was then compressed by the parallel faces of the two opposed diamonds of the DAC. The pressure and the hydrostatic conditions experienced by the sample were determined by the shift and broadening of the ruby *R*₁ lines.¹⁶ For measurements at 15 K, the cell was cooled in a helium closed-cycle cryostat. A mechanical chopper in connection with a multichannel scalar allowed for lifetime measurements in the range from 2 μs to 2s.

III. CRYSTAL-FIELD ANALYSIS

Methods of crystal-field (CF) parametrization for lanthanide energy levels in general and for Eu³⁺ in particular can be found in the literature.^{8,17-19} Here, only the basic theoretical expressions for the present calculations are recalled. The CF potential, H_{CF} , acting on the Eu³⁺ ions is conveniently expressed in the Wybourne's notation^{8,18} by

$$H_{CF} = \sum_{k,q,i} B_q^k C_q^{(k)}(i), \quad (1)$$

where the B_q^k are crystal-field parameters and the $C_q^{(k)}$ are tensor operators. The B_q^k are treated as adjustable parameters, whereas the matrix elements of $C_q^{(k)}$ can be calculated exactly. The number of parameters for H_{CF} in Eq. (1) is greatly re-

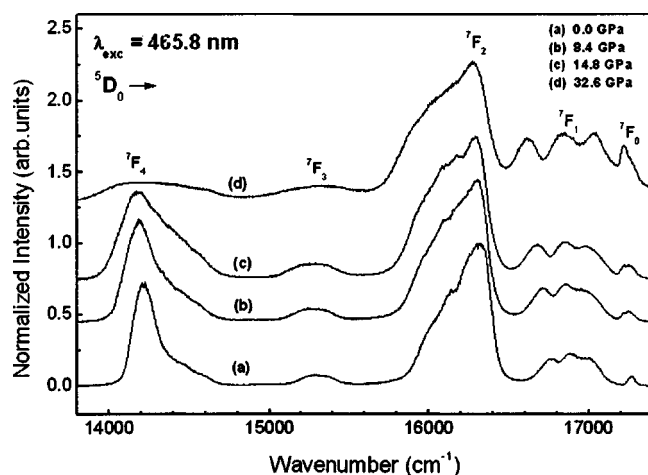


FIG. 2. Normalized emission spectra of LBEu1 glass at different pressures at 300 K.

duced by the symmetry selection rules for the point symmetry at the Eu³⁺ 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.

In the present analysis, considering the *J*-mixing interaction as a perturbation over the crystal-field interaction, the three Stark components of the 7F_1 are described by

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

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

The crystal-field strength parameter N_v has been used to simplify the description of the CF parameters due to its independence from the specific crystal structure. The N_v , considering only the second-rank CF parameters, has been determined using the following relation:^{8,20}

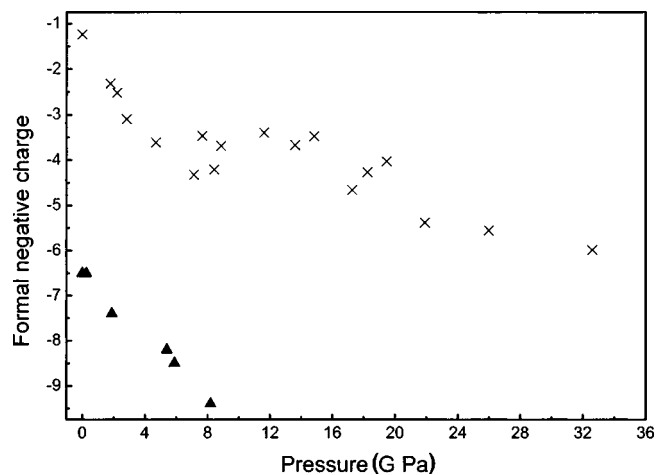


FIG. 3. Formal negative charge on ligands vs pressure at 300 K in cubic Eu₂O₃ (▲) and LBEu1 (×).

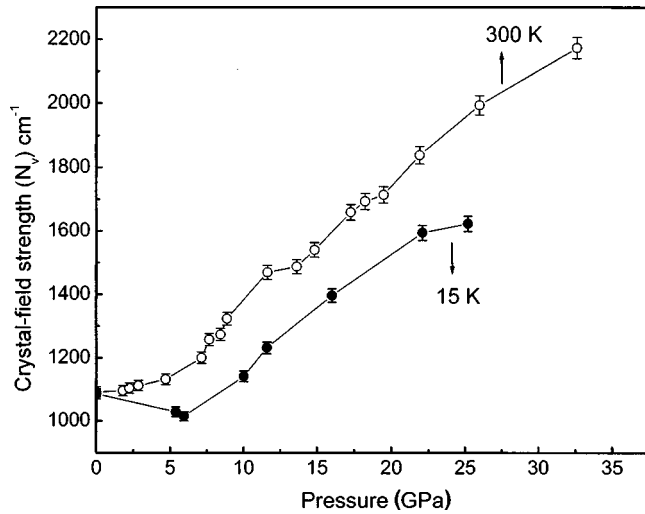


FIG. 4. Crystal-field strengths vs pressure for the LBEu1 glass at 300 K and 15 K.

$$N_v = \sqrt{\frac{4\pi}{5}[(B_{20})^2 + 2(B_{22})^2]}. \quad (3)$$

IV. RESULTS

Figure 1 presents the emission spectra of the LBEu1 glass measured at RT and 15 K at ambient pressure. Figure 2 shows parts of these emission spectra as a function of pressure. The ${}^5D_0 \rightarrow {}^7F_5$ and ${}^5D_0 \rightarrow {}^7F_6$ transitions are not shown, as they are very weak and therefore not used in the analysis with pressure variations. The spectra shown in Figs. 1 and 2 are normalized to the ${}^5D_0 \rightarrow {}^7F_2$ transition. The emission spectra corresponding to ${}^5D_0 \rightarrow {}^7F_J$ ($J=0,1,2,3,4,5,6$) transitions in Figs. 1 and 2 are very similar and comparable to those obtained for other Eu^{3+} :glasses.³⁻⁹ Figure 3 shows the variation with pressure

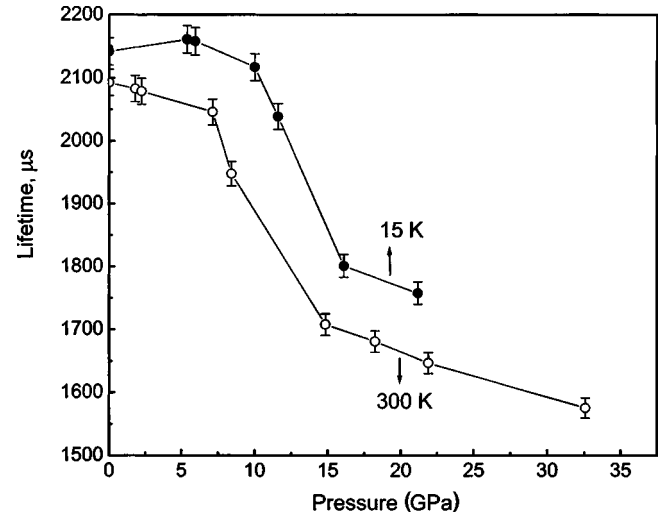


FIG. 6. Lifetime variation under pressure for the LBEu1 glass at 300 and 15 K.

for the formal negative charge on the ligands directly bonded to the Eu^{3+} ion.^{21,22} The crystal-field strength versus pressure at RT and 15 K is shown in Fig. 4. Only the Stark level splittings of the ${}^5D_0 \rightarrow {}^7F_1$ transition are considered for the CF analysis since the splittings of other transitions (${}^5D_0 \rightarrow {}^7F_{2-6}$) are not completely resolved. Typical decay curves obtained for different pressures at RT are shown in Fig. 5. The variation of lifetime as a function of pressure both at RT and 15 K is shown in Fig. 6. Table I summarizes the results obtained for different pressures at RT and 15 K for the LBEu1 glass.

V. DISCUSSION

Optical absorption and the Judd-Ofelt analysis of the LBEu1 glass has been reported in a previous paper.⁷ Here, we present a detailed study of luminescence characteristics

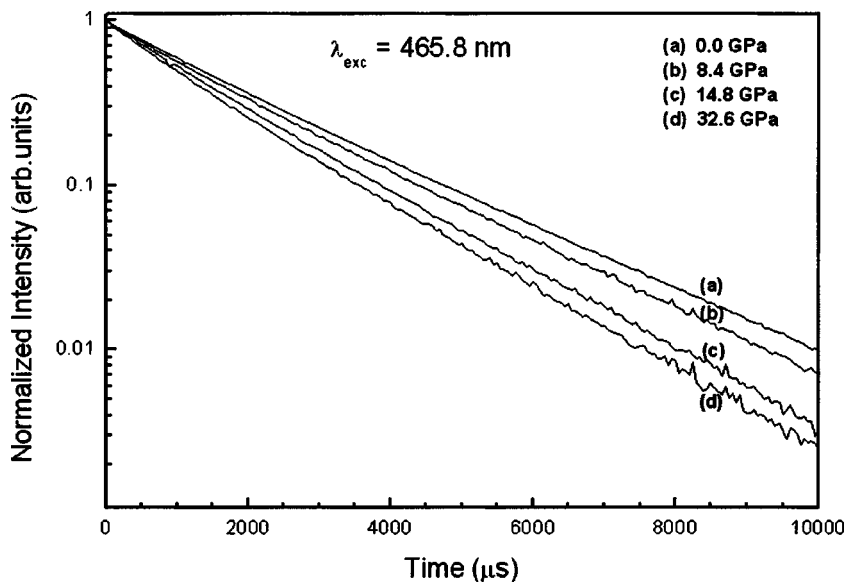


FIG. 5. Decay curves for the emission for the transition of ${}^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} in the LBEu1 glass at different pressures at 300 K.

TABLE I. Energies, crystal-field and strength parameters (B_{20} , B_{22} and N_v) (cm^{-1}), and lifetimes for the LBEu1 glass under pressure. (a) At RT. (b) At 15 K.

(a)								
Pressure (GPa)	${}^5D_0 \rightarrow {}^7F_0$	7F_1	7F_1	7F_1	B_{20}	B_{22}	N_v	Lifetime (μs)
0	17269	275.2	384.9	505.0	600	239	1092	2093
1.8	17263.6	279.7	387.9	509.8	605	236	1096	2083
2.2	17262.4	279.2	388.6	510.9	609	239	1104	2079
2.8	17258.6	281.1	391.9	514.2	612	242	1112	2079
4.7	17254.8	285.7	394.3	522.0	629	239	1132	2082
7.1	17248.8	283.2	398.0	533.1	667	253	1200	2046
7.7	17255.9	286.7	404.4	546.8	701	262	1257	1965
8.4	17249.9	281.7	404.0	545.3	705	272	1273	1948
8.9	17254.2	274.1	397.4	548.3	739	274	1323	1879
11.6	17256.4	267.0	412.9	568.0	802	328	1469	1771
13.6	17254.4	272.3	410.3	576.7	828	311	1487	1705
14.8	17255.8	272.5	417.9	586.0	852	330	1540	1708
17.3	17245.8	250.1	411.8	587.5	909	366	1659	1685
18.2	17249.4	256.5	414.9	599.6	938	361	1693	1681
19.5	17251.4	256.0	422.2	602.0	938	380	1714	1665
21.9	17238.7	233.1	406.7	604.6	1015	396	1838	1647
26.0	17236.9	255.3	439.3	648.3	1100	431	1994	1627
32.6	17232.1	196.3	400.6	627.7	1198	471	2173	1575

(b)		
Pressure (GPa)	N_v	Lifetime (μs)
0	1086	2142
5.4	1029	2161
5.9	1015	2158
10.0	1141	2117
11.6	1231	2039
16.0	1396	1801
22.1	1594	1758
25.2	1623	—

for this LBEu1 glass under pressure. As seen from Fig. 1, the emission spectra of LBEu1 at RT and 15 K consists of ${}^5D_0 \rightarrow {}^7F_J$ ($J=0,1,2,3,4,5,6$) transitions. The temperature shifts are too small to be noticed in these spectra, and the Stark levels are better resolved at lower temperatures, as seen for 7F_1 and partially for 7F_2 . The well-resolved splitting of the ${}^5D_0 \rightarrow {}^7F_1$ transition into three components suggests that the Eu^{3+} ions in the LBEu1 glass occupy low symmetry sites (orthorhombic (C_{2v} , D_2 , and D_{2h}), monoclinic (C_s , C_2 and C_{2h}), or triclinic [C_1 and $C_i(S_2)$]). The Stark level splitting for the other levels of the ${}^5D_0 \rightarrow {}^7F_{2-6}$ transitions are not fully resolved. The ${}^5D_0 \rightarrow {}^7F_5$ and ${}^5D_0 \rightarrow {}^7F_6$ emissions are comparatively very weak, similar to the situation in other Eu^{3+} :glasses.³⁻⁹

Figure 2 shows the emission spectra for ${}^5D_0 \rightarrow {}^7F_{0-4}$ transitions at pressures of 0, 8.4, 14.8, and 32.6 GPa, respectively. As seen from Fig. 2, the levels shift to a lower energy

(redshift) and the widths of the transitions become broader as pressure increases. It is interesting to note that the ${}^5D_0 \rightarrow {}^7F_4$ transition is more strongly affected under pressure than the other transitions shown in Fig. 2. All three Stark levels of the ${}^5D_0 \rightarrow {}^7F_1$ transition are resolved under pressure. The magnitude and resolution of the splitting increases under pressure.

As seen from Table I and Fig. 2, at moderate pressures up to 7.1 GPa, as well as at the higher pressures from 21.9 to 32.6 GPa, the ${}^5D_0 \rightarrow {}^7F_0$ transition shifts moderately towards lower energies; however, for intermediate pressures in the range from 7.7 to 19.5 GPa, the shift is very weak. This observation, along with spectral broadening of the ${}^5D_0 \rightarrow {}^7F_0$ transition and the increase in the crystal-field strength, can be explained by the creation of high-field Eu^{3+} sites under pressure¹² related to higher formal negative charges on the ligands.

The sum of the formal negative charges (q) on the ligands directly bonded to Eu^{3+} ion can be related to the energy (ν) of the ${}^5D_0 \rightarrow {}^7F_0$ transition:²¹

$$\nu(\text{cm}^{-1}) = 17273 + 2.29q - 0.76q^2 \quad (\text{at } T = 296 \text{ K}). \quad (4)$$

With this relation and the measured transition energies, the changes in the formal negative charges on the oxygen sites can be evaluated. The quadratic equation (4) was solved by using the values of ν (column 2 of Table I) for each pressure. The negative root of the solution of Eq. (4) was taken as the possible value for the negative formal charge. As shown in Fig. 3, the 79% increase in the value of the formal negative charge on the neighboring oxygens in this pressure range can be related to the expansion (nephelauxetic effect) of the f orbitals of Eu^{3+} . This expansion decreases the electronegativity of Eu^{3+} and causes an increase in the covalency of the Eu-O bonds, as evidenced by the redshift of the transitions ${}^5D_0 \rightarrow {}^7F_{0-4}$ under pressure in Fig. 2. Chen *et al.*²² noticed a 26% increase in this formal charge between ambient pressure and 5.4 GPa in the case of cubic Eu_2O_3 and related their results also to an expansion of f orbitals. For comparison, Fig. 3 includes both the data for the LBEu1 glass and for cubic Eu_2O_3 .

In general, the crystal-field analysis is carried out by assuming (orthorhombic) C_{2v} -point symmetry for the local structure around the Eu^{3+} ions in these glasses.^{3-9,12} The second-rank even CF parameters B_{20} and B_{22} are calculated, therefore, by diagonalizing the complete Hamiltonian (free ion and crystal field) using C_{2v} symmetry, also taking into account J mixing. From the 11 SLJ multiplets, a total of 69 JM_J states are used in the basis set for the CF calculations. During the fitting of these energy levels, all 19 free-ion parameters ($F^{2,4,6}$, ζ , α , β , γ , $T^{2,3,4,6,7,8}$, $M^{0,2,4}$, and $P^{2,4,6}$) are fixed to the values for $\text{Eu}^{3+}:\text{LaCl}_3$ (Ref. 23), and only the second-rank CF parameters are optimized. The fitting process minimizes the root mean square deviation between the experimental and calculated 7F_1 Stark energy levels.²⁴ The effect of pressure on the second-rank CF parameters (with J mixing) and on the CF strength parameter N_b [Eq. (3)] is shown in Table I and in Fig. 4 for the LBEu1 glass. Obviously, the CF strength N_b shows an almost cubic dependence on pressure at RT. At 15 K, N_b first decreases up to ~ 5 GPa, then increases up to ~ 22 GPa, and finally approaches saturation.

The decay of emission from the 5D_0 level has been measured both as a function of pressure and temperature. The 465.8 nm line of an Ar^+ laser was used to excite the 5D_2 level. A fast, nonradiative decay populates the emitting 5D_0 level. For RT, the decay of the measured emission intensity is shown in Fig. 5 for four pressures. All the decay curves are single exponential, indicating the absence of additional energy transfer processes also under pressure. On the other hand, the fluorescence decay for the ${}^4G_{5/2}$ emission of $\text{Sm}^{3+}:\text{lithium fluoroborate}$ glass shows a pronounced nonexponential behavior with increasing pressure due to energy transfer processes, even for samples with a low concentration, accompanied by a fast decrease of the lifetime.²⁵ The simple exponential decay in the present case at low temperatures is observed also at room temperature, however, with

slightly longer lifetimes. One of the reasons for the decrease in lifetime with pressure is due to the decrease in the $\text{Eu}^{3+} - \text{Eu}^{3+}$ distance which plays an important role in quenching mechanisms.

The knowledge on the effect of pressure on lifetimes of $4f-4f$ transitions is limited.²⁶⁻³⁴ Jovanic and his group²⁶⁻²⁸ reported lifetimes for the ${}^5D_0 \rightarrow {}^7F_0$ transition of the Sm^{2+} ion in SrFCl ,²⁶ SrB_4O_7 ,²⁷ and $\text{SrFCl}_{0.5}\text{Br}_{0.5}$.²⁸ In all these studies, it is found that the lifetime decreases with a pressure of up to about 10 GPa. Shen and Bray²⁹ observed an exponential decrease in lifetimes for the 5D_0 and 5D_1 level of MFCI: Sm^{2+} ($M = \text{Sr}$ and Ca) systems under pressure, up to 23 GPa, both at RT and 20 K. The lifetime for the 5D_0 level of $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ increases up to 1.7 GPa and then decreases very quickly up to 4 GPa, followed by a practically constant value up to 10 GPa.¹³ Webster and Drickamer³⁰ studied the lifetimes of the ${}^5D_{1,2,3}$ states in $\text{Eu}^{3+}:\text{La}_2\text{O}_2\text{S}$. The lifetime for 5D_1 remained more or less constant and the lifetime for 5D_2 increased from 0–2 GPa and remained constant above 2 GPa, while the lifetime for 5D_3 could be measured above 7 GPa and was found to increase up to 11 GPa. It was found that the lifetime for the 5D_0 level of $\text{Eu}^{3+}:\text{YVO}_4$ increases with pressure up to 11 GPa.³¹ In the case of the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition of Nd^{3+} in $\text{Nd}_x\text{Y}_{(1-x)}\text{P}_5\text{O}_{14}$, the lifetime decreases with pressure of up to 9 GPa.³² The lifetime of the emission from the isolated 5D_4 multiplet of Tb^{3+} in $\text{Gd}_2\text{O}_2\text{S}$ was found to be unaffected under pressure up to 5 GPa.³³

The decay time for the ${}^4G_{5/2}$ level of $\text{Sm}^{3+}:\text{lithium fluoroborate}$ glass exhibits strong decreased with increased pressure for different concentrations of Sm^{3+} ions at RT, as well as at 20 K.^{25,34} Lochhead and Bray¹² reported the lifetime for the 5D_0 level of $\text{Eu}^{3+}:\text{sodium disilicate}$ glass, which is more appropriate to compare with our present work. The lifetimes reported for $\text{Eu}^{3+}:\text{sodium disilicate}$ glass increase from 0.0–4.0 GPa and then decrease up to 21 GPa at 77 K.¹² The former trend of increasing lifetimes in the initial pressure range was explained as due to possible local structural rearrangements towards centrosymmetry and decreased admixture of opposite-parity d states. However, in the present case, the marginal variations in lifetimes up to 5.0 GPa suggest that negligible changes occur in symmetry and admixture of states. After 4 and 5 GPa in $\text{Eu}^{3+}:\text{sodium disilicate}$ and $\text{Eu}^{3+}:\text{lithium borate}$ glasses, respectively, the lifetimes decrease with pressure as a common feature.

In order to explain theoretically the variation of lifetimes versus pressure, different authors proposed and verified different models to get a satisfactory agreement between theory and experimental lifetimes under pressure,^{29,30,33,35} as reviewed in detail recently.¹⁹ All these studies indicate that, in some cases, lifetimes continuously decrease or increase with pressure^{26-30,32-34} and in some other cases discontinuities can be noticed as, for instance, when lifetime increases at initial pressures and decreases when the pressure is increased further.^{12,13} Therefore, pressure-induced changes in interatomic bond lengths and bond angles are either continuous or discontinuous, as reflected from the pressure-induced variations in lifetimes and crystal-field parameters and strengths.

As seen from Fig. 6, the variation of the lifetime with pressure shows three different regions with different slopes. At RT, the slopes per GPa are 0.002, 0.05, and 0.007 for the

pressure ranges of 0–5, 7–13, and 15–32 GPa, respectively. The trend of lifetimes at 15 K is very similar to RT.

The pressure and temperature dependencies of the lifetimes can be understood by considering a simple model³⁶ for the Eu^{3+} ion with two excited energy levels. At RT, the observed lifetime τ consists of an intrinsic lifetime τ_i and a contribution from the mixing with the higher energy level having a shorter lifetime τ_e ,

$$\tau^{-1} = (\tau_i)^{-1} + (\tau_e)^{-1} \exp(-\Delta E/kT), \quad (5)$$

where ΔE is the energy difference between the two energy levels, k is the Boltzmann constant, and T is the absolute temperature.

At RT due to thermalization, the 5D_1 level is also populated, but at 15 K, the effect of thermalization is negligible. This slight difference increases with increasing pressure, due to a decreasing energy difference between 5D_0 and 5D_1 levels.¹⁴ It is found that the difference in lifetimes between the two temperatures increases from ambient pressure (50 μs) to high pressures (125 μs), as shown in Fig. 6.

These effects of high pressure on the lifetime τ , as well as on the crystal-field strength N_v for the LBEu1 glass, exhibit nonlinear behavior. The values for τ and N_v change barely up to ~ 5 GPa and vary differently under pressure. τ decreases very rapidly from ~ 5 to ~ 12 GPa and much more slowly at higher pressures up to at least 32.6 GPa. At RT, N_v increases in the whole pressure range from ~ 5 GPa to 32.6 GPa. The trends of τ and N_v at 15 K are obviously similar to the trends at RT, as shown in Figs. 6 and 4. The correlation of a decrease in τ with an increase in N_v under pressure is similar to the previously observed variation in different hosts at ambient pressure.^{12,37} Similar variations at RT and 15 K indicate that nonradiative decay from 5D_0 is very small. Pressure-induced structural changes in LBEu1 glass, from ambient pressure to ~ 5 GPa, appear to be monotonous, as evidenced by smooth nonlinear changes in both τ and N_v .

According to Avouris *et al.*,³⁸ increases in the homogeneous linewidth, along with increases in the crystal-field strength, can result from increases in the electron-phonon coupling at the higher field sites. This observation is supported by the variation of the present lifetime data under pressure. As seen from Fig. 5, both at RT and 15 K, above ~ 5 GPa the lifetimes decrease continuously. This observation can be explained by an increase in nonradiative decay

with increasing pressure above ~ 5 GPa due to enhanced electron-phonon coupling with local vibrations, consistent with the expectation that the shortening of Eu-O bonds should increase the coupling to local vibrations. The abrupt change between 7 and 13 GPa can be related to a structural change,^{36,39} which can cause either enhanced interactions between ground and excited configurations or stronger induced vibrational interactions in the host.

The spectral shape of the ${}^5D_0 \rightarrow {}^7F_0$ transition is found to broaden inhomogeneously with pressure, which suggests that pressure induces a broader range of site distribution for the Eu^{3+} ions in the glass. This observation may need further studies in wider ranges of pressure and also with respect to hysteresis effects.

VI. CONCLUSIONS

The present study of the luminescence characteristics of Eu^{3+} ions in lithium fluoroborate glass under pressure shows new features: The shifts and the broadening of the ${}^5D_0 \rightarrow {}^7F_0$ transition indicate that the crystal-field strength increases due to charge transfer to the ligands and the creation of high-field Eu^{3+} sites under pressure. The 79% increase in the value of the formal negative charge on the neighboring oxygen under pressure is attributed to the expansion of f orbitals of Eu^{3+} , which causes an increase in the ionicity of Eu-O bonds. The decay curves of ${}^5D_0 \rightarrow {}^7F_2$ remain single exponential even under pressure, indicating the absence of additional energy transfer processes. The decrease in 5D_0 lifetimes with pressure results from the decrease in the distance between Eu^{3+} - Eu^{3+} ions; however, the temperature dependence of lifetimes under pressure is related to the thermal population of the 5D_1 level. Under pressure, a decreasing trend in τ and an increase in N_v is noticed. Similar variations of τ and N_v at RT and 15 K indicate that nonradiative decay from 5D_0 is very small. The continuous decrease in lifetimes both at RT and 15 K, above ~ 5 GPa, can be explained by an increase in nonradiative decay due to enhanced electron-phonon coupling with the local vibrations.

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