Picosecond excite-and-probe absorption measurement of the intra-$^2E_g E_{3/2}$-state vibrational relaxation time in Ti$^{3+}$:Al$_2$O$_3$

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The kinetics of vibrational transitions in the $^2E_g E_{3/2}$ electronic state of Ti$^{3+}$:Al$_2$O$_3$ is studied by exciting higher lying vibrational levels of the state by a 527-nm picosecond pump pulse, and monitoring the subsequent growth of population in the zero vibrational level and lower lying vibrational levels by a 3.9-$\mu$m picosecond probe pulse. An upper limit of 3.5 ps for intra-$^2E_g E_{3/2}$-state vibrational relaxation time is estimated.

Recently, the trivalent titanium-ion-doped sapphire (Ti$^{3+}$:Al$_2$O$_3$) has been demonstrated to be a tunable solid-state laser system with Ti$^{3+}$ as the laser-active ion. A simple energy-level structure, broader tuning range, higher gain cross section, and the lack of any significant excited-state absorption (ESA) make Ti$^{3+}$:Al$_2$O$_3$ even a more promising tunable laser crystal than such chromium-based systems as alexandrite, GGG, and emerald. This potential has stimulated the recent interest in developing low-loss high-quality crystals of Ti$^{3+}$:Al$_2$O$_3$, and in investigating its spectroscopic and laser properties. To our knowledge, there has been little effort to investigate the nonradiative relaxation processes and the kinetics of vibrational transitions in this crystal. Knowledge of these processes is crucial not only for understanding the physics behind tunable solid-state lasers, but also for characterizing new host materials for the Ti$^{3+}$ ion. In this letter, we present the first picosecond time-resolved measurement of the relaxation kinetics among the vibrational levels of the lasing state in Ti$^{3+}$:Al$_2$O$_3$.

The single optically active 3$d^1$ electron outside the closed argon core of Ti$^{3+}$ determines the optical and spectroscopic properties of Ti$^{3+}$:Al$_2$O$_3$. The Ti$^{3+}$ ion substitutes for octahedrally coordinated Al$^{3+}$ in Al$_2$O$_3$ at sites with trigonal symmetry. As shown in Fig. 1(a) the cubic component of the crystal field (CF) splits the free-ion $^2D$ term of Ti$^{3+}$ into a fourfold degenerate upper $^2E_g$ and a sixfold degenerate lower $^2T_{2g}$ manifold with an energy separation of 19,000 cm$^{-1}$. These two manifolds are further split by the trigonal component of the CF, the spin-orbit interaction, and the dynamic Jahn–Teller (JT) interaction into five Kramers doublets.

The optical absorption spectrum of Ti$^{3+}$:Al$_2$O$_3$ is characterized by a double-humped absorption band spanning 400–600 nm, and is due to transitions from the ground $^2T_{2g}$ to the JT coupling-split $^2E_g E_{3/2}$ and $^2E_g E_{1/2}$ states. The broadband fluorescence spectrum covers the range 600–1050 nm at room temperature and originates in vibronic transitions from the $^2E_g E_{3/2}$ state to the states of the $^2T_{2g}$ manifold. The vibronic four-level mode of laser action in Ti$^{3+}$:Al$_2$O$_3$ at room temperature is tunable over the 660–986 nm continuous range of this fluorescence band. The absorption band in the blue-green region of the spectrum serves as the laser pump band. Because of the strong phonon coupling and the dynamic Jahn–Teller interaction, extremely rapid nonradiative relaxation follows resulting in population in the zero vibrational level (ZVL) and lower lying vibrational (LLV) levels of the $^2E_g E_{3/2}$ state.

The kinetic of these intra-$^2E_g E_{3/2}$ vibrational transitions has been investigated in our study. A 5-ps, 527-nm pulse excites a band of higher lying vibrational (HLV) levels of the $^2E_g E_{3/2}$ state and the subsequent growth of population in the ZVL and LLV levels is monitored by a 3.9-$\mu$m infrared probe pulse. Infrared transmission measurements are used to select this probe wavelength such that there is little ground-state probe absorption. The probe transition terminates on the HLV levels of the $^2E_g E_{3/2}$ and $^2E_g E_{3/2}$ states. The pump, probe, and relaxation transitions are shown schematically in the simplified configurational coordinate diagram in Fig. 1(b). The underlying assumption here is that the 3.9-$\mu$m probe pulse investigates the relaxed excited state population. Although the possibility of pumped HLV levels absorbing 3.9 $\mu$m photons and making transitions to still higher vibrational levels may not be completely ruled out, such transitions will terminate on the high-energy end of the $^2E_g E_{3/2}$ band. The Franck–Condon overlap integrals for such transitions are expected to be small, and hence contribution to 3.9-$\mu$m probe absorption due to such transitions may be neglected. Under this assumption, the kinetics of the vibrational transitions is studied by measuring the change in the induced absorption of the probe pulse as a function of the pump-probe delay time. Details of a similar experimental arrangement, detection scheme, signal averaging, and processing technique have been reported elsewhere.

The Czochralski-grown Ti$^{3+}$:Al$_2$O$_3$ sample used in this experiment was obtained from the Electronics Division of Union Carbide Corp. The sample is a rectangular parallelepiped 22.5 mm x 10 mm x 9 mm in dimension and contains 0.12 at. % of Ti$^{3+}$. The induced absorption measurements were taken along the 9-mm path length of the sample. The radii of the pump and probe pulses at the sample position were 0.6 mm and 0.5 mm, respectively, and the pulses were made to cross the sample almost collinearly (a crossing angle of 2°).

The result of the present picosecond excite-and-probe measurement in Ti$^{3+}$:Al$_2$O$_3$ showing the time evolution of the optical density (OD) at 3.9 $\mu$m in the excited $^2E_g E_{3/2}$ state at room temperature is shown in Fig. 2. The curve is characterized by a sharp rise followed by a long decay. The
long lifetime decay reflects the depopulation of the zero and lower lying vibrational levels of the \( ^2E_g \) state via radiative transitions. Since the room-temperature fluorescence lifetime is \( 3.15 \pm 0.5 \mu s \), there is no appreciable change in the population over the time scale of this measurement.

The rise time (time for growth of OD from 10 to 90 \%\) is \( 9 \) ps. In order to account for the group dispersion effects, the transit times for both the 527-nm pump pulse and the 3.9-\( \mu \)m probe pulse through the 9-mm sample path were calculated using the dispersion characteristics of sapphire.\(^{15}\) The two transit times differ by 1.5 ps, which is the upper limit for uncertainty in the rise time from group dispersion effects. In order to extract a value for the vibrational relaxation time, we use a rate-equation analysis of the experimental data. The rate equations governing the population kinetics in the \( ^2E_g \) state are

\[
\frac{dN_2}{dt} = -k_{1R}N_2 + \alpha LP(t) ,
\]

\[
\frac{dN_1}{dt} = k_{1R}N_2 - k_RN_1 .
\]

where \( N_1(t) \) is the instantaneous population density in the ZVL and LLV levels and \( N_2(t) \) is the instantaneous population density in the pumped HLV levels of the \( ^2E_g \) state. \( k_{1R} \) and \( k_R \) are the vibrational and radiative relaxation rates, \( P(t) \) is the pump-photon flux density, \( \alpha \) is the ground-state absorption coefficient for the pump pulse, and \( L \) is the length of the sample. Equation (1) assumes \( \alpha L \ll 1 \). The rate equations were solved numerically using the fourth-order Runge-Kutta method,\(^{16}\) and the profile of the pump pulse was taken as a Gaussian\(^{17}\) of 5-ps FWHM.

The measured change in the optical absorption of the probe pulse at a particular delay time \( t_d \) is given in terms of \( N_1(t) \) by

\[
\text{OD}(t_d) = -\ln \left[ \int_0^{t_d} I(t - t_d) \exp \left[ -\sigma L N_1(t) \right] dt \right] .
\]

where \( I(t) \) is the intensity and \( \sigma \) is the excited state absorption cross section of the probe pulse, respectively. A fit of the experimental data to Eq. (3) assuming a Gaussian probe pulse of estimated 3.5 \( \pm 0.5 \) ps FWHM and using \( k_{1R} \) as a variable parameter is displayed in Fig. 2. The excited state absorption cross section \( \sigma \) is estimated from the measured optical density at much larger delay times (flat region of the curve) to be \( \approx 4 \times 10^{-18} \) cm\(^2\).

The best fit to the experimental data yields a value of 2.0 \( \pm 1.5 \) ps for the intra-\( ^2E_g \) relaxation time \( k_{1R} \) in \( \text{Ti}^{3+}:\text{Al}_2\text{O}_3 \). However, \( k_{1R} \) is less than 3.5 ps even at the extreme limit of the experimental signal-to-noise ratio. Since the observed system response is smaller than the widths of the pump and probe pulses, its precise determination depends strongly on the accurate knowledge of the duration of those pulses. The estimated group dispersion effect, though small, would cause a broadening of the rising edge of the probe absorption curve. Since all these factors contribute to an overestimation of the system response, we take 3.5 ps to be an upper limit for the intra-\( ^2E_g \) relaxation rate in \( \text{Ti}^{3+}:\text{Al}_2\text{O}_3 \). This time is much shorter than 17 ps obtained for the intra-\( ^1T_2 \) relaxation time in alexandrite,\(^{19}\) but may be comparable to vibrational relaxation times in organic molecules like fluorescein, naphthalene, parabenzquinone, rhodamine dyes, etc.\(^{20}\)

Since there is a single phonon of energy 173 cm\(^{-1}\) that interacts with the excited \( ^2E_g \) state of \( \text{Ti}^{3+}:\text{Al}_2\text{O}_3 \), a rough estimate of the "effective phonon emission time" in the \( ^2E_g \) state of this system may be made. The energy degra-
A detailed understanding of these mechanisms presents an interesting problem for further theoretical and experimental investigations.

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