Phosphate Laser Glass with Pr $^{3+}$ for Emission in the Visible Range

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The paper presents a phosphate laser glass composition doped with Pr $^{3+}$. It is well known that the spectroscopic properties of Pr $^{3+}$ in crystals and glasses are the best in order to use it as a 4f-activator element for solid state lasers emitting in the visible range. In a phosphate crystalline matrix, the level $^1D_2$ has a radiative lifetime of about 650μs. Using this idea, we formulated a phosphate vitreous matrix doped with Pr $^{3+}$ in order to obtain a material susceptible to be a laser active medium for 610 nm emission band. The fluorescence emission and other properties are presented.

1. Introduction

There are many papers reporting about the Pr^{3+} properties in various crystalline ($LiPrP_4O_{12}$; PrP_5O_{14}) and vitreous matrixes (LiBO, MgLiBO, CaLiBO, SiLiBO, BaLiBO, ZBLAN).

The main application domain of the laser glass with Pr^{3+} is the amplification filter for the optical communication window at 1300 nm [1]. For this purpose it is necessary to use glass compositions with low phonon energy in order to prevent the multiphonon relaxation phenomenon, which is responsible for the extinction of the Pr^{3+} luminescence[2].

The ZBLAN glasses and the heavy metals oxide glasses (Pb, Bi, Ga) fulfil this condition.

The spectroscopic properties of Pr^{3+} in glasses and crystals makes it suitable also as one of the best 4f elements for solid state laser with emission in the visible range of the spectrum[3].

The advantage of the phosphate crystalline matrixes (radiative lifetime of the $^1D_2$ level is high: 650 μs) leads to the idea to obtain phosphate glasses with Pr^{3+} for using in solid state lasers with emission in the visible range of the spectrum at about 610 nm.

2. Experimental

Five phosphate glasses with different Pr^{3+} concentration where obtained, in order to produce samples for spectroscopic investigations.

The basic phosphate glass consists essentially in weight percents of 69%P_2O_5, 7%Al_2O_3, 3%B_2O_3, 10%K_2O, 10% BaO and 1%Sb_2O_3.

In this type of glass the Pr_6O_{11} was introduced in amount of 1%(LPP1), 2%(LPP2), 3%(LPP3), 4%(LPP4) and 5%(LPP5).

The row materials were reagent grade. The glasses were obtained through classical laboratory procedures using small Al_2O_3 crucibles at 1300^0C and high purity graphite mould for casting. The annealing was carefully conducted in order to obtain good quality samples. The samples where optically polished.

3. Results and discutions

Transmission, excitation and fluorescence spectra were obtained using a M40 SPECORD spectrophotometer and a MQ3 CARLZEISS fluorimeter.

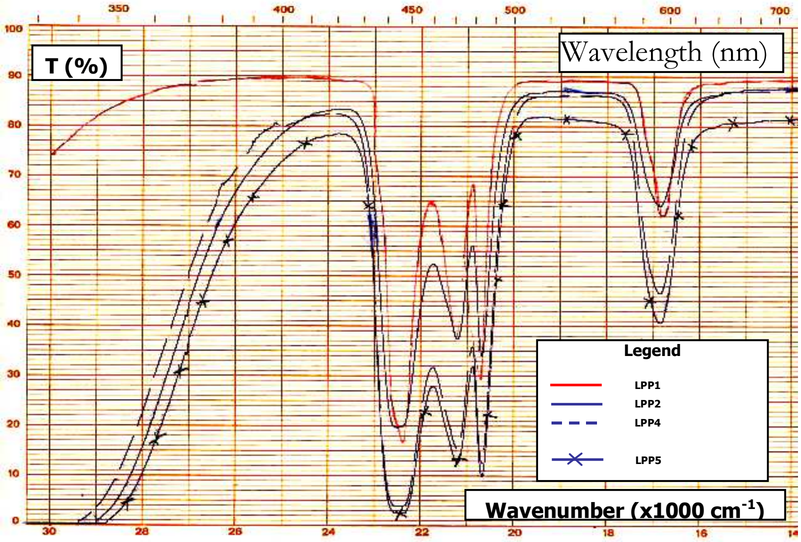

Fig. 1. Transmission spectra of LPP1, LPP2, LPP3, LPP4 and LPP5 glasses

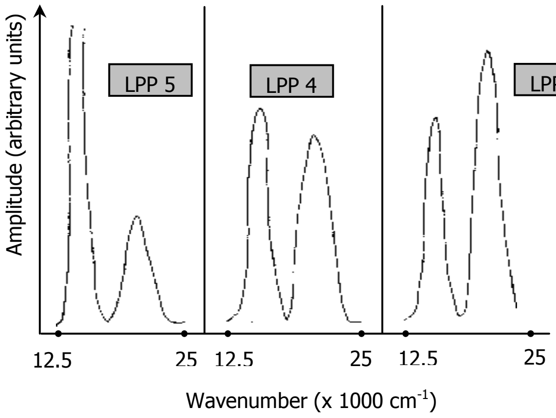

Fig. 2. Excitation spectra of LPP1, LPP4, LPP5 glasses monitored at 610nm.

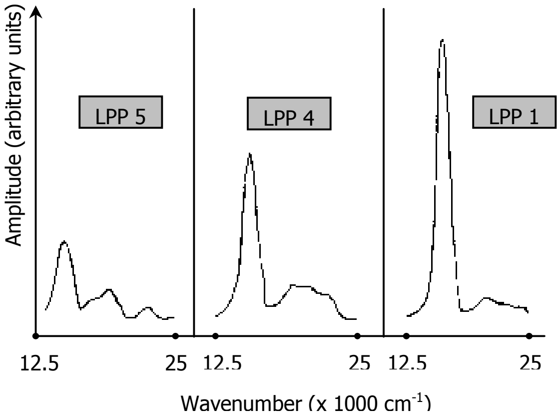

Fig. 3. Fluorescence spectra of LPP1, LPP4, LPP5 glasses excited at 444nm.

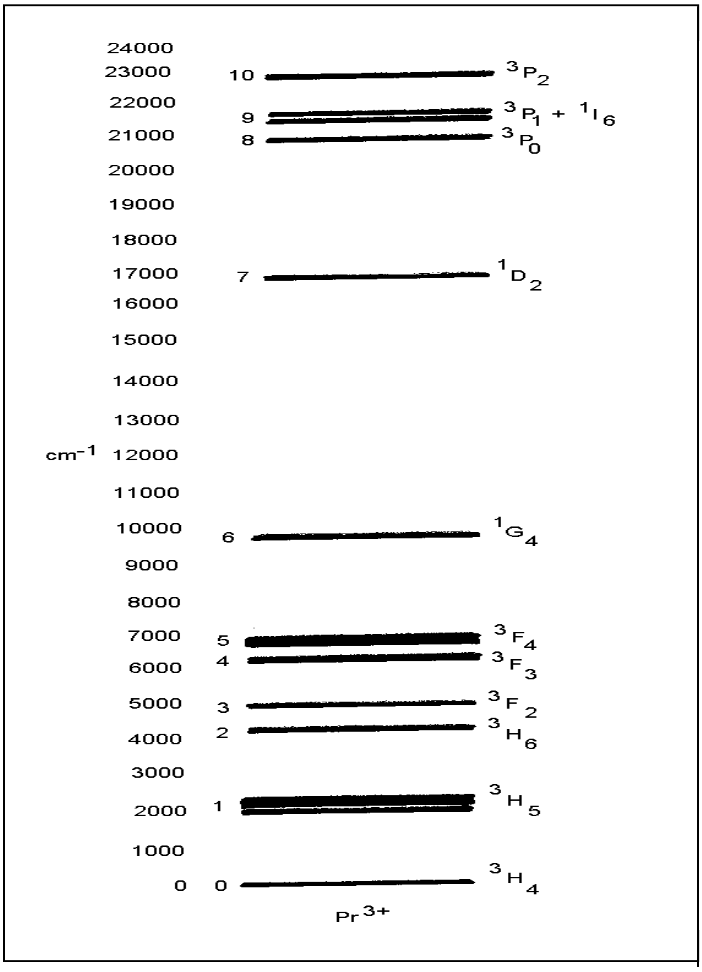

Fig. 4. Energy levels of Pr^{3+} in a ZBLAN [4]

The transmission spectra configuration presents the absorption bands at

444 nm due to the $^3P_2 \leftarrow {}^3H_4$ transition

470 nm due to the $^3P_1+{}^1I_6 \leftarrow {}^3H_4$ transition

482 nm due to the $^3P_0 \leftarrow {}^3H_4$ transition

590 nm due to the $^1D_2 \leftarrow {}^3H_4$ transition

The excitation spectra configuration presents the excitation bands at:

472 nm for the $^3P_0 \leftarrow {}^3H_4$ transition

610 nm for the $^1D_2 \leftarrow {}^3H_4$ transition.

The fluorescence spectra configuration presents the fluorescence bands at:

464 nm for the $^3P_J(J=0,1,2) \leftarrow {}^3H_J(J=4,5)$

610 nm for the $^1D_2 \leftarrow {}^3H_J\ (J=4,5)$ transition

The mechanism governing the energy transfer process in rare-earth ions has been the subject of many papers during the last five decades [5, 6, 7, 8].

The theory of a nonradiative transfer of excitation energy from a rare earth ion acting as donor to a rare earth ion acting as acceptor was developed in a classical paper by Dexter [5].

The energy transfer rate $W(r_i)$ for each ion depend on the nature of the interaction between the donor and the acceptor and can be expressed as a product between a microparameter of interaction CDA and a function of distance r_i. The microparameter CDA depends on the spectroscopic properties of the D and A ions, such as the superposition integral of donor emission and acceptor absorption, the acceptor integral absorption cross section and the lifetime of donor intrinsic emission. The various D-A interactions impose specific dependencies of $W(r_i)$: in the case of the multipolar interactions this is given by r_i^{-s}, with s = 6,8 or 10 for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions.

Due to the spectral characteristics of the Pr^{3+} ions in $^1D_2$ and $^3P_0$ states, the concentration dependence of the excitation spectrum bands corresponding to the $^3P_0 \rightarrow {}^3H_4$ (472 nm band) and $^1D_2 \rightarrow {}^3H_4$ (610 nm band) transition will be different.

The Pr^{3+} ions in the $^1D_2$ state interact strongly and for this reason the radiative relaxation is diminished and, in the same time, the nonradiative mechanisms gain a higher contribution.

In order to obtain the same intensity of the fluorescence radiation at 610 nm band, it is necessary to have a higher amplitude of the excitation band corresponding to a higher concentration of the Pr^{3+} ions.

There is a direct dependence between the Pr^{3+} ion concentration and the 610 nm band amplitude of the excitation spectra.

The Pr^{3+} ions in $^3P_0$ state interact weak and it follows that in order to obtain the same intensity amplitude of the 610 nm band it is necessary to have lower intensity of the 472 nm wavelength, corresponding to higher concentration of the Pr^{3+} ions.

The Pr^{3+} ion concentration and the 472 nm band amplitude in the excitation spectra are in reverse dependence.

4. Conclusion

The results of this approach offer preliminary data for the developing of a phosphate laser glass with emission in the visible range.

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[1] Y. Ohishi, T. Kanamori, T. Kitagawa, S.Takahashi, E. Snitzer and G.H. Sigel, Optics Letters **16(22)**, p. 1747 (1991).

[2] Y.G. Choi and J. Heo, Journ. Non-Cryst. Solids **217**, p. 199 (1997).

[3] A.R. Devi and C.K. Jayasankar, Phys. Chem. Glasses **37(1)**, p. 36 (1996).

[4] I.R. Mitchell, V.K. Bogdanov and P.M. Farrell, Optics Communications **155**, p. 275 (1998).

[5] D.L. Dexter, J. Chem. Phys. **21**, p. 836 (1953).

[6] M. Inokuti and F. Hirayama, J. Chem. Phys. **43**, p. 1978 (1965).

[7] E.E. Auzel, Proc. IEEE **61**, p. 758 (1973).

[8] A. Remillieux, B. Jacquier, C. Linares,, C. Lesergent, S. Artigaud, D. Bayard, L. Hamon and J.L. Beylat, J. Phys. **D29**, p. 963 (1996).