

Luminescence of rare-earth ion in diopside glasses of $\text{MgCaSi}_2\text{O}_6$ composition

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Introduction

The study of magnesium-calcium silicate of $\text{MgCaSi}_2\text{O}_6$ composition with a variable content of magnesium and calcium, known as a mineral of diopside, attracts the attention of researchers with a number of interesting properties. The high solubility of many metal oxides in pure colorless diopside makes it possible to obtain and study materials as phosphors [1], decorative and ornamental materials [2], due to their high biocompatibility with bone tissue as implants [3]. It is possible to obtain these materials in a glassy state in the entire range of compositions of the MgSiO_3 – CaSiO_3 system [4], the properties of which, with the exception of the structure of glasses [4, 5], are little studied.

The luminescence of rare-earth ions has been well studied in crystalline magnesium-calcium silicate [1]; there is information on the luminescence of europium and terbium ions in glass-crystalline ceramics [6, 7]. Therefore, it is of interest to study the luminescence of rare-earth ions and in glasses of $\text{MgCaSi}_2\text{O}_6$ composition and to compare with the luminescence of rare-earth ions in silicate glasses of other composition [8].

Experimental

The initial crystalline $\text{MgCaSi}_2\text{O}_6$ powder for obtaining diopside glasses was prepared by mixing the corresponding amounts of standard chemical reagents MgO , CaCO_3 and SiO_2 . The reagent mixture was calcined in an alundum crucible up to 1400° C with two grinding during heating for homogenization.

For the preparation of diopside glasses doped with rare-earth elements, in 3 g of prepared $\text{MgCaSi}_2\text{O}_6$ powder was introduced 3-5 mass. % rare earth oxide (Nd, Sm, Eu, Dy or Tb). A thoroughly mixed mixture was loaded into a glasscarbon crucible and melted using induction heating (fig.1, 2).

The glasses were obtained by quenching of the superheated to 1600° C melt. For better homogeneity, the glasses were additionally remelted.

For research, plates with a thickness of 1-2 mm were cut and polished from the prepared glasses.

Excitation and luminescence spectra of diopside glasses doped with rare-earth ions were obtained using a Fluorolog-3 spectrofluorimeter.

Results and discussion

The amorphous state of the prepared glasses is confirmed by the presented diffraction patterns (Fig. 3) obtained on a DRON-3 diffractometer.

The characteristic luminescence spectra of diopside glasses doped with rare-earth ions are shown in Fig. 4.

Three types of luminescence spectra can be distinguished.

Broadband luminescence for glasses doped with neodymium and europium with a maximum emission in the range of 460 - 490 nm and 500 - 540 nm, respectively.

Broadband luminescence for glasses doped with samarium and dysprosium with emission bands characteristic for crystalline samples.

And in the case of terbium-doped glasses, the broadband luminescence is suppressed by the luminescence bands characteristic for crystalline samples.

The luminescence of diopside glasses of samarium and dysprosium oxide doped is mainly determined by the high intensity of the emission bands of Sm^{3+} and Dy^{3+} ions. The broadband luminescence for these glasses possibly associated with cationic vacancies.

Luminescence of Sm^{3+} .

The emission spectrum of $\text{MgCaSi}_2\text{O}_6:\text{Sm}^{3+}$ consists of several typical emission peaks located at 563, 600, 647, and 708 nm, corresponding to the $4G_{5/2}$ to $6H_J$ ($J=5/2, 7/2, 9/2$ and $11/2$) emissions of Sm^{3+} . It is noted that the strongest emission peak at 600 nm ($4G_{5/2} \rightarrow 6H_{7/2}$) corresponds to the electric dipole (ED) transition of Sm^{3+} , and the weaker emission at 564 nm ($4G_{5/2} \rightarrow 6H_{5/2}$) originates from the magnetic dipole (MD) transition. Another typical $4G_{5/2} \rightarrow 6H_{9/2}$ transition obeys the selection rule of $\Delta J=2$, so it is allowed to become an electric dipole (ED) [9]. Generally speaking, the intensity ratio of the ED and MD transitions can be used to understand the symmetry of the structure in the host matrix. The greater the intensity of the ED transition, the more asymmetric the nature [10]. In our present study, the $4G_{5/2} \rightarrow 6H_{5/2}$ (MD) transition of Sm^{3+} is less intense than the $4G_{5/2} \rightarrow 6H_{9/2}$ (ED) transition, indicating the asymmetric nature of the $\text{MgCaSi}_2\text{O}_6:\text{Sm}^{3+}$ host matrix, which is in accordance with much literature [11].

Luminescence of Dy^{3+} .

The 577 nm (yellow) emission spectra of diopside glasses of $\text{MgCaSi}_2\text{O}_6:\text{Dy}^{3+}$ was associated with $4F_{9/2} \rightarrow 6H_{13/2}$ which was related to an electric dipole (ED) transition, while the 482 nm (blue) emission was associated with $4F_{9/2} \rightarrow 6H_{15/2}$, related to a magnetic dipole (MD) transition [12]. It has been known that the $4F_{9/2} \rightarrow 6H_{15/2}$ transition for Dy^{3+} is insensitive to the coordination environment. On the other hand, the $4F_{9/2} \rightarrow 6H_{13/2}$ transition is hypersensitive to the ED transitions with $\Delta J=2$, which is highly affected by the environment. Therefore, the $4F_{9/2} \rightarrow 6H_{13/2}$ transition is a forced ED transition being allowed only at low symmetries with no inversion center [13,14]. When Dy^{3+} is located at low-symmetry local site, this emission is often prominent in its emission spectrum. Generally, the intensity ratio of ED to MD (Y/B ratio) transitions has been used to determine the symmetry of the local environment of the RE³⁺ ions. The greater the intensity of the ED transition, the higher the asymmetric nature. Moreover, two additional emission peaks were also observed at 661 nm ($4F_{9/2} \rightarrow 6H_{11/2}$) and 751 nm ($4F_{9/2} \rightarrow 6H_{11/2} + 6H_{9/2}$ from the Dy^{3+} transitions).

Luminescence of Tb^{3+} .

The luminescence spectrum of diopside glass doped with terbium oxide exhibits Tb^{3+} emission bands (Fig.5,7) inherent in the crystalline state of diopside [1], which are assigned to $5D_3 \rightarrow 7F_J$ ($J=5, 4, 3$) and $5D_4 \rightarrow 7F_J$ ($J=6, 5, 4, 3, 2$) transitions, and the emission bands show a splitting pattern, such as $5D_4 \rightarrow 7F_5$ transition of Tb^{3+} (543 and 549 nm) [15]. Of the two peaks due to $5D_4 \rightarrow 7F_5$ transition of T^{3+} , the intensity of peak at 544 nm is stronger than that of peak at 548 nm. For the emission bands, the green emission transition $5D_4 \rightarrow 7F_5$ is dominant among the others, therefore, $\text{MgCaSi}_2\text{O}_6:\text{Tb}^{3+}$ produce green emission. A similar character of luminescence, determined by emission $5D_4 \rightarrow 7F_{6,5,4,3}$ transitions, was observed in germanate-silicate glass [8], although it may vary depending on the composition of the matrix. The luminescence intensity of diopside glasses doped with terbium oxide increases with an increase in the concentration of Tb^{3+} ions, suppressing the emission of $5D_3 \rightarrow 7F_J$ ($J=5, 4, 3$) transitions (Fig. 6). For a concentration of 1 mass.% terbium oxide (Fig.7), the intensity of $5D_3 \rightarrow 7F_J$ ($J=5, 4, 3$) transitions in broadband glass luminescence with a maximum in the region of 450 – 470 nm is comparable to the intensity of $5D_4 \rightarrow 7F_{6,5,4,3}$ transitions, luminescence is nevertheless determined more intense $5D_4 \rightarrow 7F_5$ transition..

Luminescence of Nd^{3+} and Eu^{3+}

Broadband luminescence for glasses doped of 1 mass.% neodymium and europium oxide with a maximum emission in the range of 460 - 490 nm is similar (Fig. 8, 9). We have not found peaks identified Nd^{3+} . The emission spectrum of Eu^{3+} ions in Fig. 4, 8 only contains the characteristic of the $4f-4f$ weak emission peak corresponding to $5D_0 \rightarrow 7F_2$ transition. The shift of broadband luminescence for glasses possibly associated with cationic vacancies.

The change in color of the emitted light from diopside glasses was confirmed by the corresponding calculated color coordinates. The values of the color chromaticity coordinates (x, y) were found to be (x = 0.373; y = 0.407) for Sm, (x = 0.265; y = 0.370) for Nd, (x = 0.329; y = 0.405) for Dy, (x = 0.344; y = 0.444) for Eu, and (x = 0.307; y = 0.407) for Tb (Fig.10).

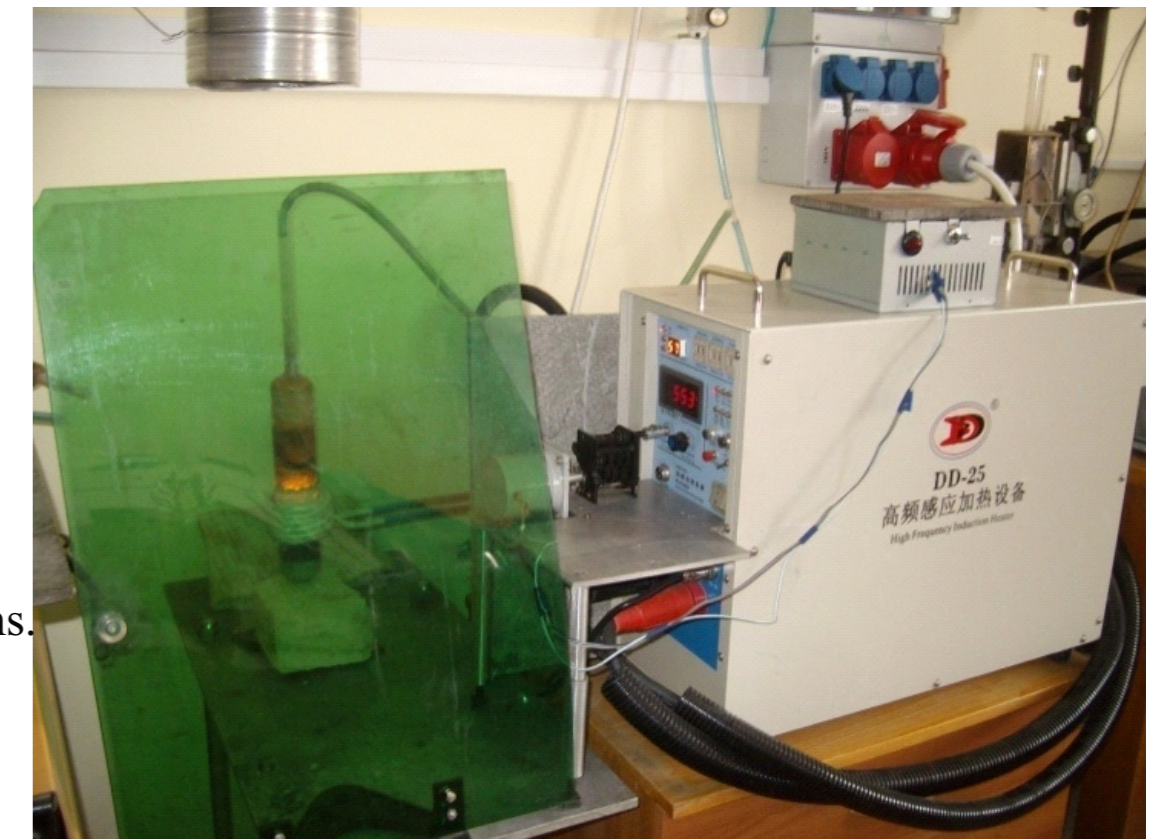


Fig.1. HF equipment for melting

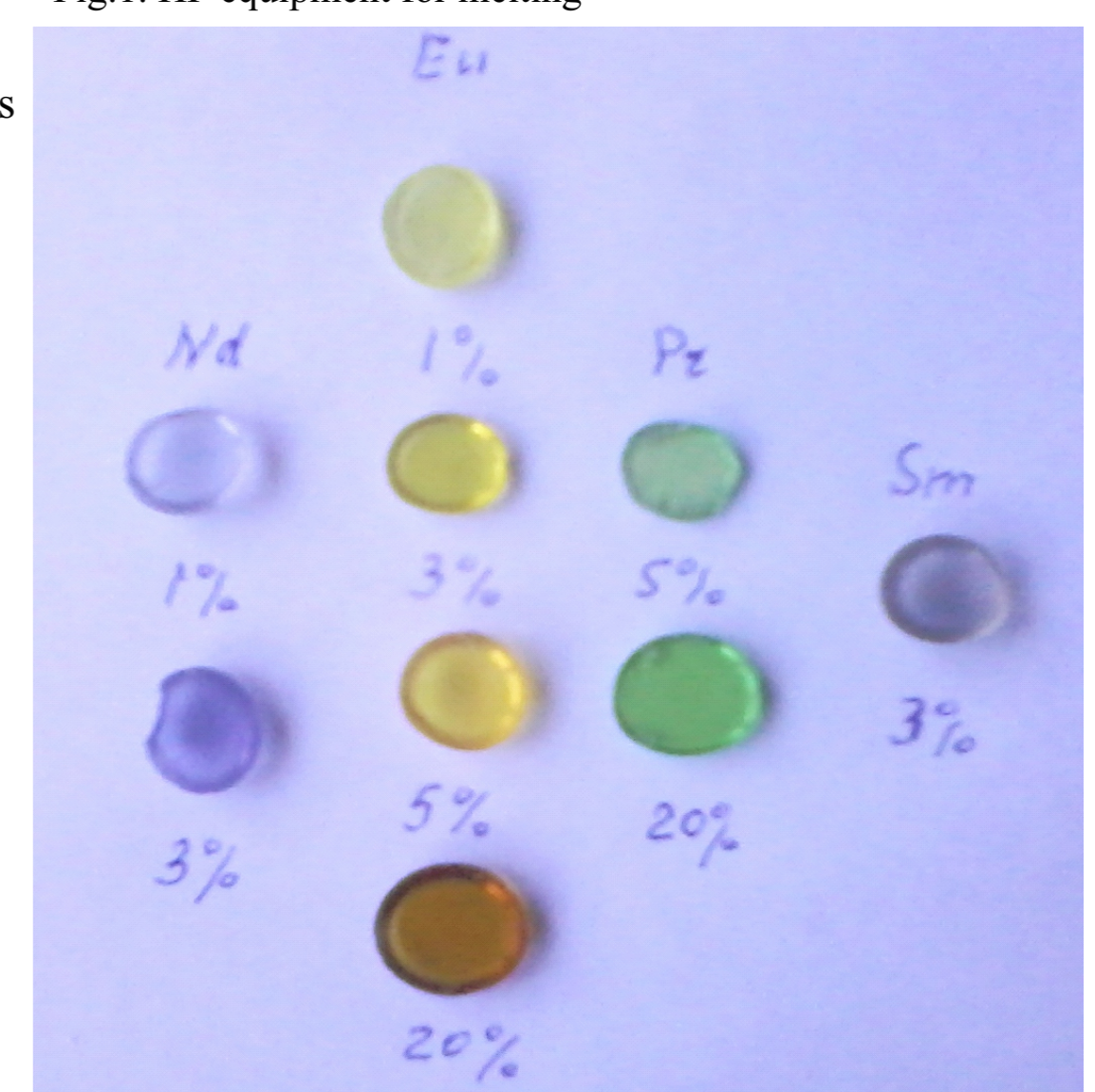


Fig.2. diopside glasses doped REE

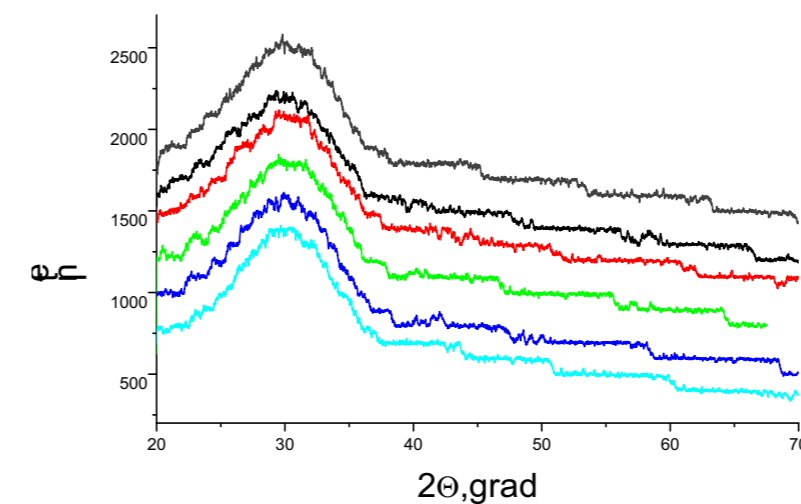


Fig.3 Diffractograms of diopside glasses: 1- 3% Nd; 2 - 3% Pr; 3 - 3% Sm; 4 - 5% Eu; 5 - 3% Dy; 6 - 3% Tb

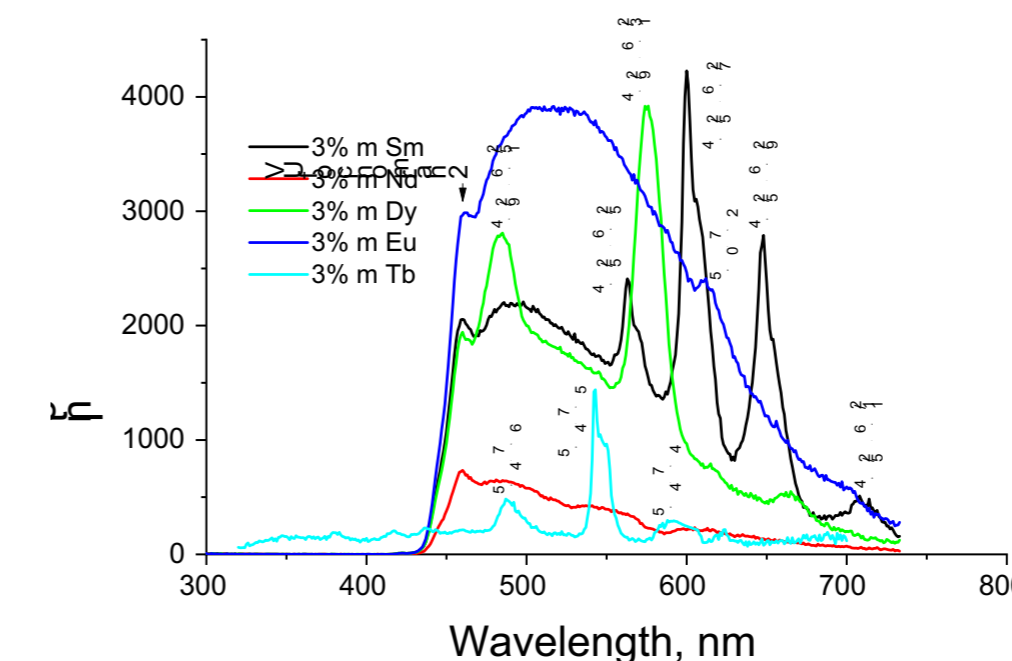


Fig.4. Luminescence spectra (Em) of diopside glass doped with 3 mass% rare earth oxide (λ_{ex} 280 nm)

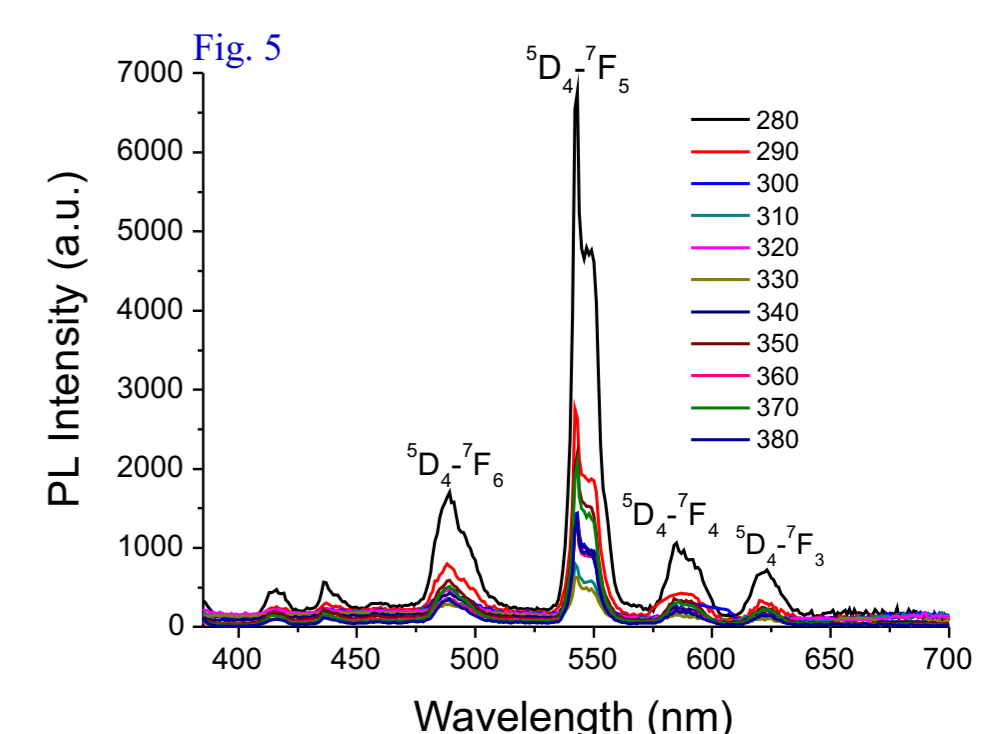


Fig.5-7. Luminescence spectra of diopside glasses doped with 3, 5 and 1 mass.% terbium oxide upon excitation at different wave lengths.

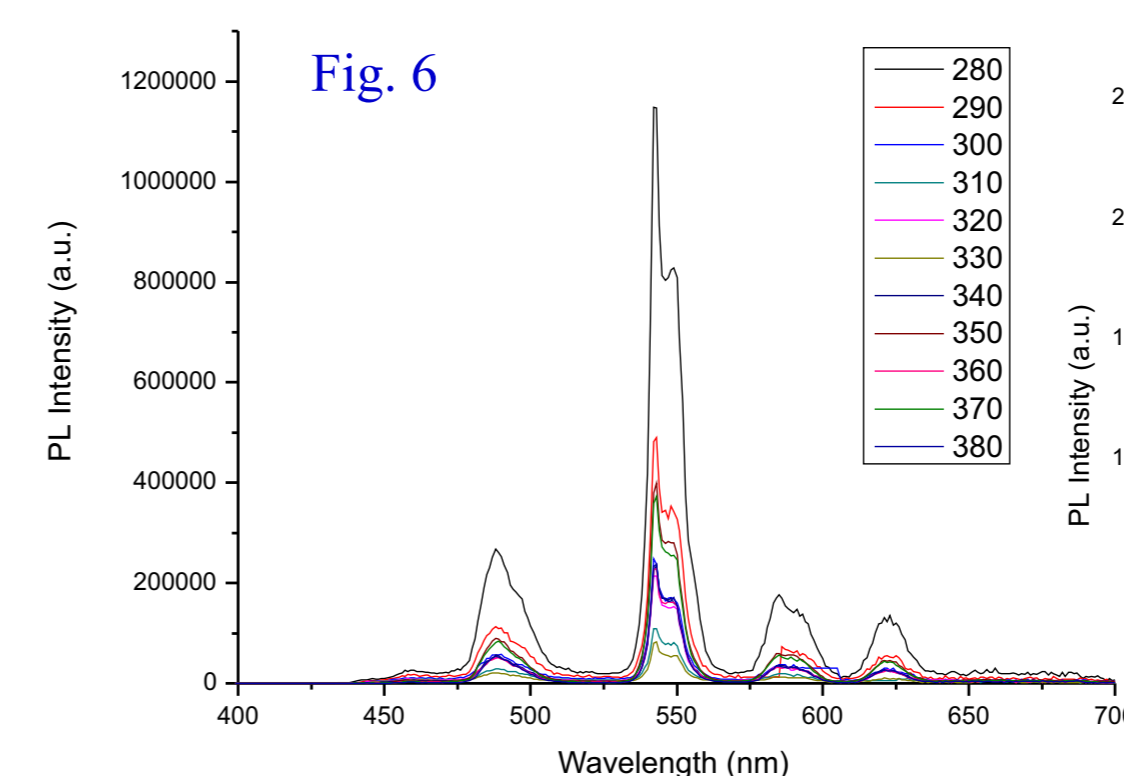


Fig.6-7. Luminescence spectra of diopside glasses doped with 3, 5 and 1 mass.% terbium oxide upon excitation at different wave lengths.

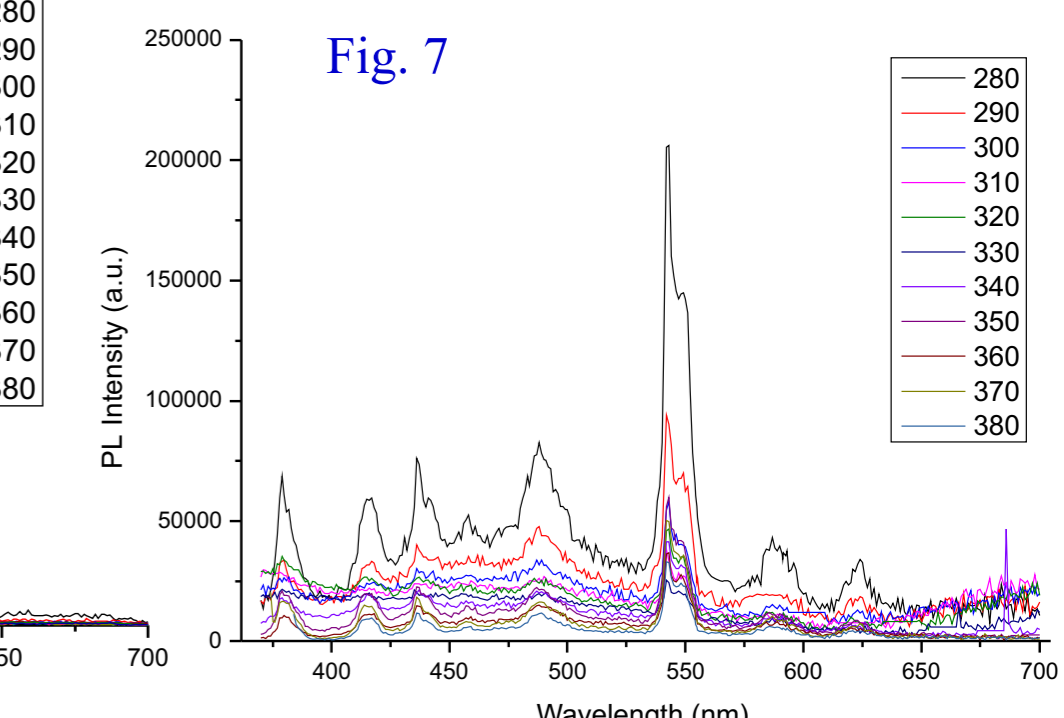


Fig.7. Luminescence spectra of diopside glasses doped with 3, 5 and 1 mass.% terbium oxide upon excitation at different wave lengths.

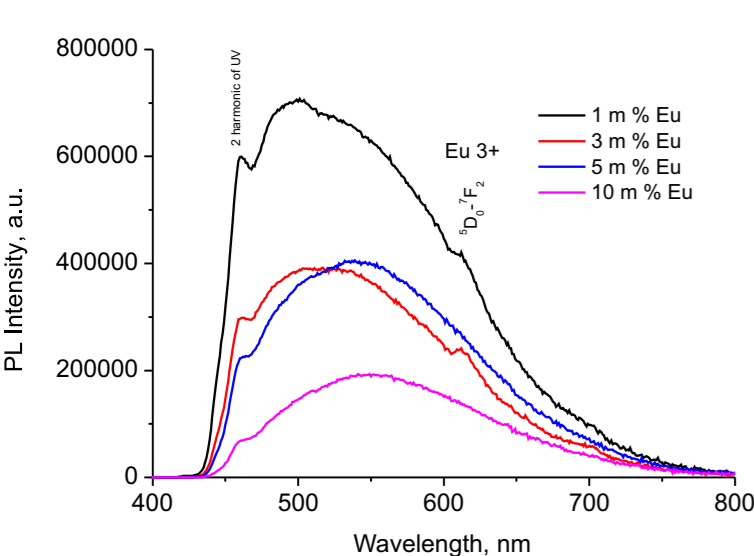


Fig.8. Luminescence spectra of diopside glass doped Eu (λ_{ex} = 280nm)

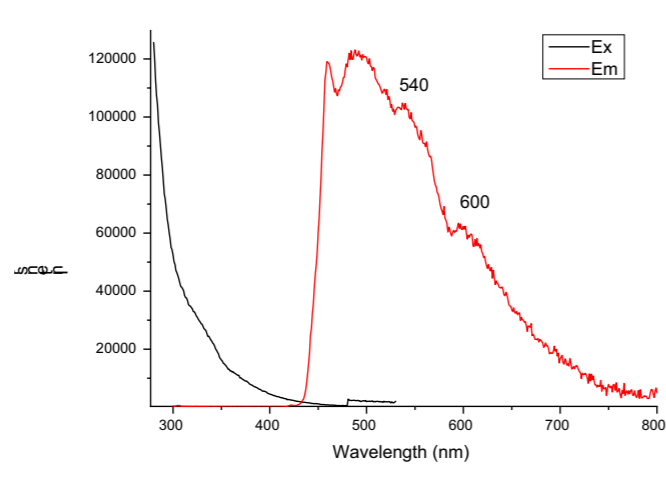


Fig.9. Luminescence excitation and emission spectra of diopside glass doped with 1 mass.% neodymium oxide.

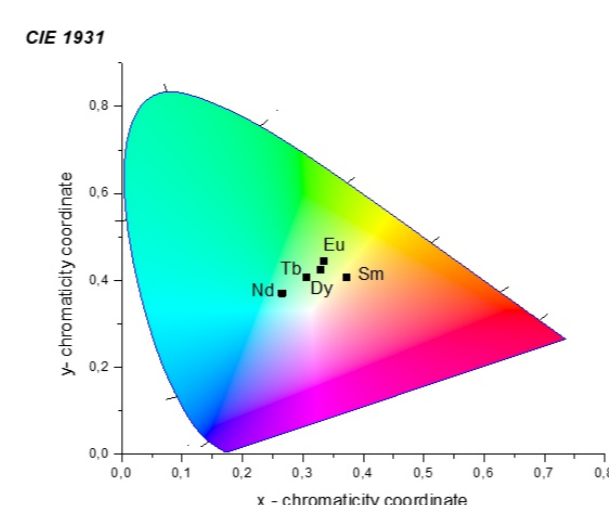


Fig.10. The CIE 1931 coordinate for diopside glasses of $\text{MgCaSi}_2\text{O}_6$ depended of rare-earth ions.

Conclusion

Some similarity of the luminescence spectra of europium in diopside glass and glass ceramics [6] and a shift of the luminescence maximum (Fig.8) to the orange-red region of the spectrum with an increase in the concentration of europium oxide in diopside glass allows us to conclude, that the nature of the spectrum is associated with the ratio of Eu^{3+} and Eu^{2+} ions in the glass and with defects arising when Ca^{2+} ions are replaced by Eu^{3+} ions.

High temperatures of preparation of diopside glass in a reducing atmosphere using a graphite or glassy carbon crucible heated by high-frequency currents can contribute to the appearance of a noticeable content of Eu^{2+} ions, especially for low doping concentrations. In the case of glass doping with Nd^{3+} ions (Fig.9), blue luminescence is most likely determined by defects in the short-range order of the glass and with their increase leads to concentration quenching of the luminescence.

The luminescence of diopside glasses of rare earth oxide doped is mainly determined by the high intensity of the emission bands of Ln^{3+} ions

More comprehensive research is needed.

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