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Light-induced ionic polarization in CdZnTe:V semiconductor crystals as a source of giant enhancement of nonlinear effects

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We report on experimental observation of a remarkable light-induced increase in the low-frequency dielectric constant in doped CdZnTe:V (CZT:V) semiconductor crystals and show that this increase is due to electric dipoles forming under illumination. Our findings provide strong evidence that CZT:V undergoes a photoinduced phase transition at room temperature from a nonpolar to polar phase. A related symmetry-breaking effect is responsible for giant light-induced enhancement of the nonlinear effects (the electro-optic effect and electrostriction) previously observed in these crystals.

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Introducing semiconductor crystals into the field of nonlinear optics is highly desirable since potential devices could be produced by advanced microelectronics technology. For example, photorefractive semiconductors seem to be promising for fast nonlinear devices since the mobility of charge carriers in them is much higher than in other photorefractives; hence, the dielectric relaxation times are much shorter for a given light intensity.[1] Moreover, the electrical and optical properties of semiconductor crystals can be manipulated via deep doping centers. At room temperature, deep centers act as traps for charge carriers; hence, the carriers' concentration is dramatically decreased as compared to undoped semiconductors.[2] This is a desired feature for space-charge-field effects since the density of the ionized traps (the source of the field) is much larger than the density of the charge carriers; thus, free charge cannot screen the space-charge field. In nonlinear optics, this situation is mainly used for stimulating photorefractive effects, in which nonuniform illumination gives rise to local variations in the density of the ionized traps, resulting in a space-charge field, which modifies the refractive index via electro-optic effects.[1] However, semiconductors exhibit weak electro-optic effects, as compared to oxide materials, such as $LiNbO_3$ or $Sr_xBa_{1-x}Nb_2O_6$.[3] Therefore, in order to obtain reasonable electro-optics refractive-index changes in semiconductors, one should apply very large electric fields or, alternatively, manipulate the local space-charge concentration to enhance the internal electric fields within the crystal.[4] Both options are very limited, altogether providing index changes well below 10^{-3}, thus hampering potential applications.

In a sharp contrast to those methods, we have recently reported on the observation of refractive-index changes in the semiconductor CdZnTe:V (CZT:V) in excess of 0.01.[5,6] This value is huge for semiconductors—possibly the largest reported in inorganic bulk materials. In further studies, we have found that the index change is accompanied by a remarkable modification of the crystalline lattice parameter (up to 10^{-3}).[6] The mechanism responsible for these huge effects is still not understood. Clearly, our findings cannot be explained by "conventional" electro-optic and electrostriction effects since the field required to support such large effects ($\sim$1.5 MV/cm) would be much larger than dielectric breakdown field for CZT ($\sim$500 kV/cm). Moreover, we observed nonzero electro-optic and electrostriction coefficients also in geometries in which these effects should be forbidden by the initial cubic symmetry of CZT. Finally, we emphasize that the enhancement of the electrostriction and the electro-optic effects *occurs also when the illumination is uniform. In fact, the effects are observed everywhere in the bulk*. This is in contrast to conventional photorefractive effects which necessitate nonuniform illumination, otherwise, when the illumination is uniform such effects appear only in a thin layer near the electrodes, where charge carriers accumulate.

Our experiments suggest that a novel mechanism is responsible for these effects, whose understanding could pave the way to long-anticipated applications. For instance, we presented a proof of concept for efficient all-optical beam steering[5] and proposed using the light-enhanced nonlinearities in CZT:V for efficient THz generation, frequency conversion, and large self-phase modulation. Our experiments[6] showed that illumination at subband-gap energies, together with a moderate applied electric field, induces large deformations of the cubic unit cell. These deformations could be a source of lattice instability leading to the formation of a polar phase. If this is correct, we expect a sharp increase in the dielectric susceptibility as the illumination intensity is increased. Here, we present experimental studies on the low-frequency impedance in CZT:V under illumination at a subband-gap energies, which support the above hypothesis.

Our $Cd_{1-x}Zn_xTe$ crystals are grown by the modified version of the horizontal Bridgman technique.[7] The nominal Zn concentration is $x=0.01$ and the nominal value of the vanadium doping is about 10 ppm. The samples used are in a form of the $5\times5\times2$ mm^3 platelets with faces oriented perpendicular to the crystallographic directions $\langle110\rangle$, $\langle1\bar{1}0\rangle$, and $\langle001\rangle$. We apply a bias electric field along the $\langle001\rangle$ direction between electrodes separated by 2 mm. We measure the resistance and capacitance of the crystal while it is illuminated with a broad circular beam [full with at half maximum (FWHM) of 6 mm] at $\lambda=980$ nm wavelength

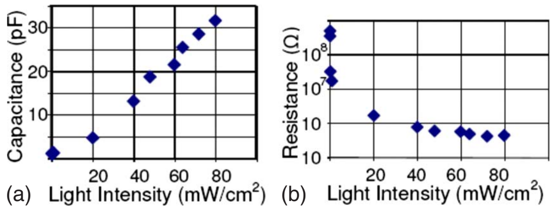

FIG. 1. (Color online) (a) Room temperature capacitance and (b) resistance of the CZT:V crystal as functions of light intensity, measured at ac voltage of 1 V and frequency of 1 kHz.

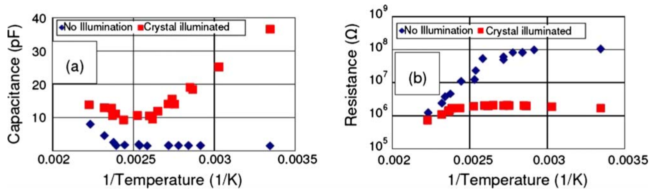

FIG. 3. (Color online) (a) Capacitance and (b) resistance of the CZT:V crystal as functions of temperature, measured at frequency of 1 kHz and light intensity of 80 mW/cm^2.

(absorption coefficient is 1.5 cm^{-1}) propagating along the $\langle 110 \rangle$ direction. The measurements are performed with a computer-controlled *LCR* Hioki impedance analyzer.

The dependencies of sample capacitance and resistance on light intensity at room temperature are shown in Figs. 1(a) and 1(b), respectively. The capacitance greatly increases with illumination intensity, implying that light indeed facilitates the formation of electric dipoles within the crystal. We estimate the low-frequency dielectric constant under these conditions to be 290, which is nearly 30 times larger than the tabulated value, $\varepsilon=10.4$, for CZT without illumination. The resistance behaves less surprisingly: as for any doped semiconductor, the resistance is inversely proportional to the light intensity (since the photoinduced free-carrier density, and hence the conductance, is proportional to the light intensity).

Studying the dependencies of the resistance and the capacitance on the electric-field frequency (in the range between 100 Hz and 1 MHz) at various light intensities, we find that the light-induced jump of the capacitance is rapidly decreasing at higher frequencies [Fig. 2(a)]. The critical frequency, at which the excess capacitance drops to half of its maximum value, depends on the light intensity and can reach a few kHz. This dependence of the capacitance on frequency could either be a result of a space-charge field or indication of an ionic polarization. It is essential to determine which one of these mechanisms causes the increased capacitance in order to deduce whether or not the enhanced capacitance is related to increased ionic polarization. For this purpose, we plot the dielectric loss (the imaginary part of the dielectric function) as a function of the electric-field frequency [Fig. 2(c)]. Under illumination, the dielectric loss has a peak around 400 Hz. The peak frequency does not depend on the light intensity and its value indicates that the characteristic time τ_d for the underlying process is about $\tau_d=400$ μs. On the other hand, by using the measured values of the dc electrical conductivity for σ (in order to estimate the carrier density) and taking again the tabulated value of $\varepsilon=10.4$ (for standard CZT without illumination), one can calculate the dielectric relaxation time, $\tau_r=\varepsilon/\sigma$, which yields $\tau_r=27$ and 5.7 μs for light intensities of 5 and 25 mW, respectively. Clearly, the dielectric relaxation time, τ_r, is more than ten times faster than the formation time of the enhanced capacitance, τ_d. In other words, the enhanced capacitance builds up much slower than the buildup of any space-charge field, the latter being related to the dielectric relaxation time. This implies that the space-charge field is not a primary source of the light-induced highly enhanced capacitance, although the ionic displacements causing the large ionic polarization in CZT:V may be initiated by the space-charge field effects.

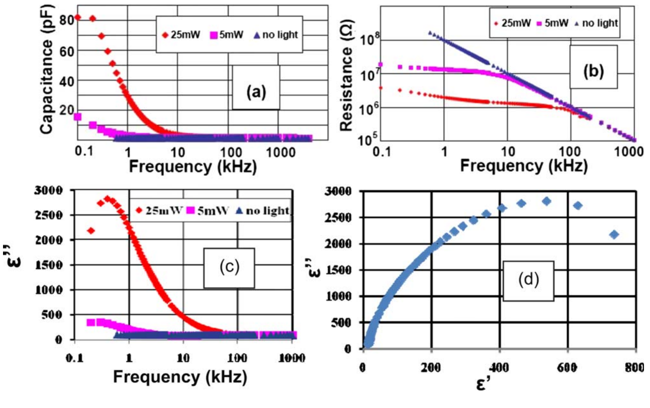

FIG. 2. (Color online) (a) Room temperature capacitance, (b) resistance, and (c) dielectric loss (ε'') of the CZT:V crystal, as functions of the electric-field frequency; (d) imaginary part of the dielectric function (ε'') vs real part (ε') of the dielectric function.

The comparison between the formation time of the enhanced capacitance, τ_d, and the dielectric relaxation time, τ_r, does not exclude the possibility that the enhanced capacitance has contributions from both mechanisms, i.e., ionic polarization and space-charge field. To clarify this issue, we plot the imaginary part of the dielectric function vs its real part, i.e., the so-called Cole-Cole diagram [see Fig. 2(d)]. A single semicircle is noticeable in the Cole-Cole diagram, which proves that, in the investigated frequency range, only one mechanism contributes to the enhanced dielectric susceptibility observed in our experiments and this is the relatively slow buildup of electric dipoles. Therefore, the data presented throughout this Brief Report provide direct evidence that the light-induced effect on the dielectric susceptibility of CZT:V is of an ionic nature.

We note that the resistance also depends on the frequency and on the light intensity [Fig. 2(b)]. In the absence of light, the resistance is systematically reduced with frequency, suggesting that the dominant conduction mechanism is hopping. Under illumination, the density of the photoexcited free carriers is increased; hence, the role of band conduction becomes substantial. At higher frequencies, the hopping mechanism prevails and all curves in Fig. 2(b) practically coincide.

Additional information can be obtained from the dependence of the low-frequency impedance on temperature with and without illumination (Fig. 3). Without illumination, the resistance is constant up to ~400 K and then it is decreasing with temperature due to thermal excitation of the deep dopant states. The slope of the resistance in the range of 400–450 K fits well the energy difference (0.75 eV) between the deep-dopant level and the bottom of the conduction band. Under illumination [Fig. 3(b)], both photoexcitation and thermal-excitation processes lead to the reduction in the resistance, making the temperature effect less pronounced. The capacitance [Fig. 3(a)] without illumination is constant up to about 400 K and then it grows with temperature. The reason for the capacitance increase at elevated temperatures is thermal excitation of localized carriers and dipole formation. Under illumination, the capacitance at room temperature is much higher than the capacitance without illumination. When increasing the temperature under the same light intensity, the capacitance decreases, in contrast to the behavior when the crystal is not illuminated. This can be explained by the following argument. When the crystal is illuminated by a light beam at 980 nm, some of deep dopants are ionized; that is, the light excites localized carriers, just as increasing temperature does without illumination. However, even a low light intensity excites more efficiently charge carriers than thermal excitations do at room temperature. Hence, under illumination, the increase in the excitation rate upon raising the temperature is negligible. On the other hand, raising the temperature increases the vibrations of the dipoles, thereby destroying their arrangement. In doing that, raising the temperature reduces the macroscopic dipole moment. At a higher temperature, the thermal-excitation rate becomes comparable to the photoexcitation rate and the capacitance increases again with temperature.

The experimental observation of how the capacitance depends on temperature is very important for understanding the light-induced large dipole moment effect because we can now clarify if light heating is the source of the effect. We measure the change in temperature upon illumination (no external heating) and find it to be 2 K at the highest intensity we use (80 $\mathrm{mW/cm^2}$). Comparing this value to values presented in Fig. 3 shows unequivocally that heating cannot explain the light-induced effect. Light heating is too small to explain the increase in capacitance.

The impedance measurements described above raise a natural question: are the ionic polarization effects confined to a thin layer near the electrodes, or are they bulk effects occurring everywhere in the volume of the crystal? Our impedance measurements, repeated at various electric-field values, unequivocally indicate that the impedance does not depend on the applied field. If the effects had taken place in a thin layer only, the thickness of this layer would depend on the field; hence, the capacitance and the resistance would have been affected. Evidently, this is not the case. Moreover, the polarization buildup occurs on a very slow time scale: the capacitance decreases substantially for frequencies above a few kHz, whereas the dielectric relaxation time in CZT is much faster ($\sim 10\ \mu$s) at the light intensities used. This suggests that the low-frequency dielectric response, which is what we actually measure, has an ionic origin rather than being related to charge transport. If so, the time scale of the low-frequency dielectric response cannot be attributed to the formation of a barrier near the electrodes. Altogether, our experiments show unequivocally that all the effects studied in this Brief Report are bulk effects.

Our findings provide a firm evidence that illuminating CZT:V crystals at room temperature by light, having a subband-gap energy, is an effective way to "prepare" a polar medium. Our results for CZT:V have some common points with those obtained in the study of deep dopant centers in GaAs.[8] In the absence of illumination, our results are similar to those of Ref. 8. However, in contrast to Ref. 8, we use light (rather than temperature) to ionize the deep traps. In such a way, we are not increasing thermal vibrations, which destroy the dipole arrangement. This fact is very important for potential applications since, as follows from our experiments, the induced dipole moment is much larger in case of photoexcitation of charge carriers as compared to thermal excitation demonstrated with GaAs in Ref. 8.

Reference 8, albeit describing temperature-driven effects, proposed a model which has relevance to our current study. In that model, the conduction and valence bands are modulated in space due to long-range potential fluctuations. Therefore, the conduction within the bands is via hopping, namely, the electrons (holes) hop from one valley (hill) in the conduction (valence) band to another. As a result, the model explains the conduction in such materials (semiconductors with deep-dopant centers), as well as the high dielectric constant and its dependence on frequency, attributing the large value of the capacitance to the creation of ionized traps. In our study, the most interesting results are the large changes in the material properties caused by illumination. It is reasonable to assume that under illumination the local density of ionized traps is changed, depending on the local variation in the energy gap. As a result, a large space-charge field is created in the vicinity of the ionized traps. Since the density of the charge carriers is more than 5 orders of magnitude lower than the density of the ionized traps, free carriers cannot screen the electric field. This leads to a strong light-induced electric field, which decays on a scale much larger than the typical distance between adjacent traps. For estimating the local electric field at the vicinity of an ionized donor, we use the fact that the electronic screening length in our material is $\sim 3\ \mu$m, much larger than the average distance between two neighboring donors (100 nm). Thus, for a distance smaller than 100 nm from an ionized donor, the electric field obeys the Coulomb law. This implies that, on the scale of tens of nanometers, the electric field created by one ionized donor can be as high as several kV/cm. In practice, since the dopants are randomly distributed, at some positions within the crystal the electric field caused by the ions can be even larger, while in other locations it may be smaller. Hence, the illumination increases the long-range potential fluctuations. Moreover, this high electric field acts on the atoms at the vicinity of the donor (on this scale there are about 10^5 atoms), causing the appearance of electrical dipoles and hence the symmetry-breaking effects discovered in our previous experiments.[6]

Based on these results, we conclude that in CZT:V light induces a phase transition from a nonpolar cubic phase to polar one with reduced symmetry. The phase transition occurs when the ionization rate due to illumination becomes comparable to the thermal ionization rate, leading to a new equilibrium state. The light intensity required for this phase transition is quite small: from previous data we estimate it as

~1.5 mW/cm^2,[9] which is well below the smallest values used in this work (see Fig. 1).

The nonuniformity of the bands also explains why we have very strong space-charge field, even though we use uniform illumination. According to Ref. 8, the charge separation under uniform illumination occurs because the local band-gap modulation provides nonuniform excitation rates. This suggests a new photorefractive mechanism, which can be used for applications requiring uniform illumination.

In conclusion, we observe very large light-induced ionic polarization in bulk CZT:V crystals at room temperature, which increases with light intensity. Under illumination, the low-frequency dielectric constant reaches 290, which is 30 times higher than its value in the absence of light. It implies that the photoexcitation of free carriers creates strong polarization of the medium mediated by the long-range potential fluctuations of the band gap. The light-induced polarization causes symmetry breaking and the related enhancement of the nonlinear effects. We believe that, under proper conditions, GaAs and amorphous semiconductors can also exhibit fascinating light-induced enhancement of their nonlinear properties.

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