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Femtosecond relaxation in Ce^{3+} ions in LiCaAlF_6 and LiSrAlF_6

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Abstract

Using femtosecond pump pulses at 266 nm and probe pulses at 292 nm we studied the temporal onset of the gain after excitation in Ce^{3+} -doped LiCaAlF_6 and LiSrAlF_6 and estimated <500 fs fast relaxation within the ${}^2\text{T}_{2g} [{}^2\text{D}(5d^1)]$ upper electronic state. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tunable ultraviolet laser oscillation and amplification have been demonstrated in Ce^{3+} -doped LiCaAlF_6 (Ce:LiCAF) [1,2] and LiSrAlF_6 (Ce:LiSAF) [2] crystals. Attempts to generate directly short ultraviolet pulses have also been reported [3] but only sub-nanosecond durations could be achieved. The gain spectra of Ce:LiSAF and Ce:LiCAF at 280–320 nm ($>4000 \text{ cm}^{-1}$) are, however, very broad and could support sub-100 fs pulse durations. They are characteristic of the $\text{Ce}^{3+} 5d^1-4f^1$ interconfigurational transition [2]. The lowest ${}^2\text{F}$ energy state of Ce^{3+} has a single $4f$ electron. The spatially diffuse $5d$ electron orbital extends outwards from the ion and the optical spectra of Ce^{3+} depend strongly on the crystal field splitting of the ${}^2\text{D}$ free-ion excited state. In YAG where the separation of the five levels belonging to ${}^2\text{D}$ is relatively large [4], fast relaxation between the lowest two levels has been observed [5,6], but the methods used (excited state absorption, growth of the yellow–green or decay of the UV emission) employed 60-ps pulses which allowed only an upper (and inaccurate) limit of 5 ± 5 ps to be estimated. In Ce:LiSAF and Ce:LiCAF the ${}^2\text{D}$ splitting is much smaller [4], and cannot be seen in the absorption spectra at room temperature.

The estimation of the relaxation time in the excited state is important for development of new techniques for extracting ultrashort light pulses from Ce:LiSAF and Ce:LiCAF lasers. Using femtosecond pulses and pump and probe technique we observed ultrafast (<500 fs) relaxation in ${}^2\text{D}$ in Ce:LiSAF and Ce:LiCAF. In the present work we studied the temporal evolution of the gain of a weak probe pulse by the stimulated emission process where the population inversion was achieved by an intense femtosecond pump pulse.

2. Absorption and emission bands due to Ce^{3+} ions

Absorption bands due to the transitions from the ${}^2\text{F}_{5/2}$ ground state to the five levels of the ${}^2\text{D}$ state in Ce:LiCAF at 17 K are observed at 276, 270, 262, 243 and 201 nm (Fig. 1), respectively [7]. Two emission bands, which have peaks at 290 and 312 nm at room temperature, are generated by the excitation into these absorption bands [2,7]. The 290 and 312 nm emission bands are due to the transitions from the lowest level d_1 of ${}^2\text{D}(5d^1)$ to the ${}^2\text{F}_{5/2}$ ground state and the ${}^2\text{F}_{7/2}$ state, respectively. Unpolarized absorption and emission spectra under 266 nm excitation for our samples of Ce:LiCAF and Ce:LiSAF are shown in Fig. 2. We measured the lifetime of the 290 nm emission band in Ce:LiCAF, which was excited with 266 nm radiation from the fourth harmonic of a Q-switched Nd:YAG laser, using a streak camera and estimated it to be 26 ns at room temperature. The excitation with 266 nm radiation corresponds to transition to the d_2 level belong-

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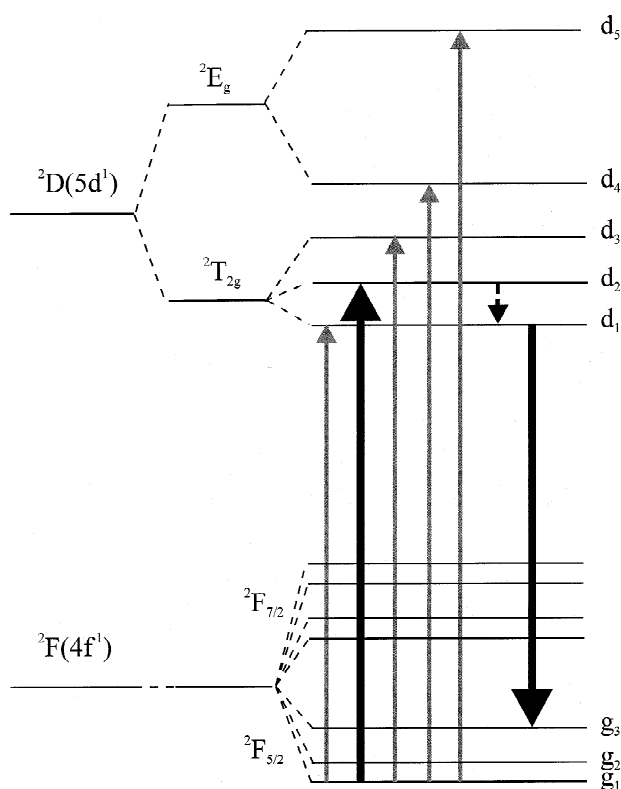


Fig. 1. A schematic energy level diagram of the Ce^{3+} ion in LiCAF in trigonal distortion [7]. The transitions related with pumping with a π -polarized 266 nm pulse and amplification of a π -polarized 292 nm probe are shown by thick vertical arrows.

ing to the ${}^2T_{2g}$ state of ${}^2D(5d^1)$. The obtained lifetime is consistent with the previously reported one (25 ns) [2]. The same result was obtained for the 312 nm emission band. This confirms that the two emission bands are due to transitions from the same excited level. Similar lifetime was obtained previously for Ce:LiSAF [2].

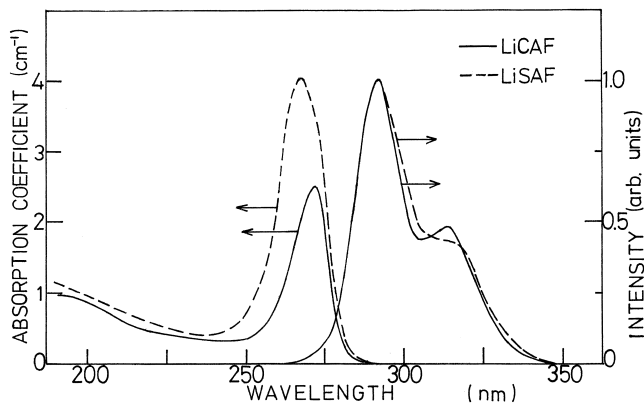


Fig. 2. Absorption and emission spectra of Ce^{3+} ions in LiCAF and LiSAF crystals at room temperature. The emission spectra were obtained by excitation with 266 nm radiation.

3. Experimental procedure

Single crystals of Ce:LiCAF were grown by the Czochralski method using a resistive heater made of high-purity graphite. A stoichiometric charge composed of commercially available high-purity (>99.99%) AlF_3 , CaF_2 and LiF was used as the starting material. The composition was 1 mol.% LiF and AlF_3 . As dopants, CeF_3 and NaF powders of high purity (>99.99%, Rare Metallic Co. Ltd.) were used. Na^+ was co-doped with Ce^{3+} in order to maintain the charge neutrality. The concentration of Ce^{3+} and Na^+ in the starting material was 1 mol%. Growth orientation was controlled by using a -axis oriented Cr^{3+} -doped LiCAF seed crystals. The pulling rate was 1 mm/h and the rotation rate was 10 rpm. The charges were loaded in $40 \times 40 \text{ mm}^2$ glassy carbon crucibles. In order to eliminate water and/or oxygen from the growth chamber, a vacuum treatment was performed before the growth. After the vacuum treatment, the furnace was flushed with argon and the material was melted at 825°C . To prevent severe cracking of the boules, the furnace was cooled at a rate of $25^\circ\text{C}/\text{h}$. Similar method was used for the growth of Ce:LiSAF crystals.

Ce:LiCAF and Ce:LiSAF single crystals with dimensions of 18 mm in diameter and 60 mm in length have been grown. Cracks, bubbles and inclusions were not observed. Under the modified growth conditions, foreign substances on the surface of the grown crystal were not formed. However, Ce:LiSAF showed a tendency to crack perpendicular to the growth axis after several days. On the contrary, Ce:LiCAF did not show cracks at any time. The effective distribution coefficient (k_{eff}) of Ce^{3+} in LiCAF and LiSAF has been determined to be 0.021 and 0.013, respectively. The k_{eff} of Ce^{3+} in LiCAF was larger than in LiSAF. This is because the ionic radius of Ce^{3+} under 6-fold coordination (0.101 nm) is closer to that of Ca^{2+} (0.100 nm) than to that of Sr^{2+} (0.118 nm), which are supposed to be replaced by Ce^{3+} [8].

The experimental set-up for the femtosecond pump and probe spectroscopy is shown schematically in Fig. 3. The set-up is similar to that described previously [9]. We used pump pulses at 266 nm (typical energy 7 μJ) produced at the third harmonic from the 100-fs output pulses of a femtosecond Ti:sapphire regenerative amplifier tuned to 798 nm. Probe pulses at 292 nm were produced by frequency doubling in a 0.3 mm thin BBO crystal of the second harmonic of the 1168 nm signal pulse available from a near-IR optical parametric generator (OPG) pumped by the same Ti:sapphire regenerative amplifier. All up-conversion stages (second and third harmonic generation) reverse the polarization because type-I BBO crystals were used everywhere. On the contrary in the OPG type-II BBO is used and the signal (idler) emerging are polarized perpendicularly (parallel) to the 798 nm pump. Thus the idler could be eliminated simply by a polarizer.

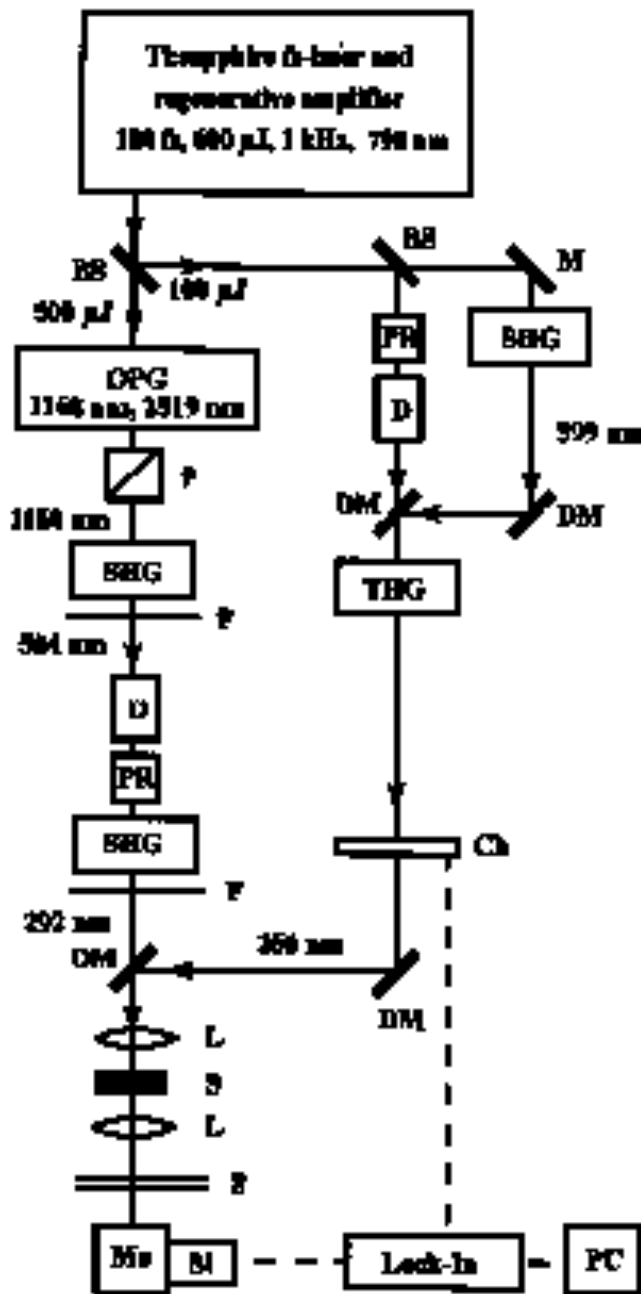


Fig. 3. Experimental set-up for the femtosecond pump and probe spectroscopy which is used in the present study. OPG, near-IR optical parametric generator; BS, beam splitter; DM, dichroic mirror; M, mirror; PR, polarisation rotator; P, polarizer; SHG, second harmonic generator; THG, third harmonic generator; Si, UV-enhanced silicon photodiode; D, delay line; S, sample; Ch, chopper; Mo, monochromator; Lock-In, lock-in amplifier; PC, personal computer; L, lens; F, filter.

Finally the polarization of the pump pulse at 266 nm and the probe pulse at 292 nm incident on the Ce:LiCAF and Ce:LiSAF samples is parallel. The zero delay point was determined by sum frequency generation of 216.7 nm light mixing the 266 nm pump and the 1168 nm signal pulse (after proper polarization adjustment) in a 0.1 mm thick type-I BBO crystal.

We used π -polarizations for maximum efficiency [2],

and both the 1.3-mm thick Ce:LiSAF and the 3.3-mm thick Ce:LiCAF samples absorbed about 30% at 266 nm (Fig. 2). The difference in the transmission of the probe beam through the pumped and unpumped samples at room temperature was measured as a function of the pump-probe delay with lock-in-modulation and averaging technique. Spectral selection was performed using an interference filter, a WG6 colour glass filter and a 0.2-m monochromator, however, both slits of the monochromator were 1-mm wide in order to suppress Kerr-type intensity dependent artifacts apparent when the two pulses were superimposed in time that had the character of induced spatial and spectral distortion of the probe beam. For the same purpose we had to operate away from the focus of the 10-cm CaF_2 lens used, at $<6 \text{ mJ/cm}^2$ pump fluence, and intentionally lengthen the pump pulses to about 600 fs by use of relatively long crystals of 2-mm and 1-mm for the frequency doubling and tripling in the THG arm (Fig. 3), respectively. The overall temporal resolution was thus determined by the length of the pump pulses since both the probe pulses and the group velocity mismatch (12 fs/mm in LiSAF and 17.6 fs/mm in LiCAF for extraordinary polarized light) were much shorter.

4. Experimental results and discussion

In both Ce:LiSAF and Ce:LiCAF we observed rise times of the gain of the order of our temporal resolution and conclude after deconvolution that the relaxation in the 2D state proceeds in a time less than 500 fs. We associate the excitation in our case with transition from the lowest g_1 level of the $^2F_{5/2}$ ground state to the d_2 level belonging to the $^2T_{2g}$ state of $^2D(5d^1)$ in trigonal distortion by the crystal field including spin-orbit interaction (see Fig. 1), which is widely used for pumping such lasers by the fourth harmonic of Nd:YAG lasers. The relaxation is to the lowest d_1 metastable level of the $^2T_{2g}$ state, which is an upper laser level. The observed amplification of the 292 nm probe pulse is related to the π -polarized 290 nm emission band (Fig. 2) corresponding to the transition from the d_1 level to the g_3 level of the $^2F_{5/2}$ state (Fig. 1).

As seen in Fig. 4, the rise time of the gain is about 600 fs in Ce:LiCAF and 800 fs in Ce:LiSAF. On the other hand, as mentioned in the introduction the relaxation from the d_2 level to the d_1 level in Ce:YAG proceeds on the picosecond time scale at room temperature [5,6]. This means that using the same excitation route, the nonradiative relaxation time to reach the metastable level d_1 from the optically excited d_2 level is shorter in LiCAF and LiSAF than in YAG.

The energy separation between the d_1 and d_2 levels of Ce^{3+} is approximately 7500 cm^{-1} in YAG, while the same separation amounts to about 860 cm^{-1} in LiCAF. The phonon energy in YAG is 480 cm^{-1} [10]. It is known that the phonon energy is larger in oxides such as YAG than in fluorides such as LiCAF. The phonon energy in LiCAF

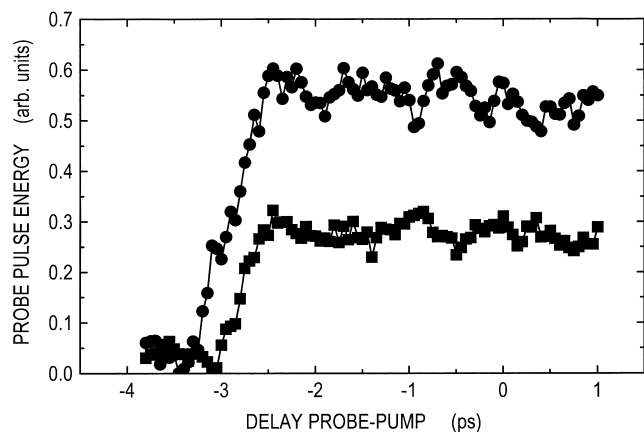


Fig. 4. Delay dependent amplification of a probe pulse at 292 nm in Ce:LiSAF (circles) and Ce:LiCAF (squares) after excitation with a 266 nm pump pulse. The onset of the gain appears at negative delays since the zero delay was experimentally determined from the coincidence of the pump pulse and the signal pulse (at 1168 nm) from the OPG. The artifact is still present in Ce:LiCAF near -3 ps.

can be estimated from the vibronic structure of the Ce^{3+} absorption spectra. From the separation between the one- and zero-phonon lines [5,6], we obtained about 104 cm^{-1} . Therefore it is suggested that the difference of the separation between the optically excited level d_2 and the metastable level d_1 in combination with the different phonon energy is responsible for the faster gain rise time in LiCAF and LiSAF than in YAG because the relaxation in the excited state is attributed to multiphonon nonradiative transitions.

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