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Author: Joanna Pisarska

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Borate glasses with PbO and PbCl₂ containing Dy³⁺ ions

JOANNA PISARSKA

University of Silesia, Institute of Chemistry, Szkolna 9, 40-007 Katowice, Poland;
e-mail: Joanna.Pisarska@us.edu.pl

Oxychloroborate glasses containing Dy³⁺ ions in the B₂O₃–PbCl₂–PbO–Al₂O₃–WO₃ system were studied using X-ray diffraction, Raman, FT-IR, absorption, excitation and luminescence spectroscopy. The results concerning glass preparation, short-range order structure and optical properties are reported. X-ray diffraction analysis evidently indicates that the fully amorphous system was prepared. Coexistence of trigonal BO₃ and tetrahedral BO₄ units was evidenced by Raman and FT-IR spectroscopy. The electronic states belonging to the 4f⁹ configuration of trivalent Dy³⁺ were determined from the absorption and excitation spectra. The luminescence bands at 480, 573 and 662 nm were registered in oxychloride glasses, which correspond to transitions originating from the ⁴F_{9/2} state to the ⁶H_{J/2} (J = 11, 13, 15) states of Dy³⁺.

Keywords: glasses, dysprosium ions, optical properties.

1. Introduction

The systematic studies of rare earth ions in different environments indicate that Dy³⁺ doped systems are known as a two primary color (yellow/blue) luminescent materials. Yellow/blue luminescence is related to ⁴F_{9/2}–⁶H_{13/2} and ⁴F_{9/2}–⁶H_{15/2} transitions of Dy³⁺. Several oxide, oxyfluoride and fluoride glass systems containing Dy³⁺ ions were studied for yellow/blue luminescence [1–15], but dysprosium-doped oxychloride glasses have not been examined yet. The preparation of oxychloride glasses and their potential applications are often limited due to low glass forming region and large tendency towards crystallization. Previously published results for oxychloride systems singly doped with Ln³⁺ are concerned mainly with Er³⁺ ions in tellurite [16], germanate [17], and phosphate [18] glasses containing PbCl₂.

Recently, the NIR luminescence of Nd³⁺ ions in B₂O₃–PbCl₂–PbO–Al₂O₃–WO₃ glass system was examined [19]. The present work deals with synthesis, short-range order structure and optical properties of the oxychloroborate glasses containing Dy³⁺ ions. The glass structure was investigated using X-ray diffraction, Raman and FT-IR spectroscopy. Visible emission due to ⁴F_{9/2}–⁶H_{J/2} (J = 11, 13, 15) transitions and its decay from ⁴F_{9/2} state of Dy³⁺ was analyzed in detail. Several spectroscopic parameters

for Dy^{3+} ions in oxychloroborate glasses were evaluated based on the absorption, excitation and emission measurements.

2. Experimental techniques

The X-ray diffraction was carried out using INEL diffractometer with $\text{Cu K}\alpha$ radiation. The Raman and FT-IR spectra were performed by Bruker spectrometer using standard KBr disc techniques. Absorption spectra were recorded using a Varian 2300 UV-VIS-NIR spectrophotometer. Luminescence spectra and decay curves were obtained using Jobin Yvon Fluoromax4 spectrophotometer. The spectral resolution was equal to 0.1 nm. Luminescence decay curves were detected with accuracy of $\pm 1 \mu\text{s}$. All spectral measurements were carried out at room temperature.

3. Results and discussion

3.1. Glass preparation and structural studies

Oxychloroborate glass samples singly doped with Dy^{3+} ions were prepared using the following composition (in wt%): $18\text{B}_2\text{O}_3-9\text{PbCl}_2-63\text{PbO}-6\text{Al}_2\text{O}_3-3\text{WO}_3-1\text{Dy}_2\text{O}_3$.

Anhydrous oxides (B_2O_3 , PbO , Al_2O_3 , WO_3 , Nd_2O_3) and lead halide PbCl_2 (99.99% purity, Aldrich) were used as the starting materials. Due to the hygroscopicity of the halide components and, in order to minimize the adsorbed water content, the batches of 4 g were weighted and stored in a vacuum furnace at 100°C . Homogeneous mixture was heated in a protective atmosphere of dried argon. Glasses were melted at 900°C in Pt crucibles, then poured into preheated copper moulds and annealed below the glass transition temperature. After this procedure, the samples were slowly cooled to room temperature. Transparent glassy plates of about 2 mm in thickness were obtained.

In order to obtain information on the crystallizing phases, the X-ray diffraction was performed. Figure 1 presents X-ray diffraction pattern of the oxychloroborate glass singly doped with Dy^{3+} ions. The XRD pattern displays two characteristic broad bands corresponding to the fully amorphous phases and does not show any strong diffraction lines due to the precipitation of PbCl_2 or other crystalline phases. In order to obtain some information on the short-range order structure of oxychloroborate glasses, Raman and FT-IR spectra were performed. Figure 2 presents the Raman spectrum, which was registered in $600-1700 \text{ cm}^{-1}$ region for oxychloride lead borate glass and then compared to the one obtained for glass sample without PbCl_2 . In this frequency region, the Raman bands are related to the vibrations of borate groups. Similarly to the previous results [20], several vibration bands at around 620, 720, 870, 925, 1050 and 1280 cm^{-1} are located, which correspond to the chain- and ring-type metaborate groups as well as diborate and pentaborate units, respectively.

Two important effects can be observed. Firstly, the intensities of the bands located at about 870 and 925 cm^{-1} (assigned to pentaborate groups [20]) due to the stretching

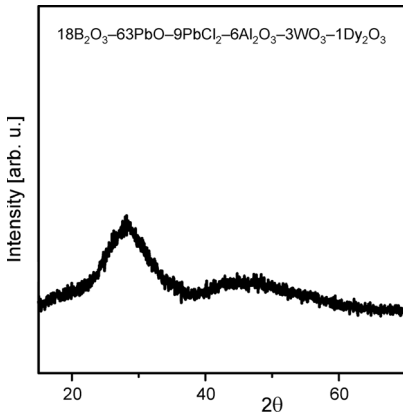


Fig. 1. X-ray diffraction pattern for the oxychloroborate glass.

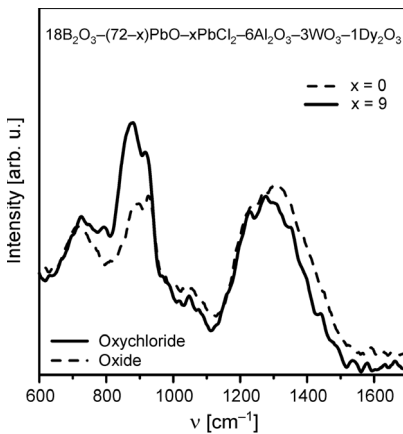


Fig. 2. Raman spectra for the glasses with and without PbCl₂.

vibrations of BO₄ units, increase with the presence of lead chloride PbCl₂. From the literature data it is known that the PbO₄ units bridge preferentially rather to BO₃ groups than BO₄ ones. Here, the partial substitution of PbO by PbCl₂ results in an increase of the Raman band intensities related to the formation of BO₄ units. Similar phenomena were observed for lead fluoroborate glasses doped with Sm³⁺ [20] in the case of BO₄ unit formation, when the oxygen atoms added to the oxyfluoride glass network reduced the effect of F ions in the PbO₄ units. Secondly, the Raman band due to the maximal phonon energy of the host slightly decreases from 1301 to 1277 cm⁻¹ in the case of the partial substitution of PbO by PbCl₂. There is a good agreement with the results obtained for other oxychloride germanate glass systems, where the maximum phonon energy slightly shifts from 819 cm⁻¹ to 805 cm⁻¹ with the replacement of PbO by PbCl₂ [21]. One can deduce that PbCl₂ plays an important role in the formation of the glass network.

Figure 3 presents FT-IR spectrum of the oxychloroborate glass containing Dy³⁺, acquired in the 4000–400 cm⁻¹ range. The spectrum exhibits the low-intense band near 3445 cm⁻¹ (2.9 μm), which is related to the characteristic stretching vibration of OH⁻ groups. The infrared bands located between 1500 cm⁻¹ and 400 cm⁻¹ are

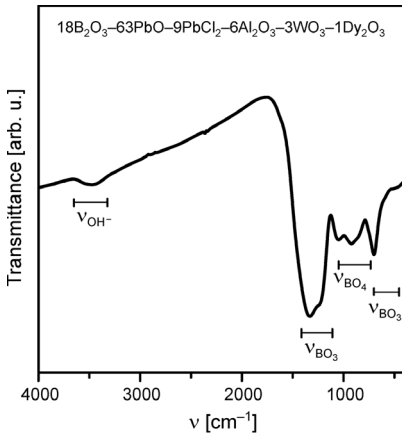


Fig. 3. FT-IR spectrum for the oxychloroborate glass.

correlated with the vibrations of borate network. The first group of bands was identified as the BO_3 bending modes ($650\text{--}700\text{ cm}^{-1}$).

The second group of bands is associated with the B–O stretching vibrations of tetrahedral BO_4 groups ($800\text{--}1050\text{ cm}^{-1}$). The antisymmetric stretching mode causes that bands are centered at 1050 cm^{-1} , whereas the symmetric stretching frequency is located in the $800\text{--}900\text{ cm}^{-1}$ infrared region. The third group of the most intense bands, centered at $1300\text{--}1400\text{ cm}^{-1}$, is due to the antisymmetric B–O stretching vibrations of trigonal BO_3 groups. It can be clearly drawn from Fig. 3 that both trigonal BO_3 and tetrahedral BO_4 units coexist in multicomponent oxychloroborate glasses.

3.2. Optical studies

The absorption spectra of Dy^{3+} ions in the glasses without and with PbCl_2 are presented in Fig. 4. The spectra consist of several inhomogeneously broadened transitions from the ${}^6\text{H}_{15/2}$ ground state to the ${}^6\text{H}_{11/2}$, ${}^6\text{F}_{11/2}$, ${}^6\text{F}_{9/2}$, ${}^6\text{F}_{7/2}$, ${}^6\text{F}_{5/2}$ and ${}^6\text{F}_{3/2}$ excited states belonging to the $4f^9$ electronic configuration of trivalent dysprosium.

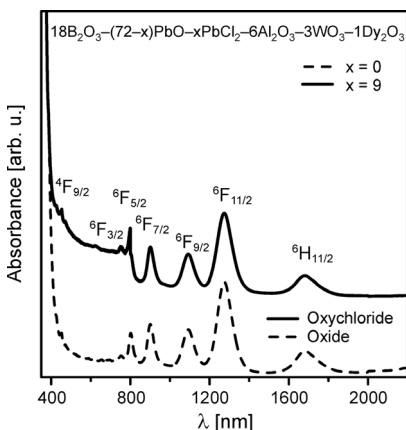


Fig. 4. Absorption spectrum for Dy^{3+} in the glasses with and without PbCl_2 .

T a b l e. Observed absorption band positions (in cm⁻¹) and bonding parameters (β and δ) for Dy³⁺ ions in the glass samples without and with PbCl₂.

Energy level	PbO–B ₂ O ₃	PbCl ₂ –PbO–B ₂ O ₃	Aquo-ion [16]
⁶ H _{15/2} – ⁴ F _{9/2}	22090	22170	22100
⁶ H _{15/2} – ⁶ F _{3/2}	13290	13328	13250
⁶ H _{15/2} – ⁶ F _{5/2}	12452	12500	12400
⁶ H _{15/2} – ⁶ F _{7/2}	11101	11101	11000
⁶ H _{15/2} – ⁶ F _{9/2}	9150	9151	9100
⁶ H _{15/2} – ⁶ F _{11/2}	7847	7853	7700
⁶ H _{15/2} – ⁶ H _{11/2}	5933	5937	5850
β	1.0078	1.0095	
δ	-0.77	-0.94	

From the absorption spectra of Dy³⁺ ions in the glasses without and with PbCl₂, bonding parameters (β and δ) were calculated using the relation [22]:

$$\delta = \frac{1 - \beta}{\beta} \times 100$$

where $\beta = \sum_N \beta^* / N$ and $\beta^* = \nu_c / \nu_a$, β is the shift of energy level position (nephelauxetic effect), ν_c and ν_a are energies of the corresponding transitions in the investigated complex and aquo-ion [23], respectively, and N denotes the number of levels used for the calculation of β values. Positive or negative sign for the δ value indicates covalent or ionic bonding between the rare earth ions and surrounding ligands. The observed absorption band positions and bonding parameters for Dy³⁺ in the glasses and aquo-ion are given in the Table. The bonding parameter δ was found to be -0.77, which indicates that the B₂O₃–PbO based glass exhibits ionic character between Dy³⁺ and surrounding ligands. This behavior is connected with the occurrence of [PbO_{4/2}]²⁻ as well as [B₃O₉]⁹⁻ anions having BO₃ and BO₄ units in the host matrix, which was evidenced by Raman and FT-IR spectroscopy (see Section 3.1). The partial substitution of PbO by PbCl₂ results in the change of δ value from -0.77 to -0.94, which indicates more ionic environment around Dy³⁺.

From the spectra it is also clearly seen that the absorption bands related to ⁶H_{15/2}–⁴F_{9/2} and ⁶H_{15/2}–⁶F_{3/2} transitions of Dy³⁺ in the visible spectral region are more intense and resolved for oxychloride glass than oxide one. Moreover, the matrix absorption in the visible region is higher for oxychloride glass as compared to oxide glass. The ⁴F_{9/2} state lies on the UV-VIS absorption edge, whereas higher-lying states of Dy³⁺ in the glass under study are not visible. For that reason, the excitation spectrum monitored at $\lambda_{em} = 573$ nm (⁴F_{9/2}–⁶H_{13/2} transition) was recorded in 300–500 nm spectral region (Fig. 5). Several narrowed bands belong to the well known higher-lying f – f electronic transitions of Dy³⁺. Any broad excitation charge-transfer bands due to Dy³⁺–O²⁻/Cl⁻ interactions were not obtained in the short wavelength spectral region.

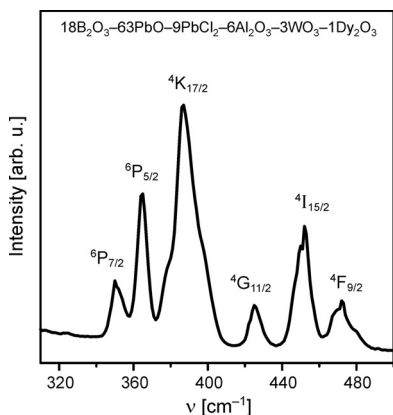


Fig. 5. Excitation spectrum for Dy^{3+} in the oxychloroborate glass.

This confirms the absence of the energy transfer process from the $\text{O}^{2-}/\text{Cl}^-$ ligands to the metal atoms. It also indicates that the interactions between Dy^{3+} ions and host lattice are rather weak. The observed bands are assigned to transitions originating from the ${}^6\text{H}_{15/2}$ ground state to the ${}^4\text{F}_{9/2}$, ${}^4\text{I}_{15/2}$, ${}^4\text{G}_{11/2}$, ${}^4\text{K}_{17/2}$, ${}^6\text{P}_{5/2}$ and ${}^6\text{P}_{7/2}$ states of Dy^{3+} . Two of them, ${}^6\text{H}_{15/2}-{}^4\text{K}_{17/2}$ (386 nm) and ${}^6\text{H}_{15/2}-{}^4\text{I}_{15/2}$ (450 nm) transitions are the most intense.

Figure 6 shows luminescence spectrum for Dy^{3+} in oxychloroborate glass. Luminescence spectra were recorded under excitation by 386 nm (${}^4\text{K}_{17/2}$ state) or 450 nm (${}^4\text{I}_{15/2}$ state) lines. Independently of the excitation wavelengths, two relative intense bands at 480 nm and 573 nm, and considerably less intense band at 662 nm have been observed. The luminescence bands correspond to ${}^4\text{F}_{9/2}-{}^6\text{H}_{15/2}$ (blue), ${}^4\text{F}_{9/2}-{}^6\text{H}_{13/2}$ (yellow) and ${}^4\text{F}_{9/2}-{}^6\text{H}_{11/2}$ (red) transitions of Dy^{3+} ions, respectively. All transitions are shown in the energy level scheme, which was constructed for Dy^{3+} ions

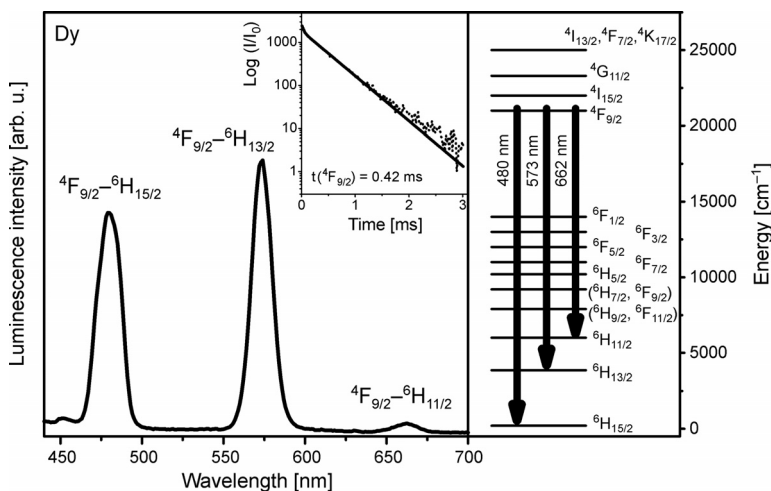


Fig. 6. Luminescence spectrum for Dy^{3+} in the oxychloroborate glass. Inset shows luminescence decay from the ${}^4\text{F}_{9/2}$ state of Dy^{3+} .

in oxychloroborate glass. Owing to small energy gaps between all states lying above 21000 cm⁻¹, the ⁴F_{9/2} state is well populated by non-radiative relaxation. Then, quite strong yellow/blue luminescence due to ⁴F_{9/2}-⁶H_{J/2} (J = 13, 15) transitions is observed. This phenomenon is related to large separation (~6000 cm⁻¹) between ⁴F_{9/2} state and the next lower lying ⁶F_{1/2} state, and the relative high phonon energy of the host (~1300 cm⁻¹).

The inset shows luminescence decay from the ⁴F_{9/2} state of Dy³⁺ in oxychloroborate glass. The luminescence decay curve is nearly single exponential. The measured ⁴F_{9/2} lifetime was determined to be 0.42 ms. It is consistent with values obtained for similar Dy-doped glasses based on ZnO-PbO-B₂O₃ [24].

4. Conclusions

Oxychloroborate glasses containing Dy³⁺ ions were studied using X-ray diffraction and various spectroscopic techniques (Raman, FT-IR, absorption, excitation and luminescence). The results concerning glass preparation, short-range order structure and optical studies are presented. X-ray diffraction analysis evidently indicates that the fully amorphous system was prepared. Coexistence of trigonal BO₃ and tetrahedral BO₄ units was evidenced by Raman and FT-IR spectroscopy. The electronic states of Dy³⁺ ions in oxychloroborate glass were determined from the absorption and excitation spectra. Luminescence spectra registered in the visible spectral region correspond to ⁴F_{9/2}-⁶H_{J/2} (J = 11, 13, 15) transitions of Dy³⁺. Decay curve for ⁴F_{9/2} state of Dy³⁺ is nearly single exponential and luminescence lifetime is close to 0.42 ms. The systematic studies indicate that multicomponent oxychloroborate glasses containing Dy³⁺ are promising solid-state materials for yellow/blue luminescence.

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