ELSEVIER

Femtosecond vibrational photon echo in CeO$_2$-doped TeO$_2$–Nb$_2$O$_5$–ZnO glass

Shian Zhang [a], Zhenrong Sun [a,*], Xihua Yang [a], Zugeng Wang [a], Jian Lin [b], Wenhai Huang [b], Zhizhan Xu [c], Ruxin Li [c]

[a] *Department of Physics, Key Laboratory of Optical and Magnetic Resonance Spectroscopy, East China Normal University, No. 3663 Zhongshan North Road, Shanghai 200062, PR China*
[b] *School of Material Science and Engineering, Tongji University, Shanghai 200092, PR China*
[c] *Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, PR China*

Abstract

Vibrational photon echo decay in the CeO$_2$-doped TeO$_2$–Nb$_2$O$_5$–ZnO glass is observed with near-infrared femtosecond laser pulse at the temperature of 7.5 and 300 K. The photon echo signals exhibit an initial fast decay followed by an exponential decay. The anharmonic frequency splitting (Δ), the dephasing rate (γ), the dephasing time (T_d) and the linewidth (Γ) are obtained. The results show that the dephasing time of the $v = 0 \rightarrow 1$ transition is dominated by the vibration state lifetime T_{1l}, and the dephasing time of the $v = 0 \rightarrow 2$ transition is determined by both the vibration state lifetime T_{2l} and the pure dephasing time T_{2d}^*.
© 2004 Elsevier B.V. All rights reserved.

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 [1–3]. They can be regarded as rather prefect nonlinear optical materials for ultra-fast all-optical switch due to their large third-order nonlinear optical susceptibility. Recently, tellurite glasses doped with heavy metal oxides or rare earth oxides, such as

* Corresponding author. Tel.: +86 21 622 33210; fax: +86 21 622 32056.
  E-mail addresses: zrsun@phy.ecnu.edu.cn, zrsun@public4.sta.net.cn (Z. Sun).

Nb_2O_5, CeO_2, or ZnO, have received great scientific interest because these metal or rare earth oxides can change their optical and physical properties [3–5].

Vibrational spectra can be responsible for inhomogeneous broadening which masks the homogeneous broadening vibrational lineshape [6,7]. When the inhomogeneous linewidth is many orders of magnitude greater than the homogeneous linewidth, inhomogeneous broadening can mask the dynamic information involving in the homogeneous broadening. The homogeneous linewidth provides valuable information on the dynamical interactions with its environment [8], so it is necessary to extract the homogeneous linewidth from the vibrational spectra. Femtosecond coherent anti-Stokes Raman scattering and Raman-induced Kerr effect [9] can measure the dephasing time of vibrational modes, but they are hard to eliminate the contributions from inhomogeneous broadening. Vibrational photon echo experiment is an important method to obtain pure homogeneous linewidth [8,10–13], and it has an additional advantage of being able to distinguish the pure dephasing and lifetime contributions to the homogeneous vibrational linewidth.

As to vibrational photon echo experiments, when the laser bandwidth is narrower than the vibrational anharmonicity, the photon echo signal only comprises of two-level transition and exhibits single exponential decay [6,7,11]. However, when the bandwidth or Rabi frequency of ultrashort excitation pulse exceeds the anharmonicity of the vibrational transition, the population can be excited to higher vibrational state. Thus a vibrational coherence among the three-level system will be created due to substantial spectral overlapping between the two transitions, which results in biexponential vibrational photon echo decays with beats at the anharmonic splitting frequency [10,12,14]. In the paper, the vibrational photon echo decay in the CeO_2-doped TeO_2–Nb_2O_5–ZnO glass is observed with near-infrared femtosecond laser pulse at low temperature (7.5 K) and room temperature (300 K), the photon echo signals exhibit an initial fast decay followed by an exponential decay.

2. Experiment

Appropriate mixtures of TeO_2 (99.99% Aldrich), Nb_2O_5 (99.99% Aldrich), ZnO (99.99% Aldrich) are melted in gold crucible for 25–30 min at 850–950 °C. Liquids are quenched to room temperature in steel molds and annealing treatments are performed at 300–350 °C for 2–4 h. TeO_2–Nb_2O_5–ZnO glass samples, doped with 0.5% CeO_2, are picked out and their surfaces are polished. As shown in Fig. 1, three absorption peaks are observed at about 585, 745, and 800 nm, which are attributed to the Ce^{4+}–O–Ce^{3+} clusters, the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ electronic transition and the $^1S_0 \rightarrow {}^1F_3$ electronic transition of Ce^{3+} ion, respectively [15,16].

A mode-locked Ti:sapphire laser (Spectra-Physics Spitfire amplifier) is used as the excitation source with the pulse duration of about 50 fs and the repetition rate of 1 kHz, as shown in Fig. 2 (a). Its center wavelength of 800 nm is resonant with the $^1S_0 \rightarrow {}^1F_3$ electronic transition of Ce^{3+} ion, and its linewidth of about 40 nm overlays many vibrational levels of the excited states. The laser beam is split into two beams by a beam-splitter (BS) with a ratio of 1.5:1. The delay between the two beams is controlled by a stepper-motor. The two beams have the same polarization (s-polarization) and are crossed in the sample with a
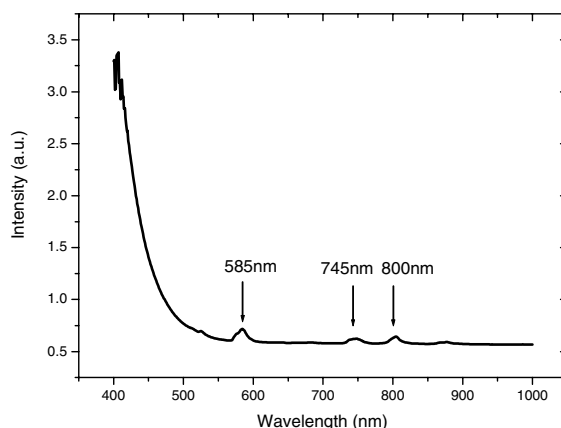

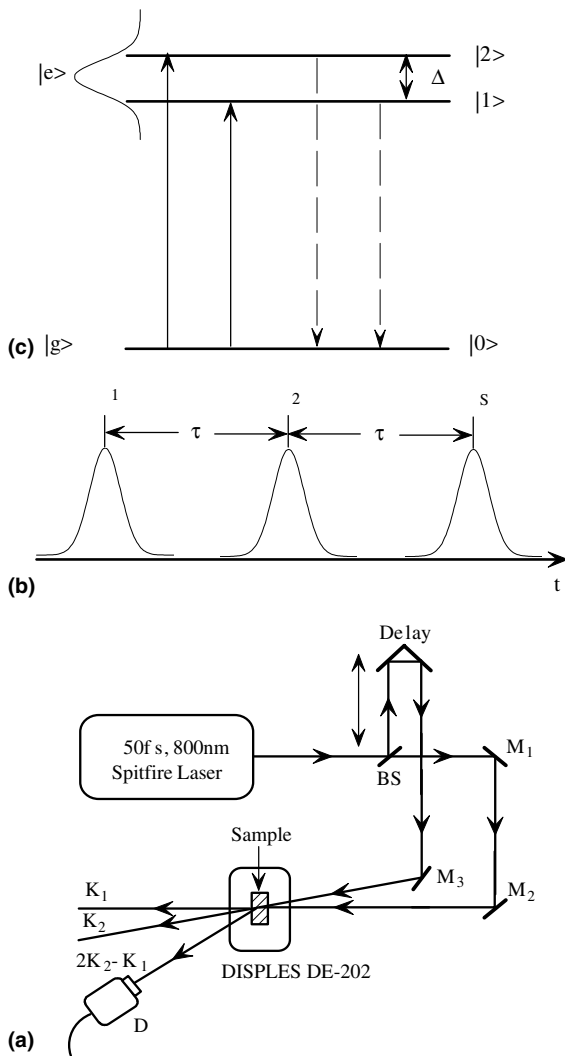Fig. 1. Absorption spectra for CeO_2 doped TeO_2–Nb_2O_5–ZnO glass.

Fig. 2. (a) Experimental setup for vibrational photon echo measurement, BS, beam-splitter; D, a silicon pin detector; M_1, M_2, M_3, mirror. (b) Pulse sequence for vibrational photon echo experiment. (c) Energy-level schematic diagram for the resonant vibrational echo experiment.

Fig. 3. The photon echo decay (dots) for CeO_2-doped TeO_2–Nb_2O_5–ZnO glass at the temperatures of 7.5 K (a) and 300 K (b), the solid curves are the theoretical fitting results by Eq. (4).

small angle about 6°. The glass sample is about 2 mm thickness and its temperature is controlled by DISPLES DE-202 system (Advanced Research Systems, Inc). Photon echo signal is determined by wave vector matching conditions $k_3 = 2k_2 - k_1$, and detected by a silicon pin detector as a function of the delay time between the two beams (the experimental results are shown in Fig. 3).
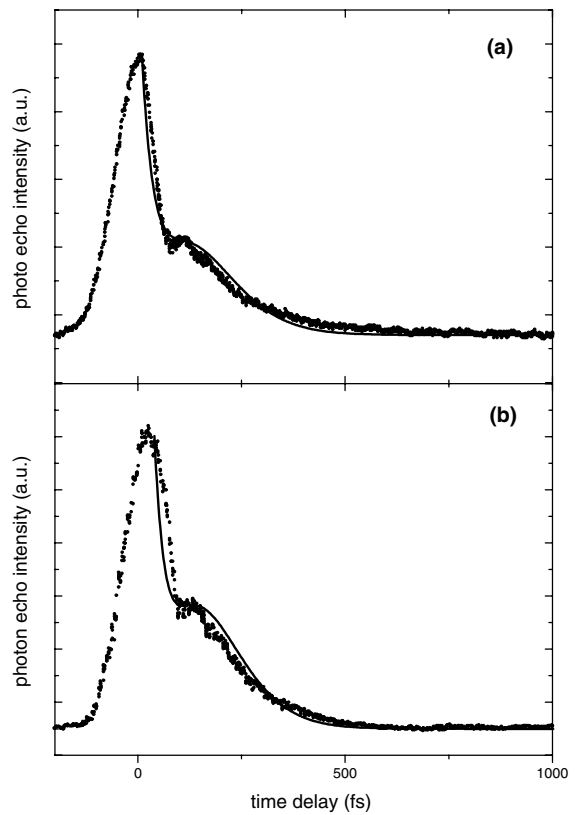
3. Results and discussion

If a relative long laser pulse is used, the photon echo decay only involves in two-level transition ($v = 0 \rightarrow 1$) for the narrow bandwidth of the laser pulse and exhibits single exponential decay, the exponential decay is usually charactered by the optical dephasing time T_d and considered as the dipole–dipole interactions of the impurity atom, ions and molecules with the thermally excited tunneling two-level systems (TLS) [17–19], which is in a good agreement with common theories of photon echo decay. For a Lorentzian homogeneous lineshape, the vibrational photon echo signal decays as

$$I(\tau) = I_0 \exp(-4\gamma t), \tag{1}$$

where $\gamma = 1/T_d$ for the $v = 0 \rightarrow 1$ transition, T_d is the homogeneous dephasing time. The echo signal decays four times as fast as the dephasing time and twice as fast as the polarization. The homogeneous linewidth Γ can be determined in view of the dephasing time T_d.

$$\Gamma = \frac{1}{\pi T_d} = \frac{1}{2\pi T_1} + \frac{1}{\pi T_d^*}, \tag{2}$$

where T_1 is the excited vibration state lifetime, and T_d^* is the pure dephasing time. The homogeneous linewidth can be determined by the excited vibration state lifetime T_1 and the pure dephasing time T_d^*. The pure dephasing time T_d^* can also be determined by the following formula:

$$\frac{1}{\pi T_d^*} = aT^\alpha + b\exp(-\Delta E/kT)/[1 - \exp(-\Delta E/kT)], \tag{3}$$

where the first term describes the influence of spectral diffusion processes, which arises from the dynamics of the tunneling two-level systems (TLS) in the impurity glass (parameter α represents the coupling between chromosphere and TLS), and the second term represents the exponentially activated processes, which is due to the coupling to the low frequency phonons.

When the bandwidth of the excitation pulse exceeds the vibrational anharmonicity, the population can be excited to the higher vibriational levels. The vibrational up-pumping is mainly determined by the magnitude of the vibrational anharmonic frequency splitting Δ, related to the excitation pulse bandwidth (Ω) or Rabi frequency. When there is substantial spectral overlap between the spectra of the $v = 0 \rightarrow 1$ and $v = 0 \rightarrow 2$ transitions (as shown in Fig. 2(c)), the ultrashort pulse excitation will create a three level coherence involving the $v = 0$, 1 and 2 vibrational levels. The three-level system is spaced by the frequencies ω_{01} and ω_{02}, where $\Delta = \omega_{01} - \omega_{02}$, and $\Delta \ll \omega_{01}$ and ω_{02}. Thus the photon echo decay can be expressed by [8]

$$\begin{aligned} I(\tau) = I(0)\exp(-2\gamma_1 t)\{&(E_1 \cdot \mu_1)^2 \exp(-2\gamma_1 t)\\ &+ (E_2 \cdot \mu_2)^2 \exp(-2\gamma_2 t) - 2(E_1 \cdot \mu_1)(E_2 \cdot \mu_2)\\ &\times \exp\left[-(\gamma_1 + \gamma_2)t\right]\cos(\Delta t)\}. \end{aligned} \tag{4}$$

Here, the subscripts 1 and 2 refer to the different excited vibrational levels. E_1 and E_2 represent the excitation laser field amplitudes for the $v = 0 \rightarrow 1$ and $v = 0 \rightarrow 2$ transitions and μ_1 and μ_2 are the respective dipole transition moments which are constants. γ_1 and γ_2 are the corresponding homogeneous dephasing decay constants, and Δ is the anharmonic vibrational frequency splitting. $I(0)$ contains all the factors that determine the strength of the signal but are not involved in either the time dependent decays or the wavelength dependence of the beats. The two former terms in Eq. (4) indicates the dephasing terms for the $v = 0 \rightarrow 1$ and $v = 0 \rightarrow 2$ transitions, respectively, the third term indicates the interaction between the two dephasing terms. Eq. (4) may recover to Eq. (1) for the narrow bandwidth case ($E_2 \cong 0$). In this case, no multilevel coherence phenomenon can be observed.

Fig. 3 displays the photon echo decay for the CeO_2-doped TeO_2–Nb_2O_5–ZnO glass at the temperature of 7.5 and 300 K. The photon echo signals exhibit a non-exponential decay: an initial fast decay followed by an exponential decay. The solid curves are fitted by Eq. (4), which are in a good agreement with our experimental data. CeO_2 is a mixed valence rather than a pure 4f compound, which involves in Ce^{4+} and Ce^{3+} ion [20]. As shown in Fig. 1, there exists Ce^{3+} ion in the TeO_2–Nb_2O_5–ZnO matrixes. When the laser pulse field interacts with the glass sample, the population will be transferred from the ground state to the excited state of Ce^{3+} ion, and there is coupling of the electronic states of Ce^{3+} ion to ballistic motion of the bath through thermally populated and low frequency modes of the TeO_2–Nb_2O_5–ZnO glass. That is, the low frequency vibrational modes are superimposed on the electronic transition of Ce^{3+} ion. The related energy level model is schematically shown in Fig. 2(c). In our vibrational photon echo experiment, the center wavelength of the femtosecond laser pulse is resonant with the $^1S_0 \rightarrow {}^1F_3$ electronic transition of Ce^{3+} ion, and the pulse linewidth of about 40 nm overlays many vibrational levels. The first pulse creates an ensemble of coherent superposition states, which begins to dephase due to inhomogeneous and homogeneous broadening. A second pulse, delayed

Table 1
Dephasing rate (γ), dephasing time (T_d), linewidth (Γ) and vibrational anharmonic frequency splitting (Δ) of the $v = 0 \rightarrow 1$ and $v = 0 \rightarrow 2$ transitions in TeO_2–Nb_2O_5–ZnO glass doped with CeO_2

Temparature (K)	γ_1 (fs^{-1})	γ_2 (fs^{-1})	T_{1d} (fs)	T_{2d} (ps)	Γ_1 (GHZ)	Γ_2 (GHZ)	Δ (cm^{-1})
300	0.0050	0.0010	200	1.0	1592	318	303.3
7.5	0.0048	0.0003	208	3.3	1531	103	303.3

by time τ, rephases the inhomogeneous contributions to the vibrational transition, and results in an echo pulse observed at time 2τ (as shown in Fig. 2(b)). In the experiment, the delay time between the two pulses is about 27.6 ps.

The vibrational anharmonic frequency splitting (Δ), dephasing rate (γ), dephasing time (T_d) and linewidth (Γ) of the $v = 0 \rightarrow 1$ and $v = 0 \rightarrow 2$ transitions are obtained and tabulated in Table 1. The vibrational anharmonic frequency splitting (Δ) is determined as $\Delta = 303.3$ cm^{-1}, which is less than the bandwidth of excitation pulse of about $\Omega = 625$ cm^{-1}. The dephasing time of the $v = 0 \rightarrow 1$ transition T_{1d} is 208 fs at 7.5 K and 200 fs at 300 K, and the dephasing time of the $v = 0 \rightarrow 2$ transition T_{2d} is 3.3 ps at 7.5 K and 1.0 ps at 300 K, which are many times larger than those of the $v = 0 \rightarrow 1$ transition. The lack of the temperature dependence of the dephasing time of the $v = 0 \rightarrow 1$ transition indicates that the dephasing time is dominated by the excited vibrational state lifetime T_{11} since pure dephasing time T_{1d}^* is temperature dependent. However, the dephasing time of the $v = 0 \rightarrow 2$ transition crucially depends on the temperature, which indicates that the dephasing time is determined by both the excited vibrational state lifetime T_{2l} and the pure dephasing time T_{2d}^*. It is deduced that the $v = 0 \rightarrow 2$ transition is related to the coupling of the $^1S_0 \rightarrow {}^1F_3$ transition of Ce^{3+} ion to the ballistic motion of the glass, but the $v = 0 \rightarrow 1$ transition is related to the $^1S_0 \rightarrow {}^1F_3$ transition of Ce^{3+} ion and no coupling to the ballistic motion of the glass.

4. Conclusion

In summary, we have observed the femtosecond vibrational photon echo decay in the CeO_2-doped

TeO_2–Nb_2O_5–ZnO glass with near-infrared femtosecond laser pulse at the temperature of 7.5 and 300 K. The photon echo signals exhibit an initial fast decay followed by an exponential decay. The vibrational anharmonic frequency splitting (Δ) is theoretical fitted as $\Delta = 303.3$ cm^{-1}; the dephasing time of the $0 \rightarrow 1$ transition is 208 fs at 7.5 K and 200 fs at 300 K; the dephasing time of the $v = 0 \rightarrow 2$ transition is 3.3 ps at 7.5 K and 1.0 ps at 300 K. It is confirmed that the dephasing time of the $v = 0 \rightarrow 1$ transition is dominated by the vibrational stated lifetime T_{11} for no coupling of the $^1S_0 \rightarrow {}^1F_3$ transition of Ce^{3+} ion to the ballistic motion of the glass, and the dephasing time of the $v = 0 \rightarrow 2$ transition is determined by both the vibrational state lifetime T_{2l} and the pure dephasing time T_{2d}^* for the coupling of the $^1S_0 \rightarrow {}^1F_3$ transition of Ce^{3+} ion to the ballistic motion of the glass.

References

[1] S.H. Kim, T. Yoko, S. Sakka, J. Am. Ceram. Soc. 76 (1993) 2486.
[2] Y. Kowada, K. Morimoto, H. Adachi, M. Tatsumisago, T. Minami, J. Non-Cryst. Solids 196 (1996) 204.

[3] A. Berthereau, E. Fargin, A. Villezusanne, R. Olazcuaga, G.L. Flem, L. Ducasse, J. Solid State Chem. 126 (1996) 143.

[4] R. EI-Mallawany, Mater. Chem. Phys. 53 (1998) 93.

[5] R. EI-Mallawany, A.H. EI-Sayed, M.M.H.A. EI-Gawad, Mater. Chem. Phys. 41 (1995) 87.

[6] D. Zimdars, A. Tokmakoff, S. Chen, S.R. Greenfield, M.D. Fayer, Phys. Rev. Lett. 70 (1993) 2718.

[7] A. Tokmakoff, D. Zimdars, B. Sauter, R.S. Francis, A.S. Kwok, M.D. Fayer, J. Chem. Phys. 101 (1994) 1741.

[8] K.D. Rector, A.S. Kwok, C. Ferrante, A. Tokmakoff, J. Chem. Phys. 106 (1997) 10027.

[9] Y. Tammura, S. Mokamel, J. Chem. Phys. 99 (1995) 9496.

[10] Q.-H. Xu, M.D. Fayer, Laser Phys. 12 (2002) 1104.

[11] K.D. Rector, M.D. Fayer, J. Chem. Phys. 108 (1998) 1794.

[12] Q.-H. Xu, M.D. Fayer, J. Chem. Phys. 117 (2002) 2732.

[13] O. Golonzka, M. Khalil, N. Demirdoven, A. Tokmakoff, J. Chem. Phys. 115 (2001) 10814.

[14] A. Tokmakoff, A.S. Kwok, R.S. Urdahl, R.S. Francis, M.D. Fayer, Chem. Phys. Lett. 234 (1995) 289.

[15] T. Otake, H. Yugami, H. Natio, Solid State Ionics 135 (2000) 663.

[16] H.M. Crosswhile, Phys. Rev. A 4 (1971) 485.

[17] E. Geva, J.L. Skinner, J. Chem. Phys. 108 (1998) 8485.

[18] W.O. Putikka, D.L. Huber, Phys. Rev. B 36 (1987) 3436.

[19] S.J. Zilker, D. Haarer, J. Chem. Phys. 105 (1996) 10648.

[20] R. EI-Mallawany, A.H. EI-Sayed, M.M.H.A. EI-Gawad, Mater. Chem. Phys. 41 (1995) 87.