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Resonance laser-plasma excitation of coherent terahertz phonons in the bulk of fluorine-bearing crystals under high-intensity femtosecond laser irradiation

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Abstract. **The dynamics of coherent phonons in fluorine-containing crystals was investigated by pump-probe technique in the plasma production regime. Several phonon modes, whose frequencies are overtones of the 0.38-THz fundamental frequency, were simultaneously observed in a lithium fluoride crystal. Phonons with frequencies of 1 and 0.1 THz were discovered in a calcium fluoride crystal and coherent phonons with frequencies of 1 THz and 67 GHz were observed in a barium fluoride crystal. Furthermore, in the latter case the amplitudes of phonon mode oscillations were found to significantly increase 15 ps after laser irradiation.**

Keywords: *femtosecond laser-produced microplasma, third harmonic generation, coherent phonons.*

1. Introduction

The range of phenomena occurring in the interaction of tightly focused femtosecond laser radiation with dielectrics is rather broad: from multiphoton and tunnel ionisation, plasma electron heating in the laser field, collisional ionisation and coherent phonon excitation to shock wave propagation and formation of residual micromodifications [1 – 7]. Special emphasis should be placed on the dynamics of coherent phonons. Not only do they provide information about the vibrational spectra of substances, but they also can be employed for controlling molecular and collective motion, obtaining special nonequilibrium states, and facilitating chemical or structural changes which may not take place under ordinary conditions [8, 9]. To describe coherent phonon dynamics, one can commonly use displacive excitation of coherent phonons (DECP), time-dependent density functional theory, and the mechanism of impulsive stimulated Raman scattering (ISRS) [10 – 18].

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The methods of registering coherent phonons may be divided into two main classes. The first class comprises those methods which involve measurements of the changes in optical material properties; the second one encompasses those methods which rely on time-resolved measurements of the parameters of the terahertz radiation generated by IR active phonons. To observe coherent phonons, pump-probe techniques with the recording of transmitted, reflected, or diffracted laser radiation are often used. For intensities of exciting laser radiation not exceeding the ionisation threshold of the material, the probe pulse signal will contain oscillations on the excited phonon mode frequenc [14, 15].

In the present work the dynamics of coherent phonons is investigated under extreme conditions (the intensity of laser radiation is $\sim 10^{13}$ W cm^{-2}, which exceeds the ionisation threshold of condensed matter) of target irradiation whereby a nonequilibrium electron microplasma is formed in the volume of a dielectric. For these purposes, advantage is taken of our previously developed nonlinear-optical technique for time-resolved probing of the bulk of a medium based on third harmonic generation in focused laser beams [19 – 23]. The generation of coherent phonons results in the temporal modulation of the cubic nonlinear susceptibility of the medium. That is why the energy of the third harmonic, which is generated in the interaction region and recorded in the experiment, will also be modulated in time with coherent phonons in the medium. This technique was used in the investigations of laser plasma dynamics in crystalline and fused quartz. We emphasise that the third harmonic signal is more sensitive to variations in a substance structure (ionisation of the medium, ion vibrations) than the signal transmitted through the sample, which was demonstrated in Refs [19 – 23]. To record coherent phonons in the probe pulse technique, an additional channel was added for recording the energy of the third harmonic generated by a probe pulse in the region of lattice vibrations [23 – 25].

The subject of our work is an investigation of the mechanisms of excitation and relaxation of coherent phonons in the regime of laser microplasma production in the volume of crystalline fluorine-containing dielectrics LiF, CaF_2, and BaF_2. In the experiments demonstrated here, all crystals were oriented in such a way that the well-known phonon vibrations at the Raman-active mode of T_{2g} symmetry were missing from the output and third harmonic signals. A distinguishing feature of the media under consideration in comparison with crystalline quartz, which was investigated in our earlier work, is the absence of 'soft' phonon modes and low-temperature phase transitions.

2. Experiment

In our experiments we employed the radiation of a Cr : forsterite femtosecond laser system ($\lambda = 1.24$ μm, $\tau = 140$ fs, $E = 01$-5 μJ, intensity contrast ratio ~250). The use of near-IR radiation broadens the potentialities of the pump-probe technique, because the third radiation harmonic falls into the transparent region of a large number of media. A schematic of the experiment is sketched in Fig. 1. A $\lambda/2$ plate with a Glan prism (*1*) was used to smoothly vary the energy of laser radiation from 0.1 to 5 μJ. The radiation was next coupled to a Michelson interferometer, a beam splitter (*2*) to guide radiation in equal portions to the probe and exciting channels. A neutral density filter (*3*) attenuated the radiation in the probe channel. The radiation of the probe and pump pulses with orthogonal polarisations was tightly focused into the bulk of a crystalline dielectric (LiF, CaF_2, BaF_2) (*8*) using a Philips CAY033 lens. The radiation of the probe channel was polarisation separated from the fundamental one with the use of a Glan prism (*1*). In the experiment we simultaneously measured the energies of the incident and transmitted through the sample probe pulses using germanium photodetectors (*4*), as well as the energy of the third harmonic of the probe radiation using a PMT (*6*) operating in a current mode; a band filter ($\lambda = 410 \pm 5$ nm) (*5*) was placed in front of the PMT. The pump and probe pulse energies were selected to respectively be above and below the plasma formation threshold in the crystalline dielectric. The sample was shifted in the plane perpendicular to the direction of laser radiation propagation at 20-μm increments with the use of a motorised translation stage, so that we realised a single-pulse regime of laser radiation interaction with the target material. The time delay between the pump and probe pulses was varied in the probe channel of the Michelson interferometer by automated mirror translation at 2.5-μm increments (8.3 fs) in the 0–300 ps range.

3. Results

All crystals investigated in our work belong to the Fm–3m group and are of O_h symmetry. Under this symmetry type the possible normal vibrational symmetries are A_{1g}, A_{1u}, A_{2g}, A_{2u}, E_u, E_g, T_u, T_g, T_{2u} and T_{2g} [26]. Coherent phonons are generated by Raman-active modes. These are modes of symmetries A_{1g}, E_g and T_{2g} for the crystals involved. For the A_{1g} vibrations the Raman tensor is completely symmetrical; the E_g and T_{2g} vibrations are doubly and triply degenerate, respectively [26]. The corresponding tensors are given in Table 1.

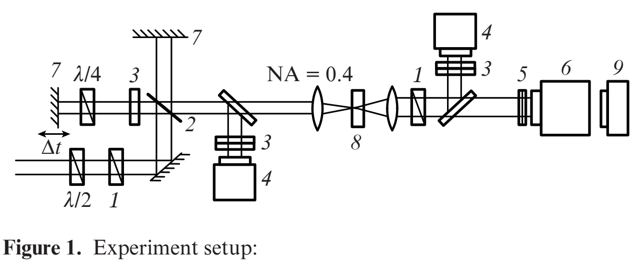

Figure 1. Experiment setup:
(*1*) Glan prisms; (*2*) 50/50 beam splitter; (*3*) neutral density filters; (*4*) Thorlabs PDA50B-EC germanium photodetectors; (*5*) band filter (410 ± 5 nm); (*6*) Hamamatsu H5784-04 PM; (*7*) silver mirrors; (*8*) sample under investigation; (*9*) CCD camera.

To determine the plasma formation threshold in fluorine-containing crystals, in the experiments we recorded the fundamental radiation and third harmonic energies transmitted through the sample as a function of the laser pulse energy (Fig. 2). For experiments with temporal resolution, the pump and probe pulse energies were taken to be respectively above and below the plasma formation threshold. For crystalline BaF_2, the ionisation thresholds E_1 and E_2 determined from the third harmonic and nonlinear absorption signals were equal to 1 and 1.1 μJ, respectively (Fig. 2a); for crystalline CaF_2, the thresholds $E_1 = 0.8$ μJ and $E_2 = 1.1$ μJ (Fig. 2b); for crystalline LiF, $E_1 = 2.5$ μJ and $E_2 = 3.5$ μJ (Fig. 2c).

To investigate the energy transfer from the laser-driven plasma produced in the bulk of the fluorine-bearing crystals to the phonon subsystem, experiments were performed for different pump pulse energies. We simultaneously recorded the transmittance and third harmonic signals of the probe pulse as a function of time delay relative to the pump one (Fig. 3). Since the third harmonic signal is more sensitive to variations of the substance properties, hereinafter in Figs 4–6 the time dependence of the transmission signal at the wavelength of exciting radiation is not given.

3.1. BaF_2 crystal

In the third-harmonic signal of the probe pulse the coherent oscillations of different phonon modes are observed. A spectral analysis of this signal confirms that it contains two quasiharmonic components with constant frequencies Ω = 1 THz and ~67 GHz (the uncertainty is equal to 20 GHz in the evaluation from the spectrum) (Fig. 4), which correspond to Raman shifts of 33 cm^{-1} [27] and 2.1 cm^{-1} [28] observed in crystalline BaF_2. The absence of the T_{2g} mode at a frequency of 241 cm^{-1} [29] is due to the crystal orientation, because the driven force $F = \Sigma_{uv}(\partial\chi_{uv}/\partial Q)E_uE_v$ ($E_{u,v}$ are components of the optical pump, Q is the normal coordinate, and χ_{uv} is the nonlinear susceptibility [15]) and the tensor of Raman scattering has only two nonzero components. Then, the integral

$$\int_{-\infty}^{t} \frac{F(\boldsymbol{r},\tau)\sin[\Omega(t-\tau)]}{\Omega}\mathrm{d}\tau$$

($\boldsymbol{r}$ is the radius vector and t is the time) vanishes and no vibrations occur. At the lower energy of the pump pulse (1.4 μJ) only the high-frequency phonon mode with a frequency of 1 THz (the dependences are not given) is observed. This component is related to the A_{1g} vibrations,

Table 1. Tensors of Raman-active modes for Fm–3m group crystals (*a*, *b*, *c* and *d* are constants).

	A_{1g}			E_g			E_g			T_{2g}			T_{2g}			T_{2g}	
a	–	–	*b*	–	–	$3^{1/2}b$	–	–	–	–	–	–	–	*d*	–	*d*	–
–	*a*	–	–	*b*	–	–	$3^{1/2}b$	–	–	–	*d*	–	–	–	*d*	–	–
–	–	*a*	–	–	$-2b$	–	–	–	–	*d*	–	*d*	–	–	–	–	–

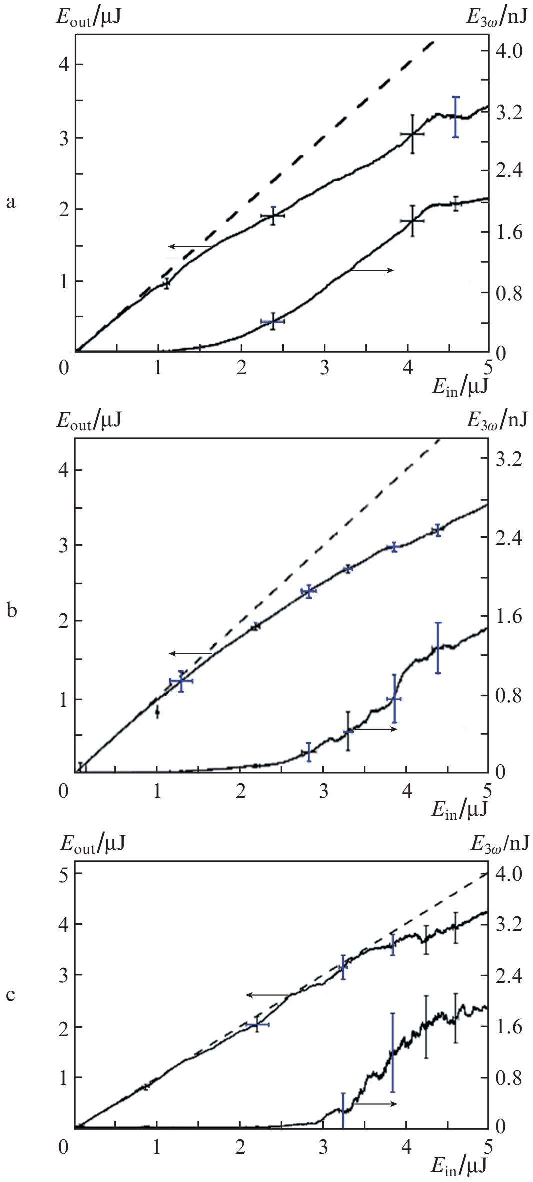

Figure 2. Energy E_{out} of transmitted laser pulse and its third harmonic energy $E_{3\omega}$ as a function of laser radiation energy E_{in} for BaF_2 (a), CaF_2 (b), and LiF (c) crystals. The dashed line corresponds to the absence of absorption.

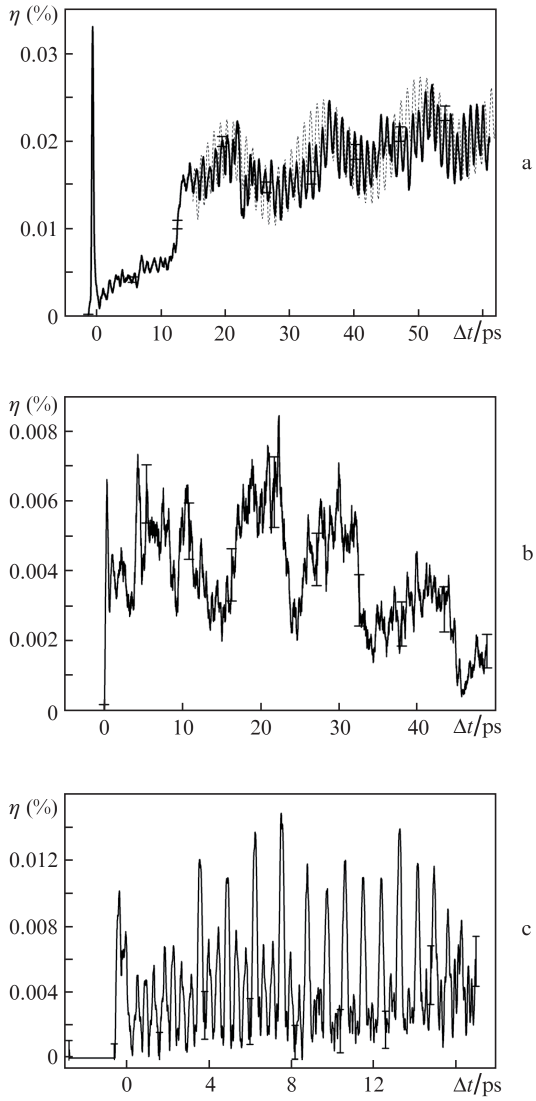

Figure 3. Generation efficiency η of the third harmonic of probe pulses in BaF_2 crystals for an exciting pulse energy E_{in} = 2 μJ (a), in CaF_2 for E_{in} = 4 μJ (b), and in LiF for E_{in} = 3.6 μJ (c) as a function of the time delay Δt between the pump and probe pulses.

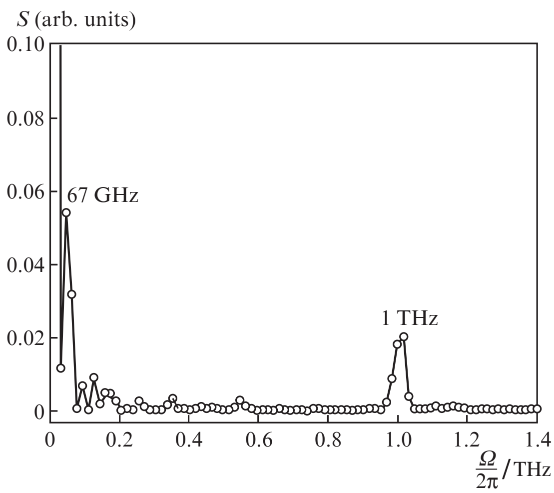

Figure 4. Spectral power density S of the third harmonic signal for a BaF_2 crystals for a pump pulse energy E_{in} = 3 μJ.

which took place at about the same frequency in other crystals belonging to the O_h group [30]. In the course of experiments on crystalline BaF_2 we also discovered that the oscillation amplitude of the signal of the third harmonic of the probe pulse increased significantly for time delays exceeding 15 ps, i.e. coherent phonons 'build up' with a delay due to plasma-electron energy transfer to the phonon subsystem rather than instantaneously on arrival of the pump laser pulse (Fig. 3a). This delay may be estimated from the deformation-potential theory [31]. In the framework of this theory the transport relaxation time τ_k, which characterises the time of energy transfer from plasma electrons to acoustic phonons, is estimated by the formula

$$\frac{1}{\tau_k} = \frac{|\xi|^2 m_e \theta_k}{\pi \rho c_s^2 \hbar^3},$$

where ξ the deformation-potential constant; m_e is the electron mass; $\theta_k = k_B T$; T is the temperature of the crystal lattice; k_B is the Boltzmann constant; ρ is the density of barium fluoride crystals; and c_s is the velocity of sound in the medium [31]. The following parameter values were employed for this estimate: $|\xi| \approx 10$ eV, which corresponds to an outer shell electron energy by the order of magnitude, $T \approx 300$ K, $\rho \approx 4.8$ g cm^{-3}, and $c_s \approx 4.29$ km s^{-1}. The wave vector $\boldsymbol{k}$ of plasma electrons was calculated proceeding from their kinetic energy equal to $\sim$4 eV. For the indicated parameter values the transport time is equal to 13 ps, which agrees reasonably well with the time delay observed in our experiment.

3.2. CaF_2 crystal

The picture observed for crystalline CaF_2 is similar to that for barium fluoride. For this crystal, the low-frequency oscillations with a frequency of 100 ± 20 GHz (Fig. 5), which correspond to a 3-cm^{-1} Raman shift characteristic of acoustic phonons [28], are also present in the third harmonic signal.

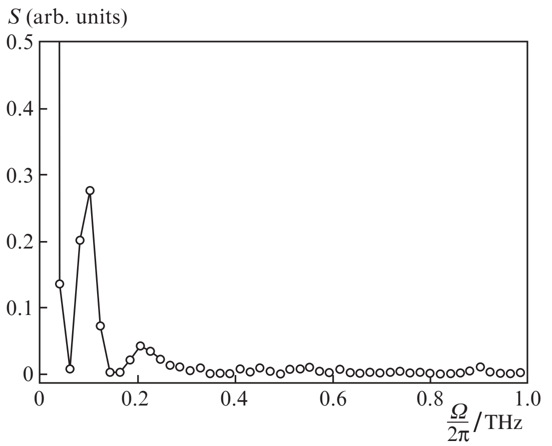

Figure 5. Spectral power density S of the third harmonic signal of the probing pulse for a CaF_2 crystal for a pump pulse energy $E_{in} = 4$ μJ.

Against the background of low-frequency oscillations in the third harmonic signal of the probe pulse we observed noisy high-frequency oscillations with different frequencies. Filtering this signal in the 0.8–1.2 THz frequency range permits extracting a low-intensity spectral component at a frequency of $\sim$1 THz.

3.3. LiF crystal

In the case of crystalline LiF, the temporal signal of the third harmonic of the probe pulse contains coherent oscillations of different phonon modes. A spectral analysis of experimental data showed that the microplasma production in the bulk of crystalline LiF results in the simultaneous excitation of several phonon modes, whose frequencies are the overtones of the fundamental 0.38-THz frequency [1, 32] (Fig. 6). In the experiment we observed an energy transfer from one phonon mode to another. The energy exchange and the presence of several harmonics of the fundamental frequency are possible in the regime of anharmonic coupling, which is realised under strong excitation, when ion vibrations become anharmonic [32]. For instance, in the 0–9 ps time interval in the third harmonic signal there are simultaneously several phonon modes – the fundamental one ($\Omega = 0.38$ THz) and a mode at a 2Ω frequency with modulation at a 6Ω frequency. However, beginning with a time delay of 9 ps, the phonon modes with the frequencies Ω, 2Ω and 6Ω vanish and there appears a mode with a frequency $3\Omega = 1.14$ THz. The anharmonic excitation of the crystal lattice of LiF results from a high specific energy input due to the relaxation of the laser-driven plasma.

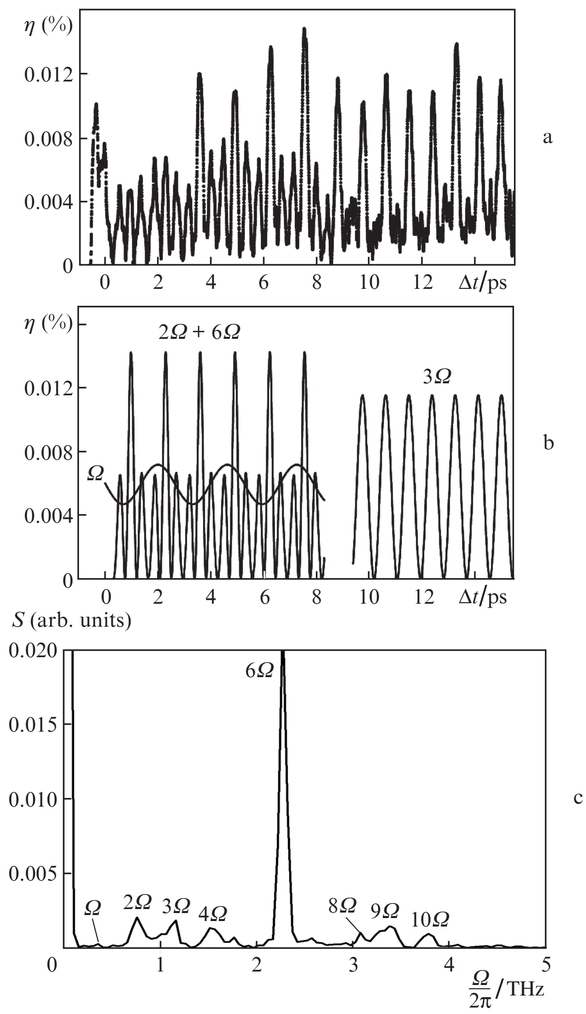

Figure 6. Same as in Fig. 3c (a), model signal with indication of phonon mode frequencies (b), and spectral power density S of the third harmonic signal of the probing pulse (c) for a LiF crystal.

4. Conclusions

In the present work we investigated the excitation and relaxation of coherent phonons for three fluorine-bearing crystals. For the first time in the third harmonic signals of the probe pulse for BaF_2 and CaF_2 samples it was possible to observe a significant increase in phonon wave amplitudes with a time delay relative to the instant of irradiation. In crystalline LiF we discovered an energy exchange between phonon modes, which is possible only in the regime of anharmonic phonon wave vibrations. It is significant that our experiments in coherent phonon generation are essentially different from the canonical ones [15, 30] by the presence of laser-driven plasma and the use of the regime of extreme laser irradiation of the target. The laser-driven plasma produced in the microvolume of crystalline dielectrics was shown to exert a significant effect on the excitation and relaxation of coherent phonons.

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