Vol 13 No 8, August 2004
1009-1963/2004/13(08)/1287-04

Chinese Physics

© 2004 Chin. Phys. Soc.
and IOP Publishing Ltd

Nonlinear optical properties of $75TeO_2$–$20Nb_2O_5$–$5ZnO$ glasses doped with CeO_2*

Zhang Shi-An(张诗按)[a], Sun Zhen-Rong(孙真荣)[a]†, Wang Yu-Fei(王宇飞)[a], Zeng He-Ping(曾和平)[a], Wang Zu-Geng(王祖赓)[a], Lin Jian(林 健)[b], Huang Wen-Hai(黄文昊)[b], Xu Zhi-Zhan(徐至展)[c], and Li Ru-Xin(李儒新)[c]

[a] *Key Laboratory of Optical and Magnetic Resonance Spectroscopy, and Department of Physics, East China Normal University, Shanghai* 200062, *China*

[b] *Department of Materials Science and Engineering, Tongji University, Shanghai* 200092, *China*

[c] *Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai* 201800, *China*

(Received 8 October 2003; revised manuscript received 30 March 2004)

Nonlinear optical properties of $75TeO_2$–$20Nb_2O_5$–$5ZnO$ glasses doped with CeO_2 have been investigated with a self-diffracted time-resolved degenerate four-wave mixing (DFWM) technique at different excitation intensities and lattice temperatures. The DFWM signal exhibits three peaks at higher excitation intensities, where a main peak appears at zero delay time and two rather weak side peaks are located symmetrically at the negative and positive time delay. Due to destructive interferences between the fifth- and third-order polarizations, the line-shape of the main peak around the zero time delay evolves from single peak into a double-peak structure with increasing excitation intensity. Two side peaks emerge at the positive and negative time delay and gradually intensify with increasing excitation intensity or lattice temperature, and their positions are independent of the pulse duration, temperature and excitation intensity, which are attributed to the many-body Coulomb interaction.

Keywords: tellurite glasses, CeO_2, degenerate four-wave mixing (DFWM), local-field corrections, many-body Coulomb interaction

PACC: 4270C, 4265M, 1130N, 7865M

1. Introduction

Tellurite glasses are very promising materials in optical communication systems for their electrical and nonlinear optical properties, such as high nonlinear refractive index, wide infrared transmittance, low melting temperature, low phonon maximum, and higher dielectric constant.[1−6] They can be regarded as rather prefect nonlinear optical materials for ultrafast all-optical switch due to their large third-order nonlinear optical susceptibility. Recently, tellurite glasses doped with heavy metal oxides or rare earth oxides,[6−9] such as Nb_2O_5, CeO_2 or ZnO, have received great scientific interest because these metal or rare earth oxides can change the optical and physical properties of the tellurite glasses. In tellurite glasses, there are symmetric or asymmetric units of TeO_4 trigonal bipyramid, TeO_3 trigonal pyramid and an intermediate TeO_{3+1} asymmetric polyhedron. TeO_4 trigonal bipyramids will transform into TeO_3 trigonal pyramids through an intermediate TeO_{3+1} trigonal polyhedron as the additional cations (such as Nb^{5+}) are introduced, and thus the addition of Nb^{5+} (d° shell) and Te^{4+} (lone pairs) can improve the nonlinear optical response of tellurite glasses.[2,6,10] CeO_2 is a mixed valence rather than a pure 4f compound; when CeO_2 is doped in tellurite glasses, CeO_2 may lower the melting point of tellurite glasses and act as a modifier without changing the glass network.[8] For the potential use of tellurite glasses doped with heavy metal oxides or rare earth oxides in optical communication systems, it is necessary to investigate their nonlinear optical properties and their mechanisms.

*Project supported by the Shanghai Priority Academic Discipline, the National Natural Science Foundation of China (Grant Nos 10234030 and 10074015), and the State Key Development Programme for Basic Research of China (Grant No 1999075204), the Programme Foundation from Shanghai Science and Technology Committee, and the Key Programme Foundation from Ministry of Education of China.

†Corresponding author. E-mail: zrsun@public4.sta.net.cn

The nonlinear optical (NLO) properties of tellurite glasses have been and are being extensively investigated. Time-resolved degenerate four-wave mixing (DFWM) is a very powerful technique to investigate the nonlinear optical properties.[11−14] With the rapid development of modern laser technique, the ultra-fast laser pulses enable us to study the ultra-fast dynamics of physical response with the above technique. In this paper, we report the line-shape of DFWM signal in $75TeO_2$–$20Nb_2O_5$–$5ZnO$ glasses with CeO_2 dopant by self-diffracted time-resolved DFWM technique at different excitation intensities and lattice temperatures, and their mechanisms are discussed in detail.

2. Experiment

Appropriate mixtures of powders of TeO_2 (99.99%, Aldrich), Nb_2O_5 (99.99%, Aldrich), ZnO (99.99%, Aldrich) were melted in a gold crucible at 780–830°C for 10–20min in air. The molten glass was poured onto a plate, annealed at 360–400°C for 4h, and then cooled to room temperature. Samples with the composition of $75TeO_2$–$20Nb_2O_5$–$5ZnO$ were instantaneously introduced with 0.5% CeO_2.

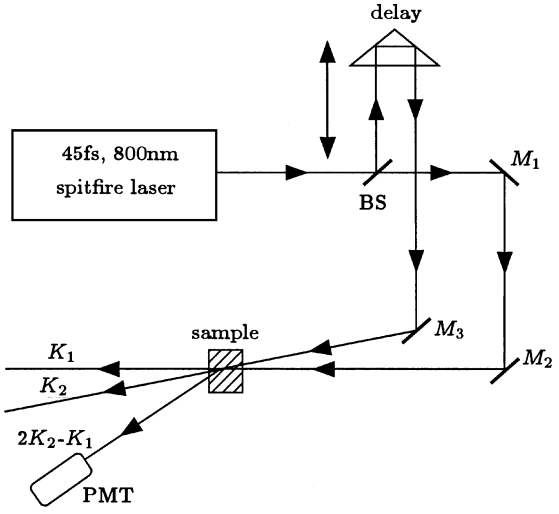


Fig.1. Experimental setup for DFWM, BS: beamsplitter; PMT: photomultiplier; M_1, M_2, M_3: reflector mirrors.

Two-pulse self-diffracted transient DFWM was performed using a Spectra-Physics Spitfire amplifier with a repetition rate of 1kHz, centre wavelength of 800nm and pulse-width of < 50fs (as shown in Fig.1). The femtosecond laser was split into two beams by a beamsplitter (BS); finally the two beams were crossed on the sample with a small angle. The two beams were of co-linearly polarized excitation (↑↑), and their average power was in a ratio of about 1.5:1. The DFWM signal was measured as a function of the pump–probe delay time.

3. Results and discussion

The line-shape of the transient four-wave-mixing signal has been systematically investigated,[12,13] and it was based on the interacting two-level model and confirmed experimentally.[12] The line-shapes usually include (a) an inhomogeneous broadening and (b) a homogeneous broadening. Figure 2 indicates the DFWM signals at the incident laser intensities of 26, 32, 37, and 39GWcm^{-2} at 300K. There appear three distinct peaks of the DFWM signal at higher excitation intensities, a main and intense peak appears at zero time delay and two rather weak side peaks are located symmetrically at the negative and positive delay time. The main peak exhibits a homogeneous broadening. Wegener and Chemla[13] have developed a model to describe the homogeneous broadening, where the local-field corrections were taken into account. For a homogeneously broadened system, one obtains

$$I_{k_3}^{\mathrm{hom}}(T) \propto \Theta(T)\mathrm{e}^{-2\gamma_2 T} + \frac{4V^2}{(2\gamma_2+\gamma_1)(\gamma_2+\gamma_1)} \times [\Theta(T)\mathrm{e}^{-2\gamma_2 T} + \Theta(-T)\mathrm{e}^{4\gamma_2 T}], \quad (1)$$

where Θ is the Heaviside step function; $V = N|\mu|^2 L$, N is the density of atoms, μ is the dipole moment between the ground and excited states, and L is the Lorentz local field factor. $\gamma_1 = 1/T_1$ and $\gamma_2 = 1/T_2$ are the longitudinal and transverse relaxation rates, respectively. According to Eq.(1), the DFWM signal indicates a rise time with a time constant $T_2/4$ and a decay time with a time constant $T_2/2$. From Fig.2, we can see that the rising and decay times remain unchanged with increasing excitation intensity; similar behaviour can be observed with increasing lattice temperature (as shown in Fig.3). The rising time is calculated to be 291fs and the decay time to be 573fs, and their ratio is generally equal to 1:2; this is in good agreement with the above theory.

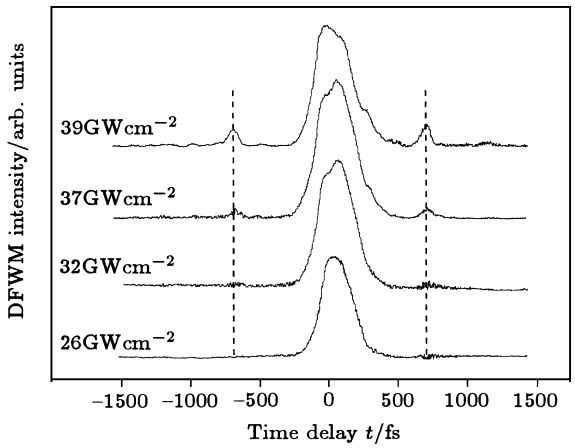


Fig.2. DFWM signal versus the delay time of the pumping and probing pulses for different excitation intensities at lattice temperature of 300K.

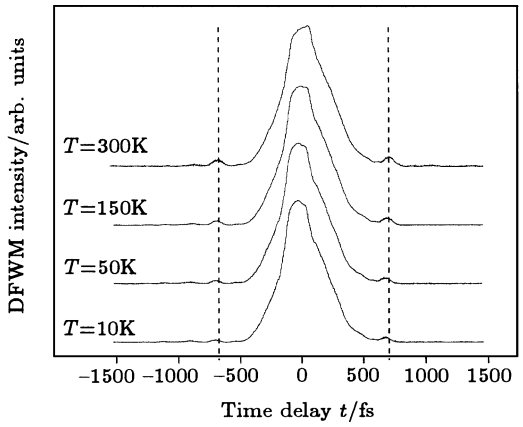


Fig.3. DFWM signal versus the delay time of the pumping and probing pulses for different lattice temperatures at the excitation intensity of 38GWcm^{-2}.

The negative edge of the main peak is related to the local-field correction and excitation-induced dephasing (EID). If pulse 1 arrives after pulse 2, there are no photons in the direction $2k_2-k_1$ diffracted from pulse 2 when the grating is formed. However, with the local-field interaction and EID, the polarization left over by pulse 2 can be diffracted by the grating in the direction $2k_2-k_1$. Wang *et al*[14] have derived an expression to describe the negative edge of DFWM signal as follows:

$$\begin{aligned} P^{(NL)} =& \kappa e^{i\delta(t-2t_2+t_1)}\{\Theta(t-t_2) \\ &\times \Theta(t_2-t_1)e^{-\Gamma_t(t-t_2)-\Gamma_1(t_2-t_1)} \\ &+ \frac{N(\sigma+i\eta)}{\gamma_e}[\Theta(t-t_2)\Theta(t_2-t_1) \\ &\times (1-e^{-\gamma_e(t-t_2)})e^{-\Gamma_t(t-t_2)-\Gamma_1(t_2-t_1)} \\ &+ \Theta(t-t_1)\Theta(t_1-t_2) \\ &\times (1-e^{-\gamma_e(t-t_2)}) \\ &\times e^{-\Gamma_t(t-t_1)-2\Gamma_2(t_1-t_2)}]\} + \text{c.c.}, \end{aligned} \quad (2)$$

where

$$\kappa = -iN\mu^4\hbar^{-3}E_2^2E_1^*\exp[-i\Omega t + i(2k_2-k_1)\cdot r],$$

$\eta = 2\mu^2L/\hbar$ and $\delta = \Omega-\omega-\varepsilon$ with $\varepsilon = N\mu^2L/\hbar$ being the static Lorentz shift. The decay rates Γ_t, Γ_t, and Γ_2 are all determined by the intrinsic dephasing rate γ. In the large bracket in Eq.(2), the first term indicates the prompt free polarization dephasing in a simple non-interacting two-level system, and the second term represents the additional FWM signal due to the EID (proportional to δ) and the local-field correction (proportional to η). From Eq.(2), we can see that the scattering of the polarization, induced by the probing pulse E_2 through the local-field correction or the EID, results in a prompt signal at $t_2-t_1>0$ (the positive time delay) and a signal at $t_2-t_1<0$ (the negative time delay).

As shown in Fig.2, the main peak changes drastically with increasing excitation intensity. A single peak of low intensity gradually evolves into two peaks around zero time delay, and then the left peak gradually rises as the excitation intensity is continually increased. It is also observed that the DFWM signal in the direction $2k_1-k_2$ has the same phenomenon for inverted delay time. The above-mentioned experimental phenomena arise from the interaction between the third-order and the fifth-order polarizations. Wegener and Chemla[13] have constructed the time-integrated DFWM signal up to fifth order in theory, and they obtained

$$\begin{aligned} I_{k_3}^{\text{hom}}(T) \propto& \Theta(T)\left[1+\frac{A_5}{A_3}\frac{5}{2}+\frac{A_5^2}{A_3^2}\frac{8}{5}\right]e^{-2\gamma_2 T} \\ &+ \Theta(-T)\left[e^{4\gamma_2 T}+\frac{A_5}{A_3}\frac{5}{2}e^{6\gamma_2 T}+\frac{A_5^2}{A_3^2}\frac{8}{5}e^{8\gamma_2 T}\right], \end{aligned} \quad (3)$$

where

$$\begin{aligned} A_3 =& -(9/16)\alpha_3\gamma_2^{-1}\Omega_0^{-4}\lambda^3E^2\delta E^*, \\ A_5 =& (25/16)\alpha_5\gamma_2^{-1}\Omega_0^{-6}\lambda^5E^3E^*\delta E^*, \\ \lambda =& 2\Omega_0|\mu|^2, \end{aligned}$$

α_3 and α_5 are coefficients. A_3 and A_5 reflect the intensities of the third- and fifth-order terms respectively, and the ratio of A_5/A_3 is proportional to the excitation intensity. From Eq. (3) we can see that at first the DFWM signal at the negative time delay becomes intense (terms linear in A_5), and then two peaks emerge (terms quadratic in A_5). The results also can be understood intuitively. The fifth-order polarization has

an opposite signal to the third-order polarization, and thus the two peaks are generated due to the destructive interference between the third- and fifth-order polarizations around zero time delay. Because the time constant for fifth-order polarization is less than that for third-order polarization, no similar destructive interference generates far away from zero time delay. This can qualitatively describe our experimental observation.

As shown in Fig.2, the two weak side peaks are located symmetrically on both sides of the main peak, and their maxima are located at the time delay of 707fs and-691fs, respectively. Their positions are independent of the pulse duration, lattice temperature and excitation intensity, but their intensities depend on the lattice temperature and excitation intensity. The two side peaks are related to the many-body Coulomb interaction, which has been extensively investigated using the transient time-resolved DFWM technique.[13,15,16] When the dephasing time $T_2 > \tau_P$ (laser pulse width), the additional DFWM signal for positive time delay, induced by the Coulomb interaction, rises slowly and reaches a maximum at a real time of $t \approx T_2$, but the additional DFWM signal for negative time delay may exist only when the DFWM signal is homogeneously broadening. Our experimental phenomena are consistent with the above-mentioned mechanism.

At low excitation intensities, the interaction of electrons and holes in the presence of external field is rather weak. With increasing excitation intensity, their interaction dramatically strengthens, the larger binding energy of the e–h pair increases the Coulomb interaction mediated many-body effects, which results in the intensification of the two side peaks. An explanation for the intensification at higher lattice temperatures is that the inclusion of CeO_2 facilitates the polaron hopping due to the hopping mechanism. In $75TeO_2$–$20Nb_2O_5$–$5ZnO$ matrices, there exists Ce^{3+} ion from the CeO_2 dopant. It is due to the existence of Ce^{3+} ion that the electrical conductivity of tellurite glasses increases with increasing temperature. At low temperatures, the 4f electron of the Ce^{3+} ions remains localized, resulting in the formation of bound polarons, and only direct hopping between localized states can occur. At high temperatures, almost all free polarons move along the Ce sites, resulting in an increase in the electrical conductivity, and therefore many-body Coulomb interaction increases. However, the influence of temperature on the many-body Coulomb interaction is not very obvious.

4. Conclusions

In summary, we have investigated the DFWM signal of $75TeO_2$–$20Nb_2O_5$–$5ZnO$ glasses with CeO_2 dopant by a time-resolved DFWM technique at different excitation intensities and lattice temperatures. The DFWM signal exhibits three peaks at higher excitation intensities. A main and intense peak appears at zero time delay and evolves into a double-peak structure from the single peak with increasing excitation intensity, which is attributed to destructive interferences between the fifth- and third-order polarizations. Two weak side peaks located symmetrically on both sides of the main peak intensify gradually with increasing excitation intensity or lattice temperature, which are attributed to the many-body Coulomb interaction.

References

[1] Kim S H, Yoko T and Sakka S 1993 *J. Am. Ceram. Soc.* **76** 2486

[2] Kowada Y, Morimoto K, Adachi H, Tatsumisago M and Minami T 1996 *J. Non-Cryst. Solids* **196** 204

[3] Weng L and Hodgson S N B 2002 *Opt. Mater.* **19** 313

[4] Nasu H, Matsushita O, Kamiya K, Kobayashi H and Kubodera K 1990 *J. Non-Cryst. Solids* **124** 275

[5] Prakash G V, Rao D N and Bhatnagar A K 2001 *Solid State Commun.* **119** 39

[6] Berthereau A, Fargin E, Villezusanne A, Olazcuaga R, Flem G L and Ducasse L 1996 *J. Solid State Chem.* **126** 143

[7] EI-Mallawany R 1998 *Mater. Chem. Phys.* **53** 93

[8] EI-Mallawany R, EI-Sayed A H and EI-Gawad M M H A 1995 *Mater. Chem. Phys.* **41** 87

[9] Ma H P, Xu S Q and Jiang Z H 2004 *Acta Phys. Sin.* **53** 1378 (in Chinese)

[10] Jeansannetas B, Blanchandin S, Thomas P, Marchet P, Champarnaud-Mesjard J C, Merle-Mejean T, Frit B, Nazabal V, Fargin F and Le Flom G 1999 *J. Solid State Chem.* **146** 329

[11] Akiyama K, Tomita N, Nomura Y and Isu Y 1999 *Physica* B **272** 505

[12] Wagner H P, Schatz A, Maier R, Langbein W and Hvam J M 1996 *Physica* E **2** 82

[13] Wegener M and Chemla D S 1990 *Phys. Rev.* A **42** 5675

[14] Wang H, Ferrio K B and Steel D G 1994 *Phys. Rev.* A **49** 1551

[15] Kim D S, Shah J, Damen T C, Schafer W, Jahnke F, Schmitt-Rinik S and Konler K 1992 *Phys. Rev. Lett.* **69** 2725

[16] Weiss S, Mycek M A, Bigot J Y, Schmitt-Rink S and Chemla D S 1992 *Phys. Rev. Lett.* **69** 2685