Tungstate fluorophosphate glasses as optical limiters

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Tungstate fluorophosphate glasses as optical limiters

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Nonlinear absorption measurements were performed on fluorophosphate glasses with high concentrations of tungsten oxide. Large two-photon absorption coefficients, α_2, were determined at 660 nm using nanosecond laser pulses. It was observed that α_2 increases for increasing tungsten oxide concentrations and, hence, the optical limiting performance of this glass composition can be controlled. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1481770]

Optical limiting (OL) materials have been intensively studied due to their potential to protect sensitive optical components and human eyes from damage as well as to smooth optical transients.[1,2] Various phenomena are exploited for OL, such as nonlinear absorption and nonlinear refraction,[1–4] nonlinear light scattering,[5] and polarization changes,[6] among others.

Organic materials are efficient optical limiters but their maximum efficiency occurs usually for long pulse durations. Other drawbacks of these materials are their poor stability and large linear absorption. On the other hand, inorganic two-photon absorbers are stable, transparent under low intensity, and present instantaneous response. For practical applications, glasses with large two-photon absorption (TPA) coefficients are important candidates for OL because their fabrication processes are more convenient than for crystals of good optical quality with appropriate size.

In this work we evaluate the nonlinear absorption behavior of fluorophosphate glasses with high tungsten concentrations for OL. It is already known that phosphate glass is not a good nonlinear absorber.[7] However, the choice of this material was due to the knowledge that transition metal ions when surrounded by oxygen atoms may generate a high optical nonlinearity.[8,9] In fact, our glasses, prepared in the $NaPO_3-BaF_2-WO_3$ system, have shown an efficient OL behavior under 660 nm excitation with nanosecond laser pulses. The TPA coefficient was determined for samples with different concentrations of WO_3 and the results are comparable to the values reported for semiconductor crystals[10] indicating a large potential of the glass composition for devices.

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The glass preparation was already reported[11] and the composition of the samples studied are presented in Tables I and II of good optical quality with dimensions of about 1 cm×1 cm×0.2 cm were obtained.

The OL measurements were performed using a dye laser (660 nm, 8 ns, 5 Hz) pumped by the second harmonic of a *Q*-switched Nd:yttrium–aluminum–garnet laser. The dye laser beam was split in 2: one beam was used to monitor the incident intensity and the other beam was focused onto the sample using a 10 cm focal lens. The intensities of the incident and the transmitted pulses were simultaneously measured using two photodetectors connected to a fast oscilloscope. The sample position was varied along the beam direction so that the incident intensity could be varied without changing the pulse energy.

The absorption spectra of the samples were measured at room temperature in the 300–1000 nm range and are shown in Fig. 1. Note that the vitreous samples are transparent in the near infrared and visible and the absorption band gap occurs at ≈400 nm. The features at ≈800 nm are due to the exchange of lamps in the spectrophotometer.

The behavior of the samples under laser excitation is illustrated in Fig. 2. Note that the sample NBW30 does not show OL whereas samples NBW40 and NBW50 present a pronounced optical attenuation as the input intensity increases. We assumed that the nonlinear absorption is due to a TPA process because the energy of two incident photons at

TABLE I. Chemical compositions and color of the samples studied in this work.

	% mol $NaPO_3$	% mol BaF_2	% mol WO_3	Sample color
NBW30	56	14	30	Transparent
NBW40	48	12	40	Yellow
NBW50	40	10	50	Yellow-gray

TABLE II. Parameters used to fit the data of Figs. 2 and 3 using Eq. (2). n_1 is the refractive index measured at 633 nm, R is the reflectance of each sample face, L is the sample thickness, and α_1 and α_2 are the one- and two-photon absorption coefficients.

Sample	n_1 (at 633 nm)	R (at 633 nm)	L (cm)	α_1 (cm^{-1}) (at 660 nm)	α_2 (cm/G W) (at 660 nm)
NBW30	1.63	0.057	0.18	0.29	···
NBW40	1.69	0.065	0.18	0.32	5.6
NBW50	1.75	0.074	0.18	0.43	11

660 nm (30300 cm^{-1}) is larger than the band gap energy of the samples which vary from 25 600 to 27 700 cm^{-1}, depending on the compositions. The transmittance of the samples, T, was calculated as the ratio among the output (transmitted) intensity and the input intensity. The results plotted in Fig. 3 show a nonlinear decrease of T as the laser intensity increases. The role played by the tungstate oxide is clear from Figs. 2 and 3.

The light attenuation through the nonlinear sample is described by

$$\frac{dI}{dz} = -(\alpha_1 I + \alpha_2 I^2), \tag{1}$$

where I is the light intensity along the propagation direction z, α_1 is the linear absorption coefficient, and α_2 is the TPA coefficient.

The solution of Eq. (1), integrated from $z=0$ to $z=L$, is given by

$$I_L = \frac{I_0(1-R)^2 \exp(-\alpha_1 L)}{1+(\alpha_2/\alpha_1) I_0(1-R)[1-\exp(-\alpha_1 L)]}, \tag{2}$$

where R is the reflectance of each sample face and L is the sample thickness. The nonlinear transmittance is given by $T = I_L / I_0$.

The value of α_2 is obtained by fitting Eq. (2) to the experimental data presented in Figs. 2 or 3, using a nonlinear curve fitting procedure. The results obtained are summarized in Table II. We observe that the values of α_2 for the samples

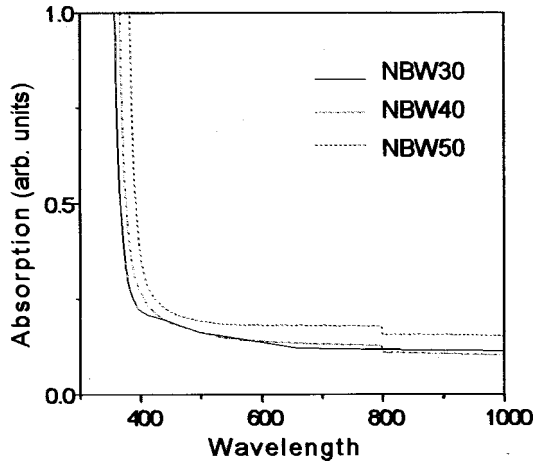

FIG. 1. Linear absorption spectra of the studied samples. The thicknesses of the samples are given in Table II.

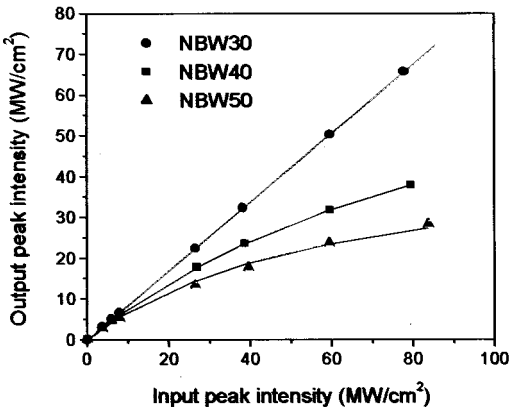

FIG. 2. Optical limiting behavior of the tungstate fluorophosphate glasses for excitation at 660 nm.

NBW40 and NBW50 are larger by more than one order of magnitude than values reported for other phosphate glasses.[7] Moreover, we note that the present values of α_2 are comparable with the TPA coefficients reported for chalcogenide glasses[12] and glass ceramics.[13,14]

The increase of α_2 for the samples with larger concentration of tungstate oxide should be correlated to possible structural changes in the glass. It was already shown by Raman spectroscopy[11] that the tungsten oxide units appears as WO_4 tetrahedral units for concentrations smaller than 30% but appears as a mixture of WO_4 tetrahedral and WO_6 octahedral units for concentrations larger than 40%, with an increase of the WO_6 proportion by increasing the tungsten oxide concentration. We recall that clusters of transition metal, including tungsten, enhance the nonlinear properties of glasses.[15] Possibly, in the present case, the enhancement of α_2 results mainly from the hyperpolarizabilities associated to W–O bonds in clusters of WO_6 octahedral units. Further structural investigations by extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) studies on the tungsten atom are in progress in order to have more precise details of the microscopic structure of the glasses.

In summary, TPA coefficients were determined for tungstate fluorophosphate glasses. It was demonstrated that the nonlinear absorption is strongly dependent on the tungsten

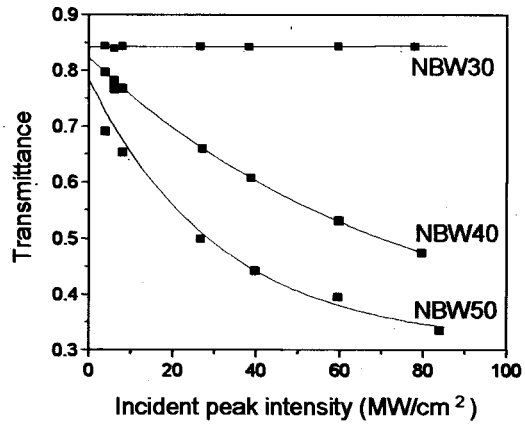

FIG. 3. Nonlinear transmittance response vs the incident peak intensity.

oxide concentration being enhanced when the fraction of WO_6 octahedral units in the glass increases. The behavior observed for samples with a high tungsten oxide concentration indicates the large potential of this glass for OL.

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