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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Light-induced symmetry breaking and giant non-linear effects in cubic semiconductor CdZnTe doped with V	**Experiment number**: MA-625
Beamline: BM 5	**Date of experiment**: from: 29 October 2008 to: 03 November 2008	**Date of report**: 10/08/09
Shifts: 15	**Local contact(s)**: Dr. Jose Baruchel	*Received at ESRF:*

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Report:

We used the BM05 beam line in order to carry out diffraction measurements, mostly in the imaging mode, with CdZnTe crystals doped by V. The measurements were performed *in situ* under laser irradiation and application of an external dc electric field. As was found by us before, the CdZnTe crystals doped by V (CZT:V) reveal enormously large electro-optic index change (about 0.01) under combined application of moderate light intensity up to 1 W/cm^2 and electric field up to a few kV/cm [1]. This finding, although not completely understood yet, opens new horizons for nonlinear frequency conversion, THz electromagnetic wave generation, electro-optic modulation, and self-deflection of optical beams.

Apparently, the giant light-induced electro-optic effect in CZT:V is due to the spatial separation of the photo-excited charge carriers under the applied electric field, which, in turn, stimulates ion displacements within unit cell. In fact, when performing dielectric measurements we found remarkable light-induced increase (30 times) of the room temperature dielectric permittivity in this material [2]. Light-induced ionic polarization is accompanied by impressive changes in the [001]-lattice *d*-spacings (up to 10^{-3}) detected by high-resolution X-ray diffraction and optical interferometry [3]. In order to explain these experimental findings, we assumed that light illumination combined with applied electric field, breaks the initial cubic symmetry of the crystal (by inducing ion displacements within unit cells) and causes significant re-structuring of all its tensors describing non–linear effects. In fact, if such light-induced phase transition takes place, we expect an enhancement of both quadratic electro-optic and electrostriction effects, which are described by tensors of the fourth rank and are quadratically dependent on the applied electric field. In our laboratory high-resolution X-ray diffraction measurements, we did find that the relative *d*-spacing changes are quadratically dependent on the applied electric field and linearly dependent on the light intensity [3].

During our experiment MA-625, we continued to study the discovered phenomena, focusing on the following issues:

- Understanding the mechanism of the light-induced phase transition and, first of all, the induced symmetry changes. This implies the measurement of relative *d*-spacing changes in different crystallographic directions.

- Homogeneity of the observed changes across the sample volume. This is an important point which allows us to separate our effect from known light-induced space charge density effects in photorefractive materials under inhomogeneous light illumination (see e.g. [4, 5]).

- Suppressing the light-induced phase transition and related effects by the diminishing the illumination area. Based on our preliminary optical measurements, we suspect that if the illuminated volume is much smaller then the volume of the crystal, the photo-excited charge density and the related (induced) electric field will not be enough to initiate the symmetry-breaking phase transition process.

For current experiment, we have prepared several crystals of different size with electrodes deposited on different crystal faces. However, valuable results were obtained with two crystals only, marked as S4 and S5, both having a cubic shape (5x5x5 mm^3) with polished faces nominally being of the [110], [1-10] and [001]-types. The deposited electrodes provided an electric field along the [1-10] direction. Other crystals revealed very high electric conductivity under irradiation by a 980 nm laser, which prevented from using them in further experiments. It also took rather long time for us the installation and learning the interlock system between the hutch door opening system and power supply of the laser, which was necessary safety requirement. In current synchrotron measurements we used (for the first time) a specially developed sample irradiation system which was separated from the sample holder and allowed much more freedom for sample movements, than previous system used in more fixed laboratory X-ray measurements. Namely, during the MA-625 experiment we used sample irradiation by the laser through a pinhole mounted in front of the sample, a 20 cm away from it.

Examples of the (220)-X-ray diffraction images taken at 15 keV from sample S4 by using an Axis 215 PTZ network camera (a 3 μm pixel size) are shown in Fig. 1. A strong effect of the light irradiation (intensity, *I*) and applied electric field, *E*, is clearly seen when comparing the upper (no light, no electric field) and lower (I = 530 mW/cm^2, E = 1.4 kV/cm) images. Lower image, as a whole, is substantially shifted to the left, i.e. far away from the direction of the incident beam. It means an increase of the Bragg angle and, correspondingly, lattice contraction along the [110]-crystallographic direction (an electric field being applied along the [1-10]-crystallographic direction). It is clearly seen that the entire crystal volume irradiated by X-rays is involved into lattice contraction, i.e. the effect is homogeneous, with no twisting or other inhomogeneous mis-orientation changes. By converting these image shifts to Bragg angles and then to the $\Delta d/d$-changes, we can quantify the combined effect of light irradiation and electric field on the CZT:V crystal. The obtained results for the relative (220)- *d*-spacing changes are plotted in Fig. 2, as a function of the applied electric field, E. The data received for several magnitudes of the electric field are grouped around the expected parabolic function (best fit is shown by solid line in Fig. 2). The maximum value, $\Delta d/d = -4 \cdot 10^{-3}$, is the highest one obtained for CZT:V crystals by using X-ray diffraction and optical measurements. With this sample, S4, we also succeeded to find one of the (111)-type reflections and carried out similar measurements, as for the (220)-reflection. The observed changes for the (111)-*d*-spacing are plotted in Fig. 3, as a function of the applied electric field, E. It is seen that the data fit well a parabolic function (solid line in Fig. 3), but the detected changes, still being negative, are 5-6 times smaller than those obtained for the (220)-reflection. It implies that the distortion of the unit cell is rather complicated which includes either positive and negative changes of certain structural parameters.

If to assume that the induced effects are morphic in nature [6], we can predict the symmetry reduction for specific experimental geometry. For example, when applying an electric field along the [1-10] direction of the zinc-blende structure, the only symmetry element which is common for the initial crystal symmetry (class *-43m*) and electric filed symmetry, is mirror

plane (*m*) containing the [1-10] and [001] crystallographic directions. It means that the initial cubic symmetry is reduced to monoclinic symmetry (class *m*) and we need four components of the symmetric strain tensor (or more exactly the tensor of the unit cell distortions) to be determined. This problem, generally, requires synchrotron X-ray diffraction measurements with four independent reflections for one investigated sample, which may be well defined goal for next beam session.

With sample S5, we studied potential influence of spatially limited (in area) light irradiation on structural changes in CZT:V crystals. In these measurements, we used three different slits: 1 mm, 0.42 mm, and 0.224 mm, mounted 6 cm away from the sample. We used (220)-reflection and light irradiation intensity, $I = 530$ mW/cm^2. Relative changes of the (220)-*d*-spacing are plotted in Fig. 4, as a function of the applied electric field (for all slits used, including no slit installed). Contrary to our expectations, we did not observe the reduction of the induced *d*-spacing changes with diminishing the slit opening. Moreover, with narrow slits we were able to reach higher electric fields (without electrically breaking the samples) and, in such a way, to obtain higher magnitudes of the relative *d*-spacing changes (see Fig. 4). It is possible that the slits used, nevertheless, are too large in order to suppress the initiation of the phase transition process. This point deserves further investigation.

In summary, the performed measurements, despite experimental difficulties mentioned, provided interesting and important results towards better understanding of light-induced phase transition in CZT:V crystals. First of all, we mention a very large contraction of the unit cell (up to 0.4%) along the [110]-direction when the electric field is applied along the [1-10]-direction. This is the highest light-induced structural change ever measured by us in CZT:V crystals. We stress that the light-induced lattice distortion is negative. As we found before, the same electric field (i.e. applied along the [1-10] direction) causes lattice expansion along the [001]-direction [3]. It means that in some crystallographic directions the positive and negative distortions can partially compensate each other, leading to much smaller effects, as we observed in this experiment with the (111)-reflection. Anyway, by measuring four or three different reflections (with the same sample) in case of electric field application along the [1-10] or [001]-direction, respectively, it is possible to completely restore the tensor of lattice changes. This will facilitate a comprehensive understanding of the symmetry reduction during light-induced phase transition in CZT:V.

References

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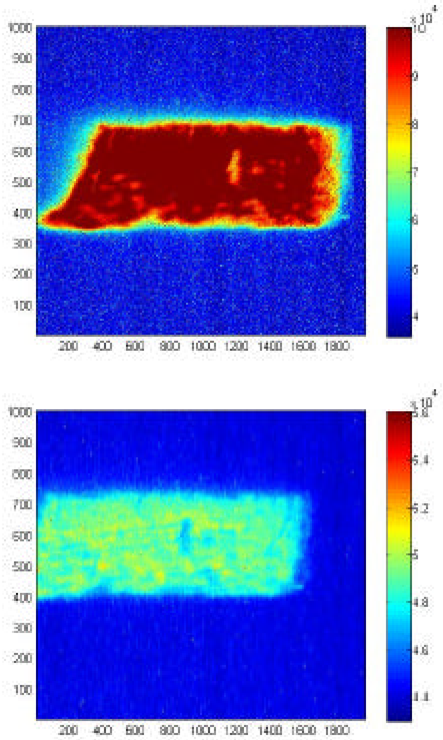

Figure 1. Diffraction images taken with a CZT crystal (S4, (220)-reflection) with no light and no electric field (upper panel) and under light irradiation and electric field application (lower panel: I = 530 mW/cm^2, E = 1.4 kV/cm).
The left-side shift of a whole image in the lower panel, as compare to the image position in the upper panel, demonstrates the net effect of the laser and electric field application. This shift corresponds to the increasing of the Bragg angle and, hence, reveals a remarkable lattice contraction along the [110]-crystallographic direction.

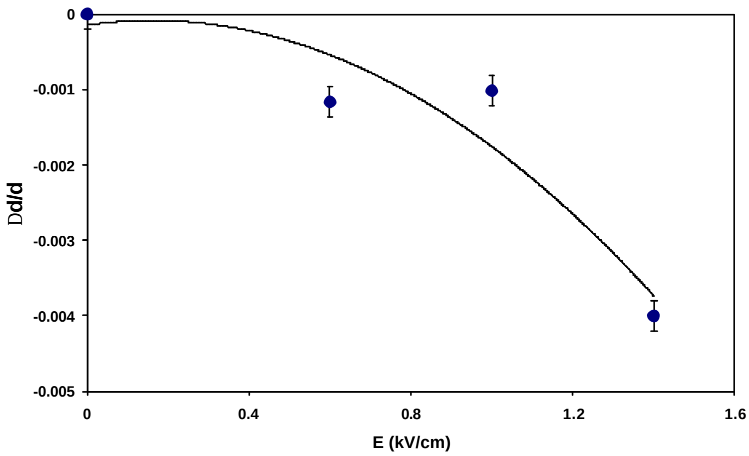

Figure 2. Relative changes, Δd/d, of the (220)-*d*-spacing in the light-irradiated CZT crystal (S4, I = 530 mW/cm^2), as a function of the applied electric field (in kV/cm).
Solid line represents best fit to parabolic function.

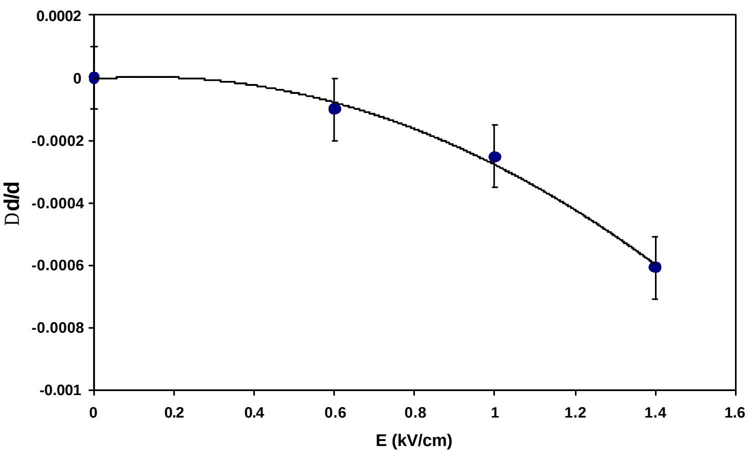

Figure 3. Relative changes, Δd/d, of the (111)-*d*-spacing in the light-irradiated CZT crystal (S4, I = 530 mW/cm^2), as a function of the applied electric field (in kV/cm).
Solid line represents best fit to parabolic function.

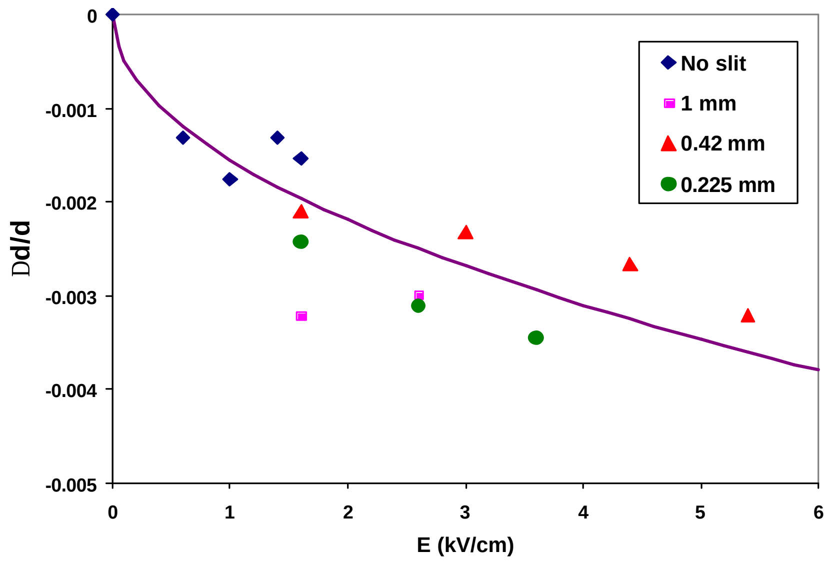

Figure 4. Relative changes, Δd/d, of the (220)-*d*-spacing in the light-irradiated CZT crystal (S5, *I* = 530 mW/cm^2), as a function of the applied electric field, E (in kV/cm). Measurements were performed with different slits, which limited the irradiated area: blue diamonds – no slit; pink squares – 1 mm; red triangles – 0.42 mm; green circles – 0.225 mm.

Solid line, showing the "center of gravity" for the whole data set, is drawn by eye.