Homogeneous broadening of absorption lines in ferroelastic crystal $NdGaO_3$ studied by four-wave-mixing spectroscopy

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The Stark-split absorption lines at 585 nm of ferroelastic crystal $NdGaO_3$ are studied by the transient incoherent four-wave-mixing (FWM) spectroscopy at low temperature. It is found that the incoherent FWM signal shows a symmetric time profile, with the envelope modulation due to quantum or polarization beats between the absorption lines, and extremely fast decay on a subpicosecond time scale. The features of the FWM signal in $NdGaO_3$ are explained by a multilevel perturbation theory, assuming that the absorption lines are homogeneously broadened by fast local-field fluctuation originating from the ferroelastic nature of $NdGaO_3$ crystal. [S0163-1829(99)05409-0]

I. INTRODUCTION

Four-wave mixing (FWM) spectroscopy has been extensively employed for the investigations of optical nonlinearity, ultrafast dynamics in various materials.[1,2] In particular, transient FWM is one of most versatile techniques in the time-domain spectroscopy that aims to directly investigate the nature of ultrafast response of material on picosecond and femtosecond time scales.[2] For example, many researchers have applied it to study the carrier dynamics in semiconductors,[3–6] the vibrational wave packet evolution in molecules[7,8] and ultrafast dephasing of chromophore due to the perturbation of the environment.[9] It is well known that the transient FWM signal tends to show the photon echo behavior for the absorption lines predominated by inhomogeneous broadening[10–12] and that the decay of the photon echo signal provides the individual homogeneous linewidth embedded in the inhomogeneous broadening. Therefore, the time profile of transient FWM signal can provide the criterion for the degree of inhomogeneous broadening of an absorption band.

In this paper we present the results of the transient incoherent FWM spectroscopy in a ferroelastic crystal $NdGaO_3$ performed with the time resolution of 0.4 and 0.14 ps. $NdGaO_3$ crystal has recently been used as a promising substrate for the growth of high-temperature superconductor material such as $YBa_2Cu_3O_{7-x}$,[13,14] and reveals the ferroelastic behavior.[15,16] The absorption spectrum of $NdGaO_3$ crystal is known to originate from the electronic transitions of Nd^{3+} ion, and an absorption band at 585 nm consists of several Stark-split sharp lines as shown in Fig. 1. We have found that the incoherent FWM signals for the Stark-split absorption lines at 585 nm show an almost symmetric time profile with respect to the time delay between two excitation pulses, including the signal modulation due to quantum or polarization beats between the lines. We have also found that the FWM signal decays extremely fast with the time constant less than 1 ps even at low temperature. The former fact is an indicative that the linewidth of the absorption lines studied is predominated by the homogeneous broadening, since it is reported that, in an incoherent FWM experiment, the FWM signal shows the symmetric time profile for the homogeneously broadened lines.[10,17] The latter is clearly in contrast to the previous observations for Nd^{3+} doped in host glasses or crystals that, at low temperature, the absorption band at 580 nm provides the long dephasing time up to a few hundred picoseconds,[18–22] corresponding to the long-lived FWM signal. These features of the FWM signal are interpreted by a multilevel perturbation theory assuming that the absorption lines are homogeneously broadened. We consider that the observed fast decay of the FWM signal is attributed to the ferroelastic nature of $NdGaO_3$ crystal in which the atomic position fluctuates randomly among the energetically equivalent positions, resulting in the fast phase modulation of Nd^{3+}.

II. EXPERIMENT

$NdGaO_3$ crystal is a ferroelastic crystal of orthorhombic with space group $Pbnm$. $NdGaO_3$ crystals used in our experiments have the size of $10\times10\times0.25$ (mm^3), whose large plane is cut normal to the (100) direction. The ferroelastic crystal is thought to have several configurations of constituent atoms corresponding to energetically equivalent potential minima and the atomic configuration is wandering randomly among the positions of potential minima.[16] Figure 1 shows linear absorption spectrum of $NdGaO_3$ crystal at 10 K. It is known that the absorption spectrum of $NdGaO_3$ coincides well with that of Nd^{3+}, meaning that optical absorption in $NdGaO_3$ occurs due to transitions between the electronic levels of Nd^{3+} ions.[15,23] The sharp absorption lines around 585 nm, indicated by arrows in Fig. 1(b), are studied by the transient incoherent FWM. The center wavelength, center wave number and absorption intensity of the absorption lines are summarized in Table I.

We perform the transient incoherent FWM spectroscopy by using two-beam excitation geometry. The experimental setup for transient FWM spectroscopy is the same as that used in our previous works.[24,25] Briefly, we employ a dye (Rhodamine B) laser pumped by the second harmonics of Nd^{3+}:YAG(yttrium aluminum garnet) laser as the excitation light source. The output pulses from the dye laser have a duration of 8 ns. The output beam from the dye laser is split into two beams, and one beam is time delayed with respect

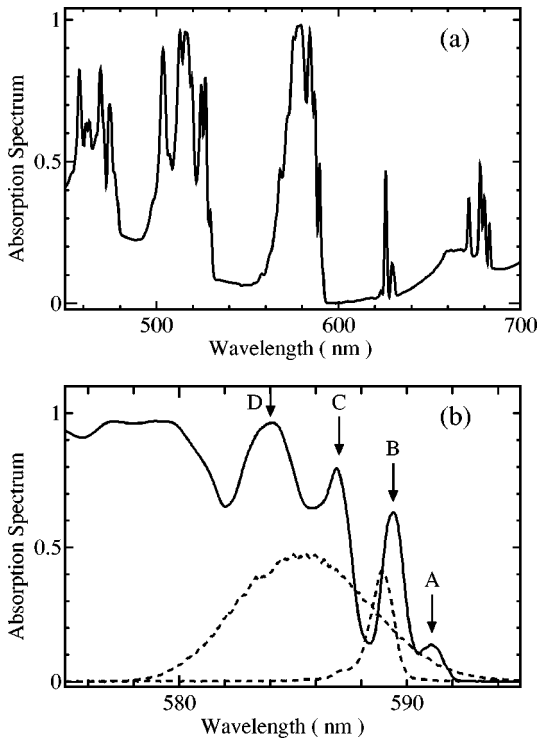

FIG. 1. (a) Absorption spectrum of $NdGaO_3$ crystal at 10 K. (b) Expanded spectrum around 585 nm. Arrows indicate the sharp absorption lines studied. Two dotted lines display the laser spectrum used to excite the sample.

to the other by a stepping-motor-driven corner reflector. After recombined to be parallel, both beams are focused onto $NdGaO_3$ crystal in a cryostat. We detect the time-integrated transient FWM signal emitted in the direction of $2\mathbf{k}_2$-$\mathbf{k}_1$ as a function of time delay τ between the two excitation beams, where $\mathbf{k}_i$ stands for the wave vector of the laser beams at the sample position. The time delay is taken to be positive when the beam $\mathbf{k}_1$ precedes the beam $\mathbf{k}_2$. It is noted that the time resolution of transient FWM in our experiment is not determined by the pulse duration but by the bandwidth of laser light,[10,19,12] since we use an incoherent (in other words, nontransform-limited) dye laser pulse. The time resolution in our experiment is adjusted to be 0.4 or 0.14 ps by changing the bandwidth of the laser with a tuning element in the laser cavity, and the corresponding output spectra of laser are shown in Fig. 1(b) by the dotted lines.

III. RESULTS AND DISCUSSION

Figure 2(a) presents a typical transient incoherent FWM signal in $NdGaO_3$ crystal measured at 10 K and 588.8 nm

TABLE I. Center wavelength, center wave number and absorption intensity (g_i) at 10 K of the sharp absorption lines indicated by arrows in Fig. 1(b).

Absorption line	Wavelength (nm)	Wave number (cm^{-1})	Absorption intensity
A	591.1	16918	0.13
B	589.4	16966	0.58
C	587.1	17033	0.71
D	584.0	17123	1.00

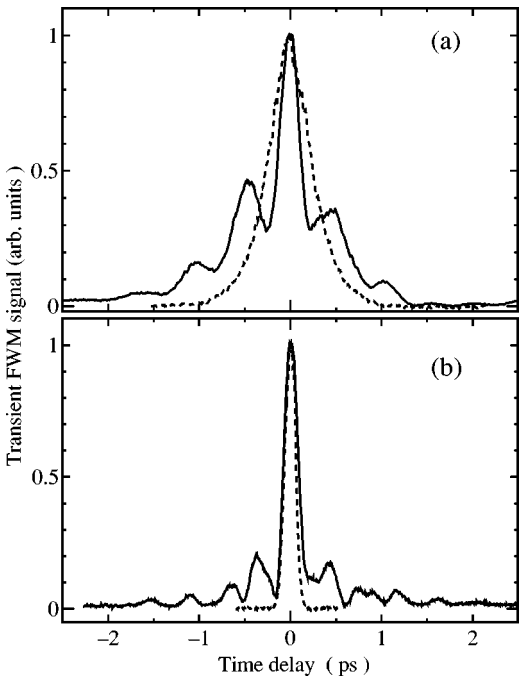

FIG. 2. Transient incoherent FWM signals of $NdGaO_3$ at 10 K measured with (a) the narrowband excitation at 588.8 nm and (b) the broadband excitation at 585.4 nm. The dotted lines represent the autocorrelation of the excitation laser light.

with the time resolution of 0.4 ps (narrowband excitation). The dotted line in Fig. 2(a) displays the autocorrelation of the laser pulse, which was measured with the same experimental configuration in a dye (Cresyl violet)-doped polymer at room temperature. The time resolution of 0.4 ps is derived from this autocorrelation trace. Compared to the autocorrelation trace, we notice two specific features of the transient FWM signal in $NdGaO_3$ crystal. One is the distinct modulation of the signal with a modulation period of about 520 fs, which is quantum or polarization beats between two absorption lines B and C in Fig. 1(b). The modulation frequency agrees well with the frequency difference between the two lines. The other is that the transient FWM signal shows the symmetric decay profile with respect to $\tau=0$, and that it decays fast with a time constant less than 1 ps. A small asymmetry around $\tau=0$ would be due to the imbalance of excitation power between two laser beams. The FWM signal for $|\tau|>1$ ps indicates that the phase information of the laser pulses is stored in the sample for a longer time than the field correlation time. As the time resolution in Fig. 2(a) is comparable to the decay time of the FWM signal, in order to further confirm the features of the FWM signal, we also perform the same FWM experiment by using a much broader excitation bandwidth with the center wavelength of 585.4 nm as shown in Fig. 2(b). In this broadband excitation, the autocorrelation time of laser light was reduced to 0.14 ps as displayed by a dotted line. Whereas the modulation pattern of the FWM signal differs from Fig. 2(a), mainly due to different excitation efficiency of the absorption lines, Fig. 2(b) more clearly gives evidence that the FWM signal is observed for both the negative and positive τ and that the signal decays fast on the subpicosecond time scale.

The specific features of our transient incoherent FWM signals in $NdGaO_3$ crystal described above are basically understood by means of the perturbation theories developed for transient incoherent FWM spectroscopy in two-level[10,12] and

multilevel systems.[17] Both theories conclude that, for the incoherent excitation, a symmetric time profile of the transient FWM signal results from the homogeneous broadening of the absorption lines, i.e., no inhomogeneous broadening. In order to derive the dephasing time T_2 of the absorption lines from the data, we perform numerical calculations based on the theory for the multilevel system developed by X. Mi *et al.*,[17] since it better fits with the absorption line structure around 585 nm of $NdGaO_3$ and can interpret the signal modulation observed in our signals. According to the theory, when the sample is excited by two incoherent laser pulses with the time delay of τ, the intensity $I(\tau)$ of the FWM signal in the direction of $2\mathbf{k}_2$-$\mathbf{k}_1$ from the homogeneously broadened lines is expressed as

$$I(\tau) \propto \left[\int_{-\infty}^{\infty} S_0(\omega) F(\omega) \cos(\omega\tau)\, d\omega \right]^2 + \left[\int_{-\infty}^{\infty} S_0(\omega) F(\omega) \sin(\omega\tau)\, d\omega \right]^2, \quad (1)$$

where $S_0(\omega)$ and $F(\omega)$ stand for the power spectrum of the laser pulse and total absorption spectrum of homogeneously broadened lines at angular frequency ω, respectively. First, we tried to calculate $I(\tau)$ by using the measured absorption spectrum and laser spectrum in Fig. 1(b) as $F(\omega)$ and $S_0(\omega)$. However, the calculated results failed to reproduce the observed FWM signals for both the narrowband and broadband excitation, since they showed much faster decay compared to the observed signals. It is probably because the resolution of 0.2 nm in the spectrum measurement made the measured linewidth broader than the true one that is estimated to be about 0.5 nm from the numerical simulation below. Then, we assume that $F(\omega)$ is a sum of four homogeneously broadened lines A, B, C, and D,

$$F(\omega) = \sum_{i=\mathrm{A}}^{\mathrm{D}} \frac{g_i}{(\omega - \omega_i)^2 + 1/T_{2i}^2}, \quad (2)$$

where Lorentzian line shape is employed with the center frequency ω_i, dephasing time T_{2i}, and absorption intensity g_i. We neglect the contribution from the absorption spectrum shorter than 582 nm, since the sharp absorption line is not observable. In the numerical calculation, the measured values listed in Table I are used for ω_i and g_i, respectively. Therefore, the dephasing time T_{2i} is only the fitting parameters in our numerical simulation.

Figure 3 shows the results of numerical simulations of the transient FWM signals for the narrowband and broadband excitation by using Eqs. (1), (2) and laser spectrum $S_0(\omega)$ as shown in Fig. 1(b). Also shown by the dotted lines are the calculated autocorrelation traces of laser expected from $S_0(\omega)$. It is noted that the theory employed here solely gives a symmetric time profile of transient FWM signal and cannot explain the asymmetry in the observed signals. Nevertheless, the numerical simulation is effective in estimating the dephasing times from the observed signal in $NdGaO_3$, since the symmetric time profile is a predominant feature of the signals. In the narrowband excitation of Fig. 3(a), the simulation is fairly in good agreement with the observed signal with simply assuming that all four absorption lines have the same value of $T_{2i}=0.8$ ps. As, in this case, the absorption lines B and C make the dominant contribution to the signal, the value of $T_{2i}=0.8$ ps corresponds to the dephasing time of the two lines. In the broadband excitation of Fig. 3(b), reasonable agreement with the observed signal is obtained with the values of $T_{2A}=T_{2B}=T_{2C}=0.8$ ps and $T_{2D}=0.5$ ps. The shorter dephasing time of line D seems convincing, by considering that line D shows a broader linewidth than other lines [see Fig. 1(b)]. It means that line D is more sensitive to the fluctuation of the environment.

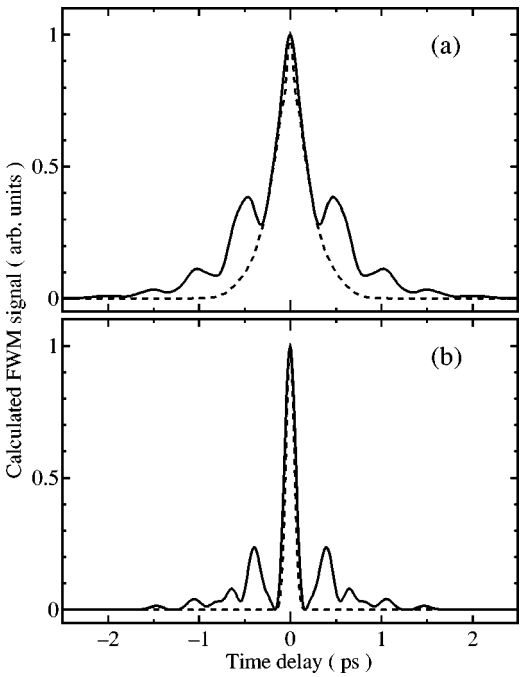

FIG. 3. Numerical simulations of the FWM signals for (a) the narrowband and (b) the broadband excitation. The dotted lines display the calculated autocorrelation traces of the laser pulse.

It should be noted that in the above modeling the signal modulation emerges as a result of the polarization beats between the independent absorption lines. Though we believe the observed signal modulation involves the effect of quantum beats from the coherence between the excited levels of the absorption lines, it is difficult to distinguish between the polarization and quantum beats in our experiments.

The simulations described above better agree with the observed signals for negative time delay, but do not interpret the complete time profiles of the observed FWM signals, especially the asymmetry in the signals. The asymmetry is more evident in Fig. 2(b) than in Fig. 2(a). In order to explain the asymmetry, it would be necessary to take into account transient effects neglected in the theory and the inhomogeneous broadening of line D comparable to the homogeneous broadening. In addition, for the broadband excitation, the contribution of the absorption spectrum shorter than 582 nm may be another reason for the asymmetry. Nevertheless, the simulations definitely indicate that the absorption lines studied have subpicosecond dephasing times even at low temperature and that the lines A, B, C are homogeneously broadened. This finding makes significant contrast to the long dephasing time measured for the absorption band at 580 nm of Nd^{3+} ions at low temperature doped in hosts,[18–22] which amounts to a few hundreds picosecond in glasses and

crystals. We attribute the homogeneous broadening and fast dephasing of absorption lines to the ferroelasticity of the $NdGaO_3$ crystal. As a result of the ferroelasticity, the atomic positions in $NdGaO_3$ crystal fluctuate randomly among the configurations corresponding to the potential minima even at low temperature, resulting in the fast phase modulation of Nd^{3+}. From the dephasing time obtained, we expect the fluctuation rate of the atomic positions is still very fast at low temperature. It would be very interesting to study the temperature dependence of the fluctuation rate by observing the transient FWM signal at different temperatures, but it is a subject for further study.

IV. CONCLUSION

We have performed the transient incoherent FWM spectroscopy for the absorption lines around 585 nm in the $NdGaO_3$ crystal. From the time profile of the FWM signals, the absorption lines are concluded to be homogeneously broadened and their dephasing time is derived to be 0.8 and 0.5 ps at 10 K by the numerical simulation based on the multilevel perturbation theory. Our analysis definitely demonstrates extraordinarily fast dephasing in $NdGaO_3$ and we ascribe its origin to the ferroelasticity of $NdGaO_3$ at low temperature.

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