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Local Structure of Niobate-Phosphate Glass Using Eu^{3+} Ion Fluorescence *

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The niobate phosphate glasses containing Eu^{3+} ions were fabricated by the melting method. The fluorescence characteristics of the glass at temperatures from 77 K to 700 K were investigated under the excitation of 488 nm light. The results show that the fluorescence intensity of Eu^{3+} ions first increases and then decreases as temperature increases. The temperature-dependent parameters of the crystal fields and the local structure surrounding Eu^{3+} ions were investigated and discussed from the situation of splitting energy level of 5D_0 - 7F_1 . The results indicate that the distance of europium and oxygen become shorter with increasing temperature and the coordination number of Eu^{3+} ion is near 8, which does not change with temperature.

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Glasses are favourable as the host materials due to their high transparency, compositional variety and easy mass production. Glasses containing Eu^{3+} ions have attracted much attention because of their potential applications in laser and optical data storage.^[1-3] Persistent spectral hole burning (PSHB) was suggested as the basis for high density frequency domain optical data storage.^[4] Recently, PSHB can be formed by a photo-induced rearrangement of the local structure surrounding the central Eu^{3+} ions doped in SiO_2 glass at liquid helium temperature, which could be developed a practical material for optical data storage.^[2] However, the distorted local structure recovers thermally with the distribution of thermal barrier height, causing the decreasing hole depth with enhancement of temperature, and finally is erased. The hole burning to low temperature by means of a liquid helium and the development of the stable host materials are the main problems impeding a practical application. Knowledge of the temperature dependence local structure around rare earth ions in glasses is important for finding the relation between optical properties of Eu^{3+} ion and their environment temperature and structure, and is helpful to search for novel materials. The structure and environment temperature of the glass strongly influences the fluorescence characteristics of Eu^{3+} ion such as the splitting of stark energy level. By analysing these temperature dependence fluorescence spectra of the stark splitting of Eu^{3+} ion energy level in the glass, the local structure of Eu^{3+} ion could be proposed and understood in detail. In this Letter, we demonstrate the preparation of Eu^{3+} doped niobate-phosphate glass, and investigate the local structure of Eu^{3+} ion with fluorescence spectra, and their lo-

cal structural change with temperature. The niobate-phosphate glass was chosen to be the host for Eu ions because of their some advantages such as the high solubility for rare earth elements to obtain high Eu^{3+} ion concentration in the glass and high emission cross section for rare earth elements.

The compositions of glass normally doped 1.0 wt.% Eu_2O_3 are listed in Table 1. BaO was introduced in the form of reagents BaCO_3 , P_2O_5 and Nb_2O_5 are 99.9% purity. The batches of 100 g were mixed in an Al_2O_3 corundum crucible under air atmosphere. After keeping at 1300°C for 2 h, the glass melt was poured on to a stainless steel plate. Each glass was annealed for 2 h at 450°C temperature and cooled it to room temperature slowly. The sample were cut into small pieces with thickness of 2 mm and well polished.

Table 1. Compositions of the host glasses.

Niobate-phosphate glass	P_2O_5	Nb_2O_5	BaO
Nb-P1	50	5	45
Nb-P2	40	15	45

The excitation and fluorescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer. In the measurements of temperature dependence emissions of Eu^{3+} , the samples were put into a liquid nitrogen cycling system. A continuous 488-nm light from an argon laser was used as the exciting light. The fluorescence was measured by a UV-Lab Raman Infinity (made by Jobin Yvon Company).

Figure 1 shows the typical emission spectrum of Eu^{3+} ion in Nb-P1 glass. The emission peaks of 5D_0 - 7F_J ($J = 0, 1, 2, 3, 4$) transitions can be observed in the glass, indicating that Eu^{3+} ions are incorporated, and show their optical properties in the glass. Figure 2

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shows the temperature dependence of the emission intensity of the Eu^{3+} ion in the two glasses. It is obvious that the emission intensity of the Eu^{3+} ion increases with temperature initially and approaches to a maximum at a certain temperature, and then it decreases as temperature increases. It can also be noted that the maximum intensity of the samples increases from high temperature to low temperature with the increasing concentration of Nb_2O_5 , indicating that the temperature-quenching increases with increasing the Nb_2O_5 content.

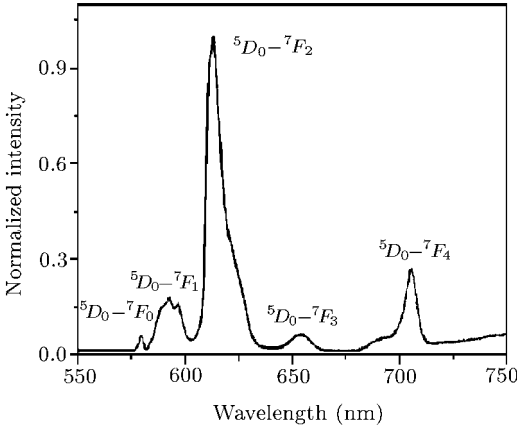


Fig. 1. Typical emission spectra of Eu^{3+} ion in the Nb-P1 glass.

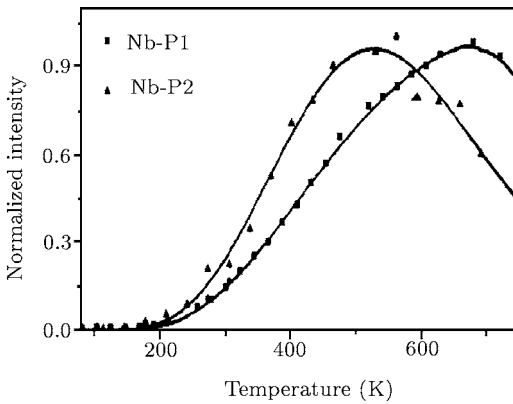


Fig. 2. Normalized emission intensity of $\Sigma^5D_0-^7F_J$ as a function of temperature.

To explain the temperature-dependent fluorescence behaviour, we show that the scheme of the energy level of the Eu^{3+} ion and the three corresponding transitions process under the excitation of the 488-nm light in Fig. 3. The energy of a 488-nm photon (20491 cm^{-1}) is lower than that of the 5D_2 level (21551 cm^{-1}) and higher than that of the 5D_1 level (18726 cm^{-1}), so the 488nm photon cannot be directly absorbed by the Eu^{3+} ions and thus there is no emission of Eu^{3+} ion at low temperature. However, as temperature increases, some electron transitions and emission processes probably occur. When the tem-

perature is high enough, photon-assistant absorption occurs. The electrons transiting from 7F_0 to 5D_2 increases, which induces increasing emission intensity and is described in process 1 in Fig. 3. On the other hand, the electrons in the 7F_0 level are thermally excited nearly to the 7F_1 and 7F_2 levels, meanwhile we consider the stark splitting of the 7F_2 level, the 488 nm light can directly excite the electrons from 7F_2 to 5D_2 , which also induces increasing emission intensity and is described in process 2 in Fig. 3. It is obvious that the temperature quenching on the 5D_0 level becomes serious when the temperature is elevated continuously, which tends to make the total emission intensity decrease. Some processes, such as the energy transfer from the 5D_0 levels to the other Eu^{3+} ions or the other impurity centres, probably occur, which is described in process 3 in Fig. 3.

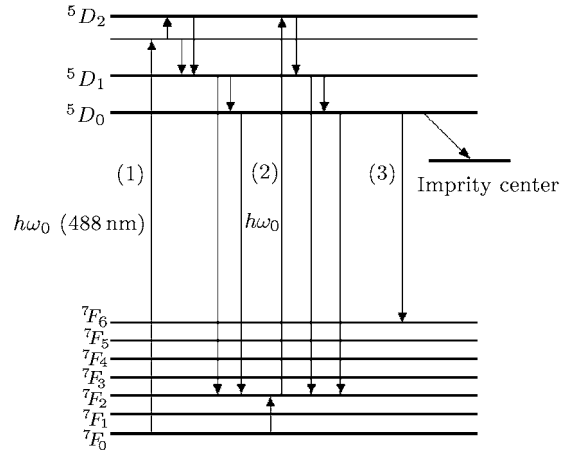


Fig. 3. Energy level of Eu^{3+} ion.

The thermally excited emission, phonon-assistant absorption and the temperature-quenching effect are mainly attributed to the variation of the emission intensity, although its detailed mechanism is not clearly clarified and understood.

Figure 4 shows the fluorescence spectra of the $^5D_0-^7F_1$ transition of Eu^{3+} from 77 K to 700 K. The fluorescence spectroscopy is useful and effective to study the local environment around the Eu^{3+} ions.^[5-9] As shown, the lines can be completely resolved into three Gaussian components ($\varepsilon_0, \varepsilon_-, \varepsilon_+$), indicating that the Eu^{3+} ions are located at sites with a symmetry of C_{2v} or C_2 or C_s . The peak energies of the Stark components of 7F_1 are plotted in Fig. 5 as a function of temperature. It can be seen from Fig. 5 that the relative intensities of $\varepsilon_0, \varepsilon_-$, and ε_+ gradually increase with increasing temperature. The peak energies of the three lines can be expressed as a polynomial function,

$$\varepsilon_+ = (17011.01 - 0.24T + 4.05 \times 10^{-4}T^2)\text{cm}^{-1}, \quad (1)$$

$$\begin{aligned}\varepsilon_- &= (16911.45 - 0.91T + 2.94 \times 10^{-4}T^2)\text{cm}^{-1}, \\ \varepsilon_0 &= (16788.21 - 0.04T + 8.95 \times 10^{-5}T^2)\text{cm}^{-1}.\end{aligned}\quad (2)$$

(3)

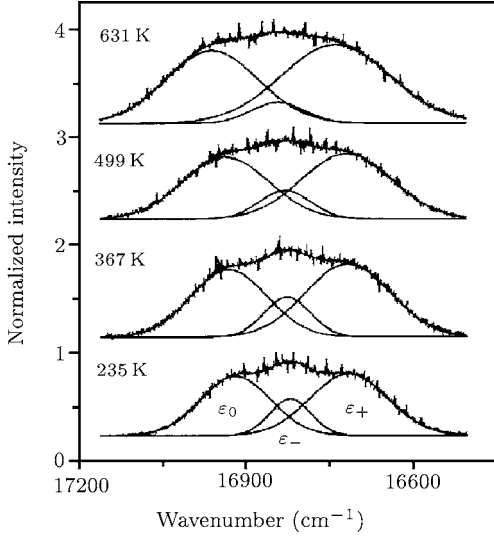


Fig. 4. Resolved emission spectra of the three crystal-field-splitting lines of the ${}^5D_0 - {}^7F_1$ transition at several temperatures.

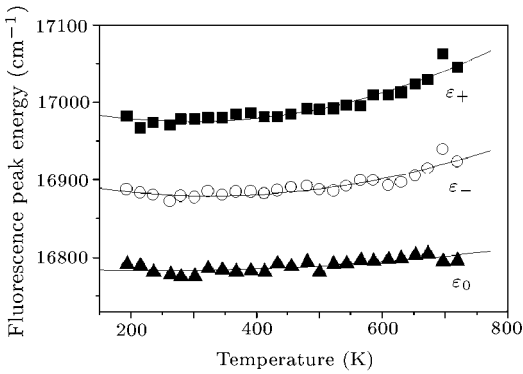


Fig. 5. Fluorescence peak energy of the three Stark splitting lines versus temperature.

In the above point symmetries, it is thought that the lowest energy of the 7F_1 lines can be assigned to the $M_J = 0$ component of the 7F_1 level, which has a large electron distribution along the z -axis. On the other hand, the other two high-energy components correspond to the electron distribution along the $x - y$ plane. Under these conditions, the z -axial and $x - y$ plane components of the second-order crystal field parameters, B_{20} and B_{22} , can be estimated from the energies of the three 7F_1 lines as follows:^[8,9]

$$B_{20} = \frac{5}{3}[2E_{\varepsilon_0} - E_{(\varepsilon_+)} - E_{(\varepsilon_-)}], \quad (4)$$

$$B_{22} = \frac{5}{\sqrt{6}}[E_{(\varepsilon_+)} - E_{(\varepsilon_-)}]. \quad (5)$$

The calculated second-order crystal field parameters B_{20} and B_{22} as a function of temperature are shown in Fig. 6. The solid lines are polynomial fitting for the data. Compared the values of B_{20} and B_{22} with these in SiO_2 and $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses, the values in $\text{P}_2\text{O}_5\text{-Nb}_2\text{O}_5$ are smaller than those in silicate glass, suggesting that the dense and hard silicate host takes more effects on Eu^{3+} ions.

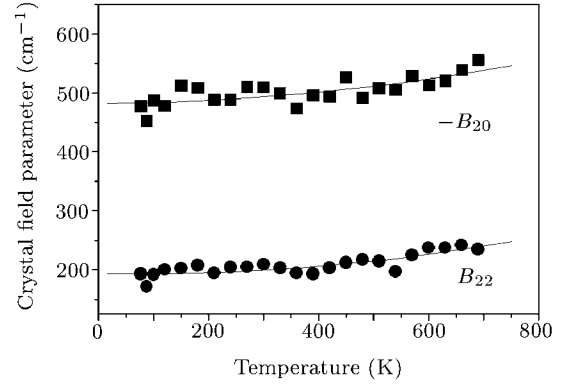


Fig. 6. Crystal field parameters B_{20} and B_{22} versus temperature.

It is known that the value of B_{20} has a portion dependence on the bond distance r between the coordinating ligands and the central ion, which is given by

$$B_{20} \propto \frac{3Z^2 - r^2}{r^3}. \quad (6)$$

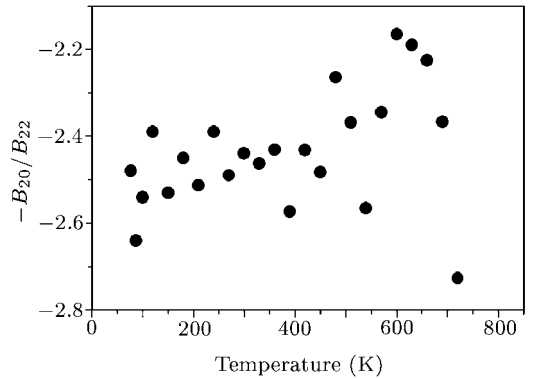


Fig. 7. Values of B_{20}/B_{22} versus temperature.

The smaller value of B_{20} implies the longer distance between the europium and the oxygen. It can be seen from Fig. 6 that the B_{20} value increases with increasing temperature, indicating that the distance between Eu and oxygen becomes shorter with increasing temperature. Brecher and Riseberg^[5,6] analysed these fluorescence spectra of the Eu^{3+} ion in oxide glasses and proposed geometric models for the coordination sphere of the Eu^{3+} ion. They restricted the ratio of the crystal parameters, B_{20}/B_{22} , to the coordination number of Eu^{3+} ions, in which the B_{22}/B_{20}

values of 2.05 and 0.23 correspond to the coordination values of 8 and 9, respectively. Figure 7 shows the values of B_{20}/B_{22} versus temperature. B_{20}/B_{22} is determined to be (2.45 ± 0.30) from Fig. 7 and almost does not change in the temperature range from 77 K to 700 K. This indicates that the coordination value of most Eu^{3+} ions is near 8 and does not vary with temperature. However, the coordination value of Eu^{3+} in silicate glass is about 9.^[2,9] The different coordinations in the glasses should be attributed to their structure and chemical composition of glass, although it is unknown in details at present.

In conclusion, the temperature-dependent behaviour of the Eu^{3+} ion has been studied in niobate-phosphate glasses. The variation of the emission intensity of Eu^{3+} with temperature is attributed to three factors, the thermally excited emission from 7F_2 to 5D_2 , phonon-assisted absorption and temperature quenching effect. The two formers tend to induce in-

creasing Eu^{3+} ions intensity with temperature, while the last one induces decreasing intensity. The distance between oxygen and Eu ion becomes shorter as temperature increases, while the coordination number of Eu^{3+} ion does not change with temperature.

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