Light-induced symmetry breaking and related giant enhancement of nonlinear properties in CdZnTe:V crystals

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Abstract: We report on enormous light-induced reversible strain effects in CdZnTe:V crystals, which lead to a remarkable enhancement of their nonlinear properties, such as electrostriction and electro-optic effects. Using both high resolution x-ray diffraction and optical interferometry we measure light-induced relative deformation of the initial crystalline lattice (changes in *d*-spacings) up to 0.15%. The experimental findings are attributed to light-induced breaking of the initial cubic crystalline symmetry. Our results point to a family of inorganic materials whose nonlinear properties can be remarkably enhanced by light, offering new possibilities for nonlinear frequency conversion, generation of Terahertz radiation, electro-optic modulation, and self-deflection of optical beams.

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OCIS codes: 190.4400 Nonlinear optics materials; 190.5940 Self-action effects

References and links

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8. Note that Δn_{eff} is positive in both geometries, suggesting that the net (electro-optic) refractive index change in the geometry depicted in Fig. 3 is somewhat larger than the one measured in the geometry shown in Fig. 2 (because $\Delta n_{eff} > 0$ in Fig. 2 whereas $\Delta L < 0$ in Fig. 3).
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1. Introduction

Semiconductor crystals are known to display a very small electro-optic response [1]. For example, the coefficients of the electro-optic (Pockels) effect in GaAs, InP, CdTe, and CdZnTe (CZT) are all in the range of 1-7 pm/V, which should be compared with 1640 and 1340 pm/V found in $BaTiO_3$ and $Sr_{0.75}Ba_{0.25}Nb_2O_6$, respectively [1]. This 2-3 orders of magnitude difference is fundamental, and is caused by the dissimilar origin of the electro-optic effect in these materials. In cubic semiconductors, the electro-optic effects are primarily of electronic origin, whereas in dielectric crystals of non-cubic symmetry (such as $BaTiO_3$ and $Sr_{0.75}Ba_{0.25}Nb_2O_6$), the strong electro-optic response is associated with ionic displacements. Recently, however, we have reported on an anomalously large electro-optic response in CdZnTe doped by vanadium (CZT:V) [2]. The index change depends linearly on light intensity and reaches $\Delta n \approx 0.01$. This corresponds to an effective electro-optic coefficient of ~900 pm/V. This finding cannot be understood through the conventional electro-optic effect in CZT, because to support such a giant index change the electric field would have to be of the order of the local atomic field in the crystal. Moreover, we observed large refractive index changes in experimental geometries for which the electro-optic coefficients should be zero according to the initial cubic symmetry of the crystalline lattice.

Here, we investigate the physical origin of the large refractive index change detected in our previous experiment [2]. We demonstrate experimentally that light, combined with an electric field induces enormously large reversible strain in CZT: V crystals, breaking the crystalline symmetry and leading to a drastic enhancement of their nonlinear properties, such as electrostriction and electro-optic effects. Using high-resolution x-ray diffraction and optical interferometry we measure light-induced deformations of the crystalline lattice which depend linearly on light intensity and quadratically upon the applied electric field. We measure values as large as 0.15% in lattice deformations (change in *d*-spacings), which are three orders of magnitude higher than the value calculated with the tabulated piezoelectric coefficients [3]. We emphasize that the lattice deformations observed in our experiments are induced by light and are reversible, in sharp contradistinction with the results of all previous studies on CZT, where structural deformations have been identified as a consequence of elemental replacements or ordered growth of epitaxial layers, both irreversible (see, e.g., [4,5]). We therefore conclude that the large enhancement of the nonlinear electro-optic and electrostriction effects observed in CZT: V under illumination arises from light-induced crystalline symmetry-breaking.

2. Experiments and results

Our $Cd_{1-x}Zn_xTe$ crystals are grown by the modified version of the horizontal Bridgman technique [6]. The nominal Zn concentration is x = 0.01, and the nominal value of the V doping is ~ 10^{17} cm^{-3}. We measure the in-situ lattice strain by using high-resolution x-ray diffraction, while the crystal is biased by an electric field, and illuminated (uniformly) with a laser beam of $\lambda = 980$ nm wavelengths. The x-ray measurements are carried out in the Bragg scattering geometry using a Bede D^3 multi-purpose diffractometer combined with a 18 kW Rigaku rotating anode generator and a channel-cut crystal-monochromator and analyzer for the incident and diffracted beams. High accuracy ($\Delta a/a \approx 5\cdot 10^{-5}$) absolute measurements of the lattice parameters are performed by the Bond method [7]. The samples for this study are of a 5x5x1 mm^3 rectangular shape, with faces oriented in directions perpendicular to the crystallographic directions <110>, $<1\bar{1}0>$, and <001>. Metallic electrodes were deposited on the 5x1 mm^2 faces. In this geometry, the bias electric field is applied along the <110> crystallographic direction, while the light propagates along $<1\bar{1}0>$. High-resolution (004) x-ray diffraction profiles are taken from the (001) atomic planes parallel to the 5x5 mm^2 faces. Figures 1(a) and 1(b) show the (004) *d*-spacing (left-hand axis) and the induced strain (right-hand axis) as functions of the applied electric field and light intensity, respectively.

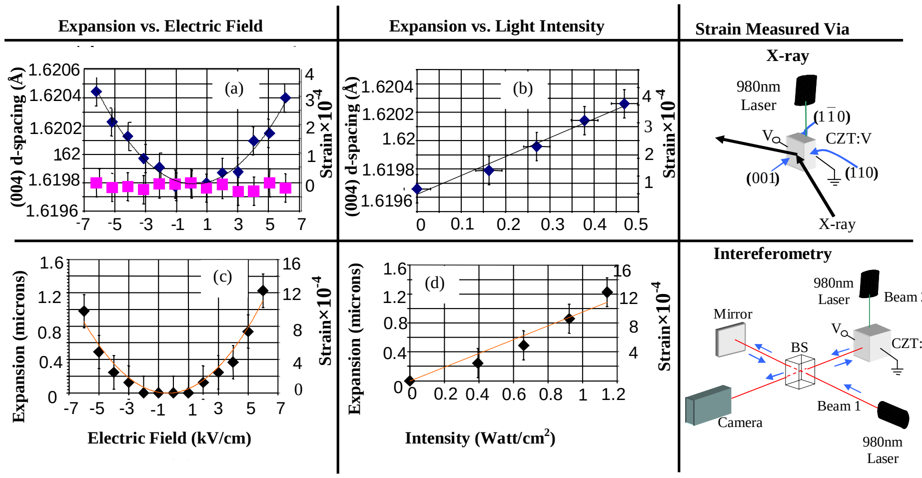

Fig. 1. Experimental results displaying light-induced tensile strain (lattice expansion) measured through x-ray diffraction (a, b) and optical interferometry (c, d). The interferometric method is illustrated at the bottom right panel.
(a) Light-induced change (blue diamonds) and change in the absence of light illumination (pink squares) in the (004) *d*-spacing (left-hand axis) and strain (right-hand axis) vs. an applied electric field. The light-induced strain measurements are taken at a constant light intensity of 253 mW/cm^2.
(b) Light-induced change in the (004) *d*-spacing (left-hand axis) and strain (right-hand axis) vs. light intensity at a fixed applied electric field of 6 kV/cm.
In both (a) and (b) experiments, x-ray diffraction is taken from the (001)-plane.
(c) Light-induced expansion of the crystal (left-hand axis) and strain (right- hand axis) vs. an applied electric field at a constant light intensity of 730 mW/cm^2.
(d) Light-induced expansion of the crystal (left-hand axis) and strain (right- hand axis) vs. light intensity at a fixed applied electric field of 6 kV/cm.
All interferometric measurements represent light reflection from the (001)-plane, and are taken with an electric field applied in the direction and the light beam propagating through the crystal along the $<1\bar{1}0>$ direction. The intensity of Beam 1 is roughly 1 mW/cm^2, which is negligible compared with the intensity of Beam 2.

The results of x-ray measurements shown in Figs. 1(a) and 1(b) provide direct evidence for the strong modifications of the lattice *d*-spacings under the experimental conditions, and exemplify the crucial role played by the light beam causing these changes. Specifically, in the absence of illumination [pink squares in Fig. 1(a)], the measured strain is zero within the accuracy of x-ray measurement. With illumination, the strain increases quadratically with the applied field and linearly with the light intensity, reaching the value of $\Delta a/a \approx 4 \cdot 10^{-4}$ (blue diamonds in Figs. 1(a) and 1(b). However, the x-ray penetration depth (under our experimental conditions) is only several microns (~10,000 atomic layers) beneath the surface of the sample. To obtain information on the light-induced deformation in the sample bulk, we use optical interferometry-by replacing one of the mirrors in a Michelson interferometer with the CZT: V crystal while keeping the far end of the crystal fixed (see lower right panel in Fig. 1). A direct comparison between the strain measured via x-ray diffraction and the strain as deduced from the interferometric measurements can establish whether the induced strain is indeed a bulk effect, in which all unit cells are deformed collectively. Typical results are shown in Fig. 1(c) and 1(d), depicting the absolute crystal expansion (left-hand axes) and relative deformation (right-hand axes) as functions of applied field and light intensity. The

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interferometric results are indeed consistent with those obtained by x-ray diffraction to within 20%. The remaining difference is attributed to surface charge, which to some extent reduces the electric field near the surface, thereby influencing the x-ray diffraction results. These experiments unequivocally prove that the light-induced deformation is a bulk effect.

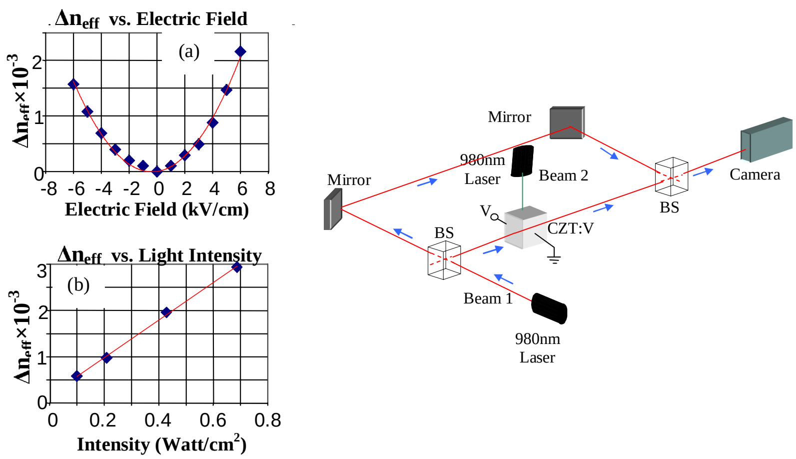

Fig. 2. Experimental results of $\Delta \mathbf{n}_{\mathbf{eff}}$ measurements. (a) Δn_{eff} vs. applied electric field at a constant light intensity of 730 mW/cm^2. (b) Δn_{eff} vs. light intensity at a fixed applied electric field of 6 kV/cm. All interferometric measurements represent Δn_{eff} in the <001> direction, and are taken with the electric field applied in the <110> direction and the light beam inducing Δn_{eff} propagating through the crystal along the $<1\bar{1}0>$ direction.

Another way to track the effects of light-induced crystalline deformation is by monitoring the phase changes accumulated by a wave propagating through the crystal, which experiences simultaneously a light-induced length change and an electro-optic index change. Such an experiment compares the magnitude of two nonlinear effects, electrostriction and the electro optic effect, which in CZT: V are both enhanced by light. To perform a direct comparison, we construct a Mach-Zehnder interferometer and insert the crystal in one of its arms (see Fig. 2). When both the refractive index and the length of the crystal vary with light intensity, the effective index change is $\Delta n_{eff} = \Delta n + n(\Delta L / L)$, where Δn the index change is, *L* is the crystal length, *n* is the refractive index, and ΔL is the length change. Figure 2 shows Δn_{eff} as a function of applied electric field and light intensity. Comparing the measured values of Δn_{eff} and strain, we find that both depend linearly on the light intensity and quadratically on the applied electric field.

Finally, we repeat both interferometric experiments in a different crystalline geometry: applying electric field along <001>, light propagation along $<1\bar{1}0>$, the strain and phase changes (electro-optic + strain) along <110>. The results are shown in Figs. 3(a)-3(d). The values of the observed strain are very close to those obtained in the geometry depicted in Fig. 1, with one exception: now the crystal exhibits contraction rather than expansion [8].

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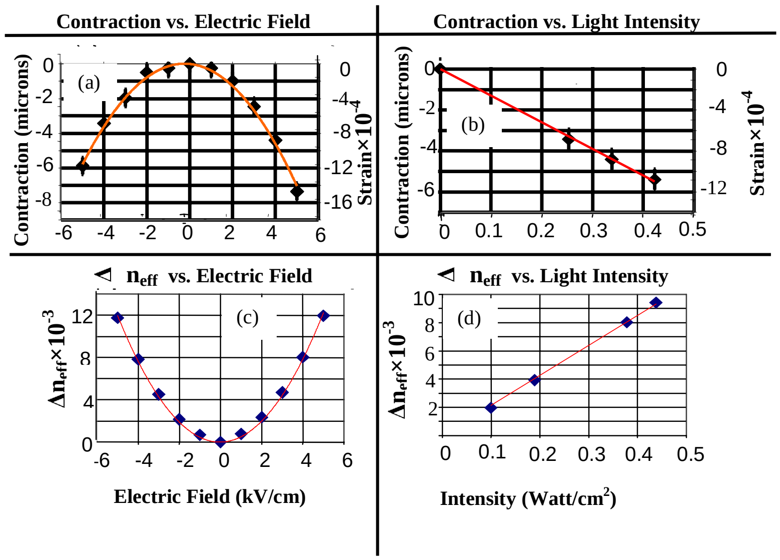

Fig. 3. Experimental results presenting light-induced compressive strain (lattice contraction) in the crystal and $\Delta\mathbf{n}_{\mathbf{eff}}$ in an experimental geometry (with respect to the crystalline axes) different than that of Figs. 1 and 2. Results are taken through interference measurements, with the electric field applied in the <001> direction and the light beam propagating through the crystal in the $<1\bar{1}0>$ direction. The data in (a, b) is taken with the interferometer of Fig. 1, through light reflection from the (110) plane. The data in (c, d) is taken with the interferometer of Fig. 2, by propagating the probe beam through the crystal in the <110> direction

(a) Contraction of the crystal (left-hand axis) and the induced strain (right-hand axis) vs. applied electric field measured at a constant light intensity of 331 mW/cm^2.

(b) Contraction of the crystal (left-hand axis) and the induced strain (right-hand axis) vs. light intensity measured at a fixed applied electric field of 4 kV/cm.

(c) Δn_{eff} vs. applied electric field measured at a constant light intensity of 378 mW/cm^2.

3. Discussion

Our experiments have shown that, under illumination, the changes in the refractive index and lattice strain depend quadratically on the applied electric field. Formally, one could attribute the quadratic field dependence to the “conventional” dc Kerr effect and electrostriction, respectively, which are both described by the fourth rank tensors. However, these tensors have certain zero components for the CZT $\bar{4}3m$ point group [9]. This should prohibit the observed electrostriction and dc Kerr effect in some of the experimental geometries we have used. For example, the g_{41} coefficient of the dc Kerr effect and the e_{14} tensor element of electrostriction are both zero for the CZT point group, implying that in the experiment of Fig. 3 (electric field applied along <001> with the light propagating along <110>), neither electrostriction nor electro-optic index changes should have been observed. Our experiments, however, reveal the opposite: the measured light-induced effects are in fact very strong, and they are insensitive to the polarization of both light beams (i.e., the beam causing the effect and the probe beam, marked as Beams 1 and 2 in Fig. 1, respectively). The fact that the observed effects are insensitive to the light polarization fundamentally contradicts the properties of the dc Kerr effect.

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We emphasize that the observed strain cannot be attributed simply to thermal effects induced by the incident light beam, because we find that the temperature increase in the presence of the most intense beams we used (~ $1W/cm^2$) is only 2^oC. By using the tabulated values for the thermo-optic effect ($1.4\cdot10^{-4}K^{-1}$) [10] and the thermal expansion coefficient ($5.9\cdot10^{-6}K^{-1}$) [3], one should expect to observe $\Delta n=2.8\cdot10^{-4}$ and a tensile strain of $1.2\cdot10^{-5}$. These values are about two orders of magnitude smaller than those found by us experimentally. Moreover, the thermal expansion coefficient is a second rank tensor, and hence is isotropic in cubic crystals. This means that in cubic crystals, heating can only lead to isotropic lattice expansion, which clearly stands in a sharp contrast to our results. For example, thermo-optic effects cannot explain the lattice contraction displayed in Fig. 3. In a similar vein, thermo-optic effects in CZT can account only for expansion of the crystal unit cell, hence they cannot explain the contraction effect displayed in Fig. 3. The refractive index change cannot be attributed to elasto-optic effects for the same reasons that rule out attributing the observations to the dc Kerr effect. Namely, the elasto-optic effect is highly sensitive to light polarization, and is also described by a fourth-rank tensor with the same zero components as the dc Kerr effect, both are with a sharp contradiction with our experimental findings.

Our experimental findings suggest that the large refractive index changes and the huge strain we observe arise from light-induced breaking of the initial cubic symmetry of the CZT crystals. The light excites charge carriers that are subsequently separated by the electric field and then re-trapped, thereby establishing a strong internal space-charge field. The space-charge-field leads to collective ion displacements within the crystalline lattice, thereby breaking the initial cubic symmetry of the CZT crystals.

All experimental results described above are obtained for CZT crystals doped with V. To elucidate the role of the doping, we have performed a series of experiments with nominally undoped CZT crystals, in the same configurations and under the same experimental conditions described above. We find that the electro-optic response of undoped CZT is much weaker than in doped CZT. In fact, undoped CZT crystals behave exactly as expected from the electro-optic coefficient r_{41}=5.5pm/V, the values provided by conventional electro-optic effects in cubic semiconductors.

4. Conclusion

In conclusion, we have demonstrated that laser light causes significant lattice deformation within the bulk of CdZnTe: V crystals, which increase linearly with light intensity and quadratically with an applied electric field up to 0.15%. This light-induced electrostriction is accompanied by an enormous enhancement of the electro-optic effect, resulting in a giant refractive index change of about 0.01. To our knowledge, such light-induced deformation and refractive index changes are the highest ever reported for a bulk semiconductor, and cannot be explained through intrinsic electrostriction and the dc Kerr effects. The CZT: V is, most probably, not the sole crystal in which the observed phenomena can occur. We believe that such light-induced symmetry-breaking effects will take place in the family of inorganic materials of cubic symmetry, containing ions weakly bonded and easy to move, and doped with midgap dopants. The symmetry breaking itself, being of ionic nature, occurs in time scales of the order of the dielectric relaxation time, which, for the ~ $1W/cm^2$ intensity used in our experiments, is of the order of a few msec. However, once the initial symmetry is broken and the crystal acquires strong internal dipole moments, all of its nonlinear properties arising from ultrafast electronic origins are enormously enhanced as well. We therefore anticipate that, under illumination, CZT: V will be an efficient medium for nonlinear frequency conversion, optical rectification, and for generation of THz electromagnetic waves.

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