International seminar on Nanoscience and Technology- conference proceedings. Sept- 2016
Volume 3, Special Issue - Available Online: http://ijrset.in/Volume3,Special-Issue-I.php Pages: 33-36

ISSN 2394-739X
International Journal for Research in Science Engineering and Technology

LOW DOSE IRRADIATION (γ-RAYS) EFFECTS OF MORPHOLOGICAL AND OPTICAL STUDY ON ZnCd $(SCN)_4$

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ABSTRACT- Low dose irradiation effects in Single crystals of bimetallic $ZnCd(SCN)_4$ (abbreviated as ZCTC) irradiated with γ-rays. The crystal was grown by slow cooling method and third order optical nonlinearities are investigated by single beam Z-scan technique with a He:Ne laser operated at 632.8 nm. The nonlinear refractive index, absorption coefficient and third order susceptibility are estimated to be -1.99×10^{-12} cm^2/W, 5.62×10^{-6} cm/W and 3.94×10^{-9} esu respectively. The full width at half maximum (FWHM) of the diffraction curves is 5.5 arc s, which is very close to that expected from the plane wave theory of dynamical X-ray diffraction. The surface feature is investigated by AFM.

Keywords- [Crystal growth; Z-Scan; HRXRD; Atomic force microscopy]

1. INTRODUCTION

The search for new materials with enhanced nonlinear optical (NLO) properties has increased considerably over the recent years as a result of wide range of applications in optical communication, photonics, electronics and optical storage systems. Hence, there is a demand for materials with large NLO figure of merit, high resistance to laser damage, good environmental stability and overall high performance [1]. Hence, researchers are focusing their attention on organometallics, which combine the advantages of both organic and inorganic materials. Among the different types of organometallic NLO materials, the thiocyanate (SCN) ligand based bimetallic crystals possess several advantages due to their high transparency, better nonlinear optical response and, moderate mechanical and thermal stability, which make them potential materials for crystal engineering based three dimensional (3D) coordination networks. The organic ligand is usually more dominant in the NLO effect. Especially, the SCN organic ligand with medium sized π-electron systems such as benzene derivatives has its SHG efficiency higher than that of urea. ZCTC belongs to tetragonal system, space group $I\bar{4}$ with a=11.445(2) Å, c=4.202(1) Å, V=550.4(2) Å^3, Z=2, D_c=3.2148 g/cm^3. High optical quality ZCTC single crystals were grown by Yuan et al [2]. Though the growth of ZCTC crystal has been achieved by the crystal growers, there are still challenges pertaining to the growth of large size single crystals free from defects. The aim of the present work is to carry out the growth of organometallic crystal of ZCTC and investigate its Z-scan study and atomic force microscopic study (AFM) studies are also carried out to expedite the use of the crystal for device fabrication. Crystalline perfection of the grown crystals by high resolution X-ray diffraction (HRXRD) studies

2. GROWTH OF CRYSTAL

High purity (E-Merck, AR grade) starting materials were used. The following reaction is expected to take place;

$$4NH_4SCN + ZnCl_2 + CdCl_2 \rightarrow ZnCd(SCN)_4 + 4NH_4Cl$$

The synthesized product of ZCTC was purified by recrystallization and dissolved in mixed solvent of ethanol and water (1:1). In accordance with the solubility data, saturated solution of 200 ml of ZCTC was prepared and kept in cryostate for slow cooling. The temperature was then reduced from 45 °C at a temperature lowering rate of 0.1 - 0.2 °C per day and crystals of dimension up to 10 x 9 x 3 mm^3 were obtained. When the sample is irradiated by using ^{60}Co-gamma source with a dose of 200Gy.

3 RESULTS AND DISCUSSION

1.3. Z-Scan Study

Development of high power laser sources has motivated an extensive research in the study of nonlinear optical properties and optical limiting behaviour of materials[3,4]. For the usage of the crystals to be efficient, it is necessary to have quantitative information about their nonlinear optical properties. Such nonlinear optical phenomena as nonlinear refraction and absorption can seriously affect the operation of laser devices. In part, intensity dependent refraction index of laser material causes the changes in the spatial distribution of laser field and can lead to self-focusing of the radiation and breakdown of device. It is the main factor which restricts the light intensities used and output laser power.

In the present investigation, the sample of ZCTC was translated in the Z–direction along the axis of a focused Gaussian beam from the He-Ne laser at 632.8 nm and the far field intensity is measured as a function of the sample position. By properly monitoring the transmittance change through a small aperture at the far field position (closed aperture), it is possible to determine the amplitude of the phase-shift. By moving the sample through the focus and without placing an aperture at the detector (open aperture), the intensity dependent absorption of the sample can be measured. When both the methods (open and closed) are used for the measurements, the ratio of the signals determines the nonlinear refraction of the sample.

The real and imaginary parts of the third order nonlinear optical susceptibility ($\chi^{(3)}$) are defined as

$$\text{Re}\ \chi^{(3)}\ (\text{esu}) = 10^{-4}\ (\varepsilon_0 c^2 n_0^2 n_2)\ /\pi\ (cm^2/W) \quad (1)$$

$$\text{Im}\ \chi^{(3)}\ (\text{esu}) = 10^{-2}\ (\varepsilon_0 c^2 n_0^2 \lambda\beta)\ /4\pi^2\ (cm/W) \quad (2)$$

Where, ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum.

Figure.1 and 2 shows the open and closed aperture Z-scan curves for ZCTC crystal. In the closed aperture Z-scan curve, the pre-focal transmittance peak is followed by the post focal valley, which is the signature of negative nonlinearity [5]. The nonlinear refractive index, absorption coefficient and third order susceptibility are estimated to be $-1.78\times10^{-12} cm^2/W$, 8.66×10^{-6}cm/W and 6.025×10^{-9}esu respectively.

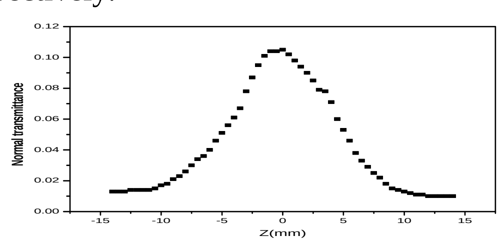

Figure 1- Open aperture Z-scan curve of ZCTC

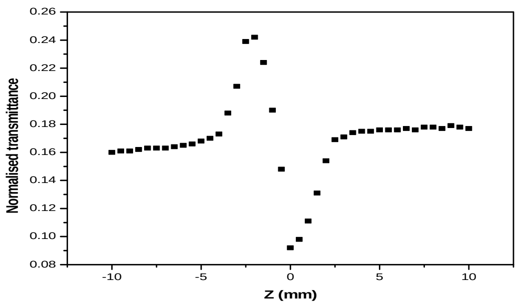

Figure 2- Open aperture Z-scan curve of ZCTC

3.2. HRXRD study

Figure 3 shows the DC recorded for ZCTC crystal using (2 0 0) diffracting plane in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer described above. As seen in the figure.3, the DC is quite sharp without any satellite peaks which may otherwise be observed either due to internal structural grain boundaries due to epitaxial layer which may sometimes form in crystals grown from solution [6].

The full width at half maximum (FWHM) of the diffraction curves is 5.5 arc s, which is very close to that expected from the plane wave theory of dynamical X-ray diffraction [7]. The single sharp diffraction curve with very low FWHM indicates that the crystalline perfection is extremely good. The specimen is a nearly perfect single crystal without having any internal structural grain boundaries. high-resolution DC recorded for a typical ZCTC single crystal specimen using (2 0 0) diffracting plane. On de-convolution of the diffraction curve, it is clear that the curve contains an additional peak, which is 23 arc s away from the main peak. This additional peak depicts an internal structural very low angle (tilt angle, α < 1 arc min) boundary [6] whose tilt angle [misorientation angle, α (please see the inset in the Figure) between the two crystalline regions on both sides of the structural grain boundary] is 23 arc s from its adjoining region.

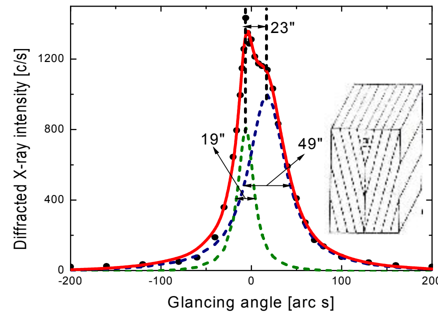

Figure 3- Diffraction curve for ZCTC single crystal for (2 0 0) diffracting plane

3.3. Atomic Force Microscopy Study

To better understand the morphology of a surface a quantitative description of the surface topography must be carried out. The topography matrix data should be treated in each profile line (2D) or over all profiles extending the analysis to surface (3D). The surface profile parameters are usually separated in four categories: amplitude, spacing, hybrid and functional.

Figure 4 show the 10, 0000 x 10, 000 nm^2 image morphologies of ZCTC crystal on the (1 0 0) face of sample. It is evident from the image (Fig.3) for ZCTC that the sample possesses almost smooth surface, Surface skewness (S_{sk}) values of ZCTC (0.226) and Roughness average (S_a) (4.77 nm). It has been reported that if the height distribution is asymmetrical and the surface has more peaks than valleys, the Skewness moment is positive, and if the surface is more planar and the valleys are predominant then the Skewness is negative [8].

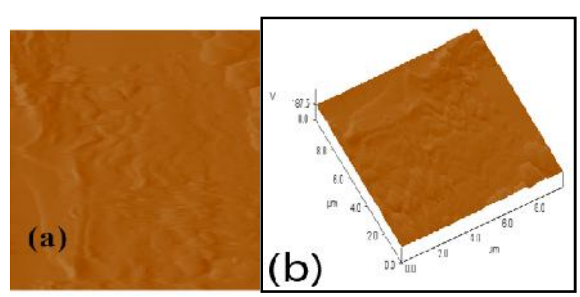

Figure 4- (a) AFM image and (b) 3D image of ZCTC

CONCLUSION

Organometallic single crystals of ZCTC was grown and by using the open and closed aperture Z-scan curves, parameters like nonlinear refractive index, nonlinear absorption coefficient and third order nonlinear optical susceptibility of these crystals were measured. The large magnitude of the third order nonlinear coefficients of these crystals shows that they are promising candidates for further materials development and possible photonic device applications. The negative sign of the nonlinear refractive index indicates that these materials exhibit self defocusing optical nonlinearity. From the HRXRD, the DC value indicated that the good crystalline quality of the ZCTC crystal.

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