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Photoinduced non-linear optical diagnostic of InI ferroelastic nanocrystals

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Abstract

Photoinduced second harmonic generation was established in the centrosymmetric layered crystals of InI. The effect was grounded on occurrence of photoinduced optical second harmonic generation in the ferroelastic phase of the InI crystals. As a subject of investigations layered ferroelastic crystal of InI was chosen. It was found that the ferroelastic phase disappears during decrease of the nanolayers from 15 nm up to 6 nm. Such effects are explained by occurrence of anharmonic phonon modes confined by the walls of the layered crystals. We have found that the effect may be of importance for the further investigations of the layered nanocrystals. At the same time the giant value of the photoinduced SHG indicates on a possible using the nanolayered crystals like promising non-linear optical crystals.

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Keywords: Nanocrystallites; Non-linear optics

1. Introduction

Single crystals of InI possess layered structure and point group mmm. Due to existence of layered structure one can receive the InI samples with thickness up to several nanometers. These samples may serve like model nanocrystalline materials. In the paper [1] in InI was discovered ferroelastic phase transition at low temperature. Due to existence of inversion symmetry it is necessary to apply photoinduced SHG [2], which induces the acentric charge density distribution by external pumping polarized light. The observed effects are originated from a superposition of nano-confined effects and vacancies [3].

Generally, ferroelasticity is closely related to the dimensions of particular layers [4]. Possibility of receiving the samples with sizes below 7 nm opens a new era in novel nanotechnology. Besides low dimensions of the layers possessing perfect surfaces such sheets may be used for operation by temperatures of the corresponding phase transitions. It is a consequence of a fact that low dimensions of the layered crystals may change their electron–phonon interaction constants and temperature of corresponding phase transitions. Simultaneously, the nanosizes may lead to appearance of nano-confined states favoring different kind of non-linear optical susceptibilities, particularly described by third rank polar tensors [5].

The main goals of the present work are as follows: to study an influence of the nano-sized dimensions on behavior of the photoinduced optical second harmonic generation described by third rank polar tensors. Particularly, to establish the role of electron–phonon anharmonicity in the effects observed. Despite it is important to investigate role of the nano-confined effects on the shift of temperature for the corresponding ferroelastic phase transitions.

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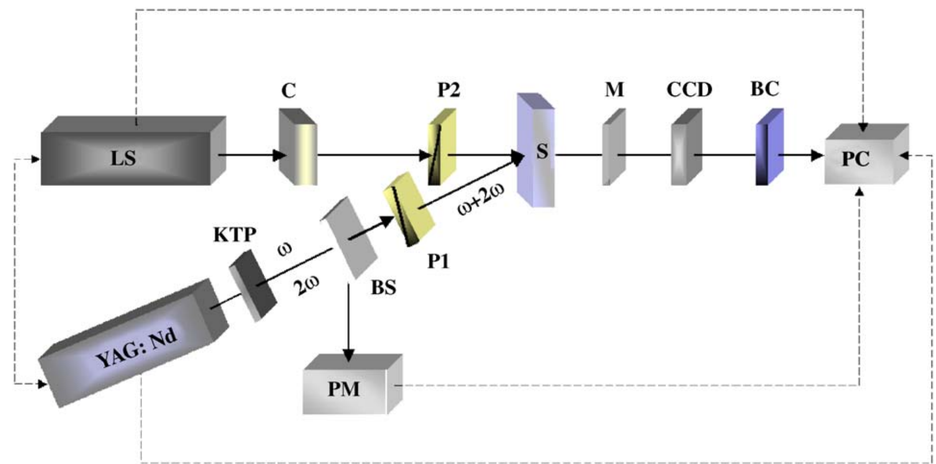

Fig. 1. Principal set-up for the measurements of the PISHG. **YAG: Nd**—pumping laser, **LS**—probing laser, **C**—chopper, **BS**—beam splitter, **S**—sample, **M**—monochromator, **CCD**—camera, **BC**—electronic boxcar, **PC**—personal computer, **PM**—photomultiplier, **P1, P2**—polarizes, **KTP**—crystal for double frequencies.

2. Experimental

Generally, the principles of the measurements were described in Ref. [6].

Typical experimental set-up is given in Fig. 1. The Nd-YAG laser with wavelength 1.06 μm was used as a source of the fundamental laser beam. The pump duration of the laser was varied within the 1–40 ps with pump power densities changed up to several GW/cm^2. The KTP crystal was used for the doubling of the fundamental wavelength due to optical SHG. The beam-splitter BS was used for monitoring of the fundamental wavelength power density. The investigated sample S was put in the thermoregulated cryostat. The polarisers P1 and P2 were applied for the polarization of the probing and pumping laser beams. The laser source from the optically parametrized Nd-YAG laser source (LS) was used as a fundamental laser beam with pump duration varying within the 1–35 ps. The chopper C allowed to achieve changes of the laser signal power densities within the several pulses. The monochromator M was applied for separation of the fundamental, second harmonic generation and scattered light backgrounds. The registration was performed by CCD camera connected with the electronic boxcar (BC) and personal computer (PC). The output SHG signal was measured using the PC.

3. Results and discussion

Varying the sample's thickness (6–12 nm) and temperature (4.2–100 K) we have measured dependences of the optical second harmonic generation versus the pumping light power density at different temperature. Maximal signal was observed for parallel polarization between the pumping and probing beams.

The principal results of the measurements are presented in the Figs. 2–6. For convenience all the experimental data are presented in the three-dimensional form.

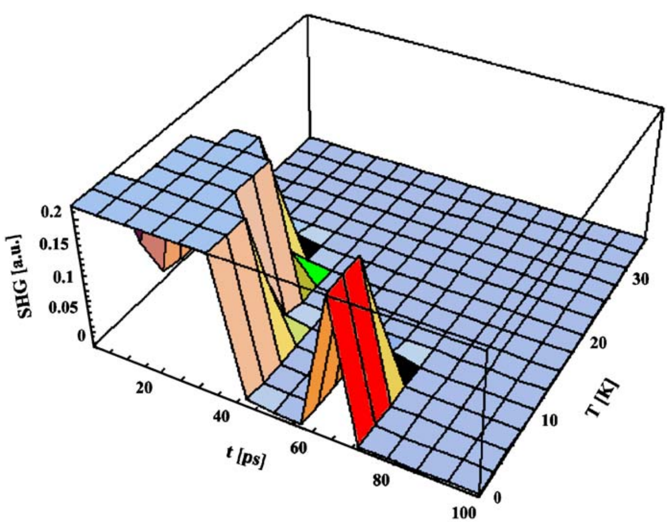

Fig. 2. Temperature dependence of the SHG for the InI nanocrystallites at different pump-probe delay time for the samples of the thickness 6 nm.

From Fig. 2 one can see that for the samples with thickness about 6 nm (where nano-confined effects should be more pronounced) the output SHG occurs at temperatures below 20 K. This one correlates well with appearance of low-temperature interlayer (membrane-like) anharmonic phonon modes in InI [7]. Moreover there are two clear pump-probe SHG temporary maxima. The first one—at 10–30 ps and the second one—at 60 ps. With increasing layer thickness (compare Figs. 3 and 4) the first temporary bands substantially increases and the second one is suppressed. Simultaneously the second temporary SHG maximum is shifted towards less temperatures (up to 10 K).

It is clearly shown that the second oscillator is almost disappeared for the samples possessing thickness higher than 12 nm (see Fig. 5). Here one can say about a superposition of the electronic nano-confined levels with the electron–phonon anharmonic interactions due to ferroic effects.

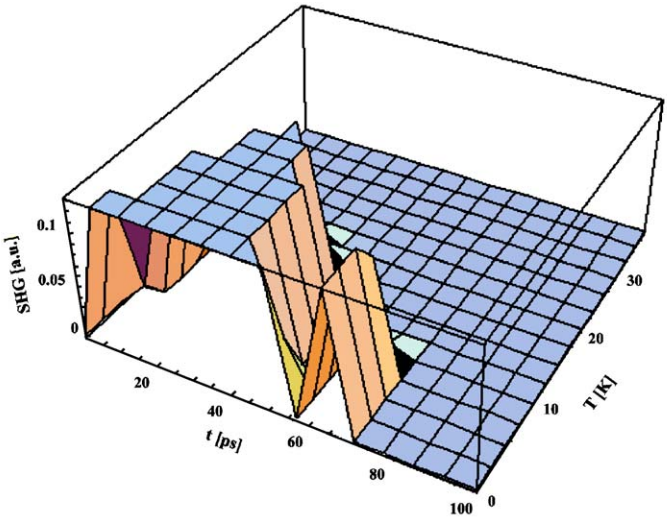

Fig. 3. Temperature dependence of the SHG for the InI nanocrystallites at different pump-probe delay time for the samples of the thickness 8 nm.

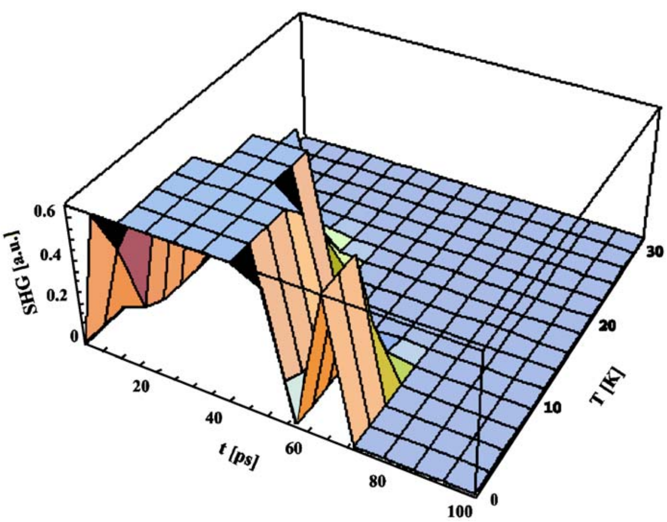

Fig. 4. Temperature dependence of the SHG for the InI nanocrystallites at different pump-probe delay time for the samples of the thickness 10 nm.

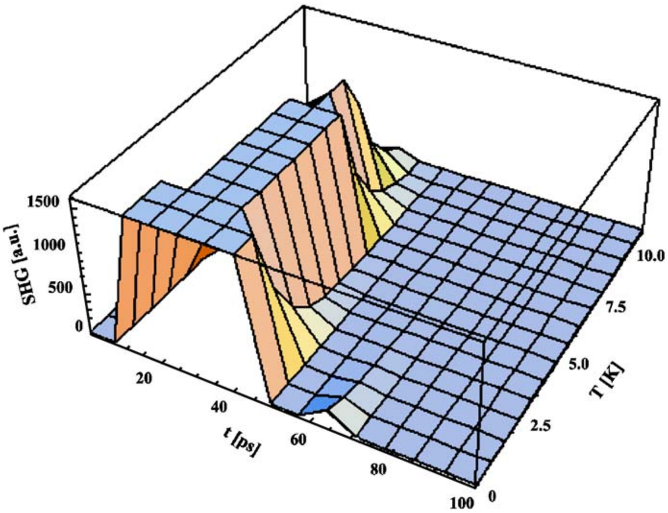

Fig. 5. Temperature dependence of the SHG for the InI nanocrystallites at different pump-probe delay time for the samples of the thickness 12 nm.

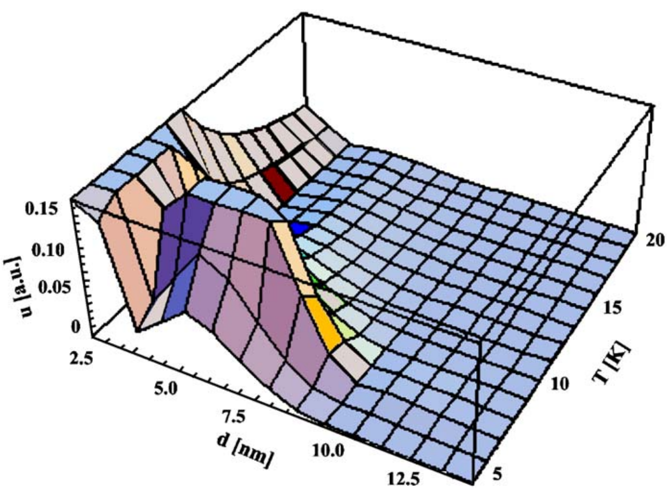

Fig. 6. Dependences of dilatometry measured relative deformation versus temperature and crystalline size.

For better understanding of the physical insight of the observed low-temperature anomalies we have done additional dilatometric measurements by a method described in Ref. [1] at low temperatures for the InI samples possessing different sizes. The method has used RF signal as a probing one. One can see that below 10 K there appear anomalies of the corresponding relative deformation **u**. So there exists a close relation between the spontaneous mechanical stresses in ferroic states, defining low-temperature anharmonic electron–phonon interaction and the observed SHG values.

4. Conclusions

In the present report we have established substantial influence of the layered sizes of the InI on the photoinduced SHG. Simultaneously, it was discovered temperature shift of the existed SHG maxima. There exist at least two electron–phonon relaxation systems, which are determined by low-temperature anharmonic inter-membrane rigid phonon modes. It is also important that during decrease of the InI crystal sizes from 12 to 6 nm the beginning of the ferroelastic transition is shifted from 10 to 28 K. Maximal pump-probe splitting is observed at crystal sizes equal to about 6 nm and at sizes about 12 nm it completely disappeared being very similar to the bulk-like crystals.

Maximal photoinduced SHG (about 0.8 pm/V) was observed for the crystalline sizes below 6 nm.

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