Study on optical nonlinearities of ZnO-Nb_2O_5-TeO_2 glass with time-resolved four-wave mixing technique

Li Jiang (江 丽)[1], Shi'an Zhang (张诗按)[1], Yufei Wang (王宇飞)[1], Zhenrong Sun (孙真荣)[1], Zugeng Wang (王祖赓)[1], Jian Lin (林 健)[2], Wenhai Huang (黄文昱)[2], Zhizhan Xu (徐至展)[3], and Ruxin Li (李儒新)[3]

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

[2] *School of Material Science and Engineering, Tongji University, Shanghai 200092*

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

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We investigated nonlinear optical properties of ZnO-Nb_2O_5-TeO_2 glass excited by a femtosecond laser with time-resolved four-wave mixing (FWM) technique. The unusual FWM signals were observed in samples with ZnO dopant. The mechanism for the optical nonlinearities was discussed.

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Tellurite glasses have gained much attention among the new developing nonlinear optical glasses due to their good electrical, optical and magnetic properties. As promising materials in optical switching and optical memory devices, they possess many excellent properties such as large second- and third-order nonlinear optical susceptibility, large nonlinear refractive indices, wide infrared transmission range, etc.[1−3]. Tellurite glasses are good hosts of rare earth and heavy metals because weak Te-O bands can make the glass network more open[4,5]. Tellurite glasses, doped with metal oxides, are regarded as potential candidates for up-conversion lasers and optical fiber amplifiers with small multi-phonon decay rates[6−8]. Zinc oxides play an important role in forming the glass network and can improve the thermal and chemical stabilities of tellurite glasses. Recently, some researches have focused on zinc tellurite glasses for its more stable structures[9−11]. Furthermore, the hyperpolarizability of the Nb-O band induces high refractive index, thus the metal Nb is usually added into tellurite glasses to improve optical nonlinearity and vitrification of tellurite glasses[2].

We used time-resolved four-wave mixing (FWM) technique to study the optical nonlinearities in glass sample ZnO-Nb_2O_5-TeO_2 with a femtosecond laser. The mechanism of unusual FWM signals was discussed.

Glass was prepared from the spectral grade ZnO, Nb_2O_5 and TeO_2 with the composition of xZnO-$20Nb_2O_5$-$(80-x)TeO_2$. The powder was weighed precisely, mixed thoroughly and melted in a platinum crucible at 780 − 830 °C for 15 − 20 minutes in air. The melting glass was poured onto a plate, annealed at 360 − 400 °C for 4 hours, and then cooled to the room temperature. The resultant glass sample was cut into 1.5-mm-thick plates and polished on two surfaces for the following experiments.

In time-resolved FWM experiments, we used a Spectra-Physics Ti:sapphire femtosecond laser as excitation source with the final output wavelength of 800 nm, pulse-width of about 40 fs and the repetition rate of 1 kHz. The laser beam was split into two linearly parallel polarized beams, one beam as probing is delayed by T with respect to another beam as pumping, then to spatially overlap on the sample. In this technique two pulsed laser beams with wave vectors k_1 and k_2 interfere in a sample to produce a diffracted beam in the direction $k_3 = 2k_2 - k_1$. The magnitude of the diffracted signal in the direction k_3 is then recorded as a function of the time delay T. Signals detected by a photodiode were amplified by a lock-in amplifier and then sent into a computer.

Figure 1 shows FWM signals as a function of the delay time for xZnO-$20Nb_2O_5$-$(80-x)TeO_2$ glass samples with the excitation power of about 60 mW for various ZnO content x. Without ZnO doping, the time-resolved signal for the sample $20Nb_2O_5$-$80TeO_2$ is almost a typical FWM signal with peak maximum near zero delay.

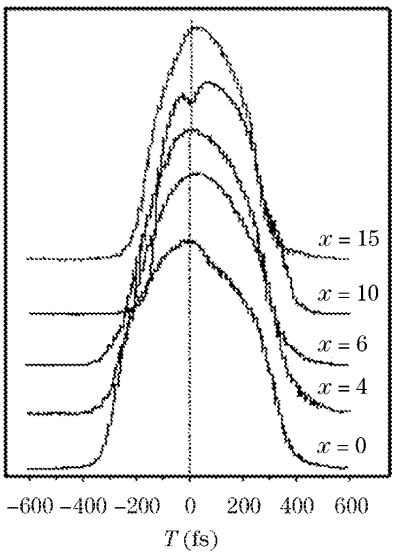

Fig. 1. FWM signals for the sample xZnO-$20Nb_2O_5$-$(80-x)TeO_2$ versus delay time T.

When ZnO content is increased, FWM signals evolve gradually into asymmetrical line-shape with fast negative rising and slow positive decaying wings. As ZnO content up to 10%, a peculiar temporal profile of FWM signal that is two distinct maxima and a valley near zero delay appears. Such a double peak structure disappears when ZnO content in the sample increases to 15%.

Double-peak for the FWM signals has been experimentally observed and theoretically proven in semiconductor structures such as GaAs/AlGaAs quantum wells[12−14]. It is believed that double-peak phenomena arise from high order optical nonlinearities of excitons. Generally, the destructive interference of various orders of nonlinear polarization causes single-peak FWM signals which evolve into double-peak signals. The peak for FWM signal due to the third-order term $\chi^{(3)}$ may be compensated by the contribution of the fifth-order term $\chi^{(5)}$ with the opposite sign, resulting in a pronounced destructive interference close to zero time delay. This destructive interference takes away energy from the time-integrated signal and thus leads to a minimum of the signal close to zero time delay. So, the double-peak can be seen very nicely in the time-dependent polarization close to $T = 0$[15]. In the region away from zero delay, the contribution of $\chi^{(5)}$ disappears because it decays with faster time constants.

The concentration of ZnO dopant is related to high order optical nonlinearities in ZnO-Nb_2O_5-TeO_2 glass samples. With ZnO dopant increasing, more Nb^{5+} can rather easily join the network structure from outside of the entities. As the Nb-O bond and the d orbital of Nb^{5+} cations located in the network structure have more contributions to the nonlinear optical property, some quantity of ZnO dopant can improve third-order optical nonlinearity and thus fifth-order optical nonlinearity, and their destructive interference results in peak evolution. However, it is difficult to accommodate more Nb^{5+} when the network participant gets saturation, thus the optical nonlinearities have a maximum limit. Moreover, more $[TeO_4]^{4-}$ network units depolymerize and transform into $[TeO_3]^{2-}$ clusters with ZnO increasing, which may also impair the large optical nonlinearity of the sample. In our case, 10ZnO-20Nb_2O_5-70TeO_2 glass sample shows the strongest interaction of high order optical nonlinear terms. As ZnO content increases to 15%, the optical nonlinearity of the sample becomes weaker.

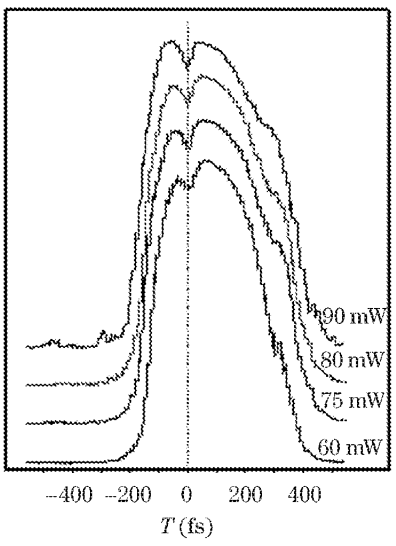

Fig. 2. FWM signals for the sample 10ZnO-20Nb_2O_5-70TeO_2 versus delay time T with different excitation powers.

Time-resolved FWM experiments on each sample excited with different laser power were examined as well. Time-resolved signals for the sample 10ZnO-20Nb_2O_5-70TeO_2 are shown in Fig. 2. Peak evolution can be clearly seen from the figure. With the excitation intensity increasing, left peaks in double-peak structure rise quickly and become higher than right ones in higher excitation intensity. It is explained that for a homogeneous line the time-integrated diffracted signal up to fifth order is[15]

$$I_{k_3}^{\mathrm{hom}} \propto \Theta(T)\left[1+\frac{5}{2}\frac{A_5}{A_3}+\frac{8}{5}\frac{A_5^2}{A_3^2}\right]\mathrm{e}^{-2\gamma_2 T} +\Theta(-T)\left[\mathrm{e}^{4\gamma_2 T}+\frac{5}{2}\frac{A_5}{A_3}\mathrm{e}^{6\gamma_2 T}+\frac{8}{5}\frac{A_5^2}{A_3^2}\mathrm{e}^{8\gamma_2 T}\right],$$

when $T < 0$, the first term is equal to zero. For positive time delays, one finds an exponential decay of the polarization. The time constant of the time-integrated signal is $T_2/2$[16]. For negative time delays, the constant is $T_2/4$. Double-peak structure, evolving with the excitation intensity, has also been observed in semiconductor system[17]. In the sample 10ZnO-20Nb_2O_5-70TeO_2, the effect of destructive interference becomes stronger with excitation intensity increasing, and thus double peak structure was influenced drastically by laser power.

In summary, the optical nonlinear properties for the sample ZnO-Nb_2O_5-TeO_2 were studied by using time-resolved FWM technique. The unusual FWM signals result from the high order nonlinear properties of excitons.

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