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Third Order Non - Linear Optical Properties of Ammonium Bromide Single Crystals by Z-Scan Technique

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Abstract: Single crystals of Ammonium Bromide were grown by the solution growth method using methanol as a solvent. The crystal structure was studied by X-ray diffraction. The UV–Visual absorption spectra indicate a good transparency between 200 and 900 nm. The nonlinear refractive index n_2 and susceptibility $\chi^{(3)}$ have been measured through the Z-scan technique. Ammonium Bromide exhibits saturation absorption and self focusing performance. Non-linear absorption Co-efficient β is determined as $7.7627\times10^{-4}\,cm/W$. Non-linear refractive index n_2 measured at the wavelength of 632.8 nm is calculated as $1.6421\times10^{-8}\,cm^2/W$. The real and imaginary parts of $\chi^{(3)}$ have been measured at 632.8 nm and were found to be $1.2065\times10^{-7}\,esu$ and $2.7998\times10^{-6}\,esu$ respectively. Also, the absolute value of the third order Non-linear optical susceptibility $\chi^{(3)}$ is $2.8024\times10^{-6}\,esu$.

Keywords: Growth from solution, Ammonium Bromide, single XRD, U-V Spectrum, Z-Scan.

1. Introduction

The Z-Scan technique[1-3] is a popular method for the measurement of optical non-linearity of the material. It has the advantage of high sensitivity and simplicity. One can simultaneously measure the magnitude and sign of the non-linear refraction and non-linear absorption, which are associated with the real part $\chi_R^{(3)}$ and imaginary part $\chi_I^{(3)}$ of the third order non-linear susceptibilities. The Z-Scan technique has been used to measure the non-linear optical properties of semiconductors [4,5], dielectrics [6,7], organic or carbon-based molecules [8,9] and liquid crystals[10,11]. In this work, we present the growth of Ammonium Bromide single crystals by the solution growth method using methanol as a solvent. Single X-ray diffraction, optical absorption spectrum and Z-scan measurements were carried out. Z-Scan results reveal that it is a potential candidate for the optical switching [12] and optical limiting [13].

2.Experimental

Single crystals were grown using AR grade chemical and de-ionized water as a solvent by slow evaporation technique. By repeated re crystallization, water-clear plate like crystals of $0.5\times0.5\times1.1cm^3$ are obtained within 24 days. The grown crystals present good optical transparency. Grown crystals were as shown in the figure 1.

Figure 1 Grown Crystals of Ammonium Bromide

3. Results and Discussion

3.1 Single Crystal XRD

Single crystal X-ray diffraction analysis for the grown crystals has been carried out using ENRAF NONIUS CAD4 X-Ray diffractometer to confirm the lattice parameters of Ammonium Bromide. The single crystal data of Ammonium Bromide is given in Table 1.

Table 1. The single crystal X-ray data for Ammonium Bromide

System	**Monoclinic**		
Lattice parameter	$a =$ 15.8861	$b =$ 7.4891 $\AA$	$c = 17.1018$ $\AA$
	$\alpha = 90°$	$\beta = 117.45°$	$\gamma = 90°$
Volume (V)	1805.6 $\AA^3$		
Space group	P_{21}		

3.2 Optical Studies

The UV-Vis-NIR absorption spectra are very useful tool in the transmission range of the crystal for the study of NLO behaviour. Absorption spectra of the grown single crystals of Ammonium Bromide were recorded using Varian Cary 5E UV spectrophotometer in the range 200-900 nm. The spectra reveal a low UV cut off value at 340 nm for Ammonium Bromide. The absorption is found to be low in range 340 to 900 nm for Ammonium Bromide. Figure 2 shows the UV-Vis-NIR spectra of Ammonium Bromide.

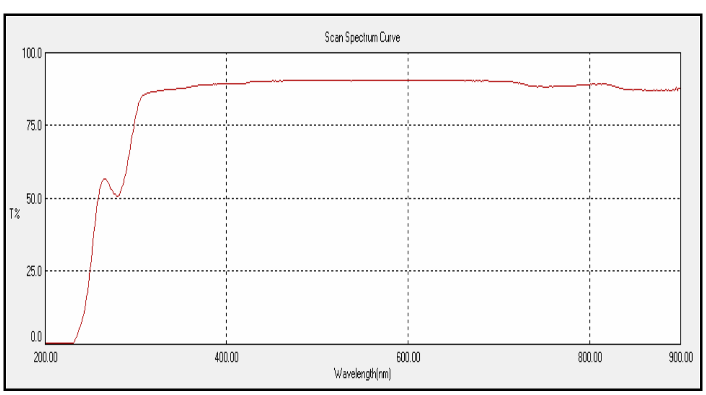

Figure 2. UV-Vis-NIR Spectra of Ammonium Bromide

3.3 NLO Measurements

3.3.1. SHG Measurement

The second harmonic generation efficiency of the grown crystals were carried out using the powder technique [14]. The sample is irradiated at 1064nm Nd:YAG pulsed laser. The second harmonic signal was absent for this sample and it confirms the centro-symmetry nature of this crystal.

3.3.2 Third Order Non-Linear Optical Measurement using Z-scan Technique

A spatial distribution of the temperature in the crystal surface is produced due to the localized absorption of a tightly focused beam propagating through the absorbing sample. Hence a spatial variation of the refractive index is produced which acts as a thermal lens resulting in the phase distortion of the propagating beam. The difference between the peak and valley transmission $\left(\Delta T_{P-V}\right)$ is written in terms of the on axis phase shift at the focus as,

$$\Delta T_{P-V} = 0.406\left(1-S\right)^{0.25}\left|\Delta\Phi_0\right| \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where, nonlinear phase shift with the sample at focus (Z=0)

$$\Delta\Phi_0 = \frac{2\pi}{\lambda} n_2 I_0 L_{eff} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The nonlinear refractive index is given by

$$n_2 = \frac{\Delta\Phi_0}{K\ I_0\ L_{eff}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where, $\Delta\Phi_0$ is the phase shift with the sample at focus (Z=0), $K = \frac{2\pi}{\lambda}$ (λ is the laser wavelength), 'L_{eff}' is the effective thickness of the sample $= \frac{\left(1-e^{-\alpha L}\right)}{\alpha}$ 'L' is the thickness of the sample. 'I_0' is the intensity of the laser beam at the focus (Z=0) .

"S" is the transmittance of the aperture in the absence of a sample and calculated using the relation

$$S = 1-\exp\left(\frac{-2\ r_a^2}{\omega_a^2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where, "r_a" is the aperture and ω_a is the beam radius at the aperture.

From open aperture Z-scan data, the non-linear absorption coefficient is estimated as

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where, ΔT is the one valley value at the open aperture Z-scan curve.

The value of β will be positive for saturable absorption and negative for two photon absorption. The real and imaginary parts of the third order Non-linear optical susceptibility $\chi^{(3)}$ are defined as

$$\mathrm{Re}\ \chi^{(3)} = \frac{10^{-4}\times\left(\varepsilon_0 c^2 n_0^2 n_2\right)}{\pi} \quad (esu)$$

$$\mathrm{Im}\ \chi^{(3)} = \frac{10^{-2}\times\left(\varepsilon_0 c^2 n_0^2 \lambda\ \beta\right)}{4\pi^2} \quad (esu)$$

$$\ldots\ldots (6)$$

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. The absolute value of the third order Non-linear optical susceptibility $\chi^{(3)}$ is calculated from the formula

$$\chi^{(3)} = \sqrt{\left(\mathrm{Im}\,\chi^{(3)}\right)^2 + \left(\mathrm{Re}\,\chi^{(3)}\right)^2}\ (esu) \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Figure 3 shows the normalized transmittance for the Open Aperture (OA) curve of Ammonium Bromide. The transmission is symmetric with respect to the focus (Z = 0), where it has a Maximum transmission. This indicates that the materials exhibit Saturation Absorption (SA).

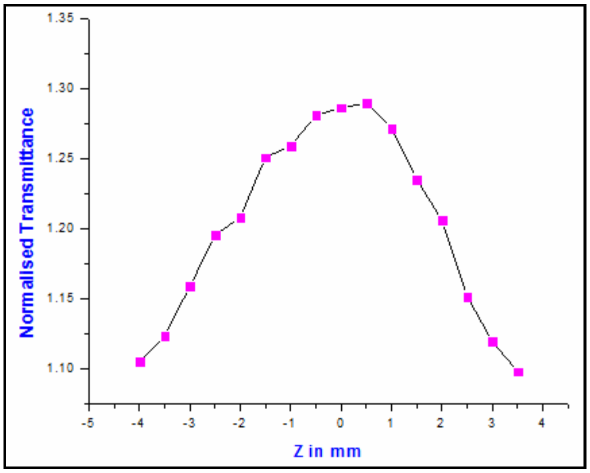

Figure 3. Open Aperture curve of Ammonium Bromide

Figure 4 shows the normalized transmittance for the Closed Aperture (CA) curve of Ammonium Bromide. The valley to peak configuration of the curve (Figure 4) suggests that the refractive index change is positive, exhibiting a self focusing effect. This may be an advantage for the application in protection of optical sensors. As seen from the closed aperture Z-scan curve, the prefocal transmittance valley is followed by the post focal peak which is the signature of positive nonlinearity [15].

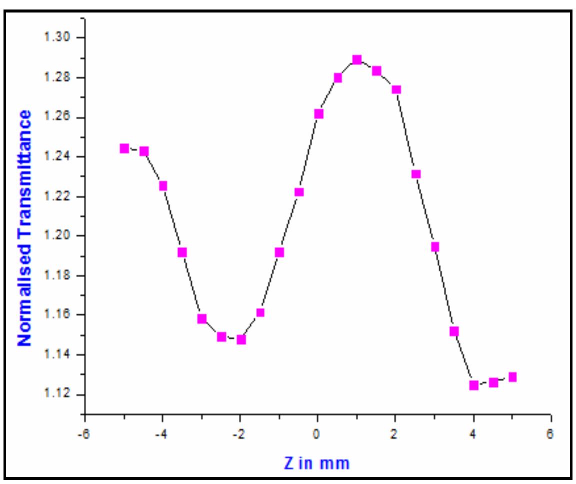

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Figure 4. Closed Aperture Curve of Ammonium Bromide

Figure 5 shows the division curve of the grown sample by combining OA and CA curves. The division curve is used to calculate third order susceptibility of the grown material.

The calculated value of the nonlinear refractive index n_2 is found to be $1.6421 \times 10^{-8}\ cm^2/W$. As the material has a negative refractive index, it results in self de– focusing nature of the material. From the open aperture Z-scan curve, it can be concluded that the nonlinear absorption is regarded as saturation absorption. The nonlinear absorption coefficient (β) is found to be $7.7627 \times 10^{-4}\ cm/W$. The real and imaginary parts of $\chi^{(3)}$ have been measured at 632.8 nm and were found to be $1.2065\times10^{-7}\,esu$ and $2.7998\times10^{-6}\,esu$ respectively. Also, the absolute value of the third order Non-linear optical susceptibility $\chi^{(3)}$ is $2.8024\times10^{-6}\,esu$. The value of $\chi^{(3)}$ is found to be larger than the other well known compounds [16] and it is due to the p-electron cloud movement from the donor to acceptor which makes the molecule highly polarized. The value of the $\chi^{(3)}$ of Ammonium Bromide single crystals reported here is of the same order of the magnitude of the materials such as Chaclogenide glasses [17] and C60[18] etc.

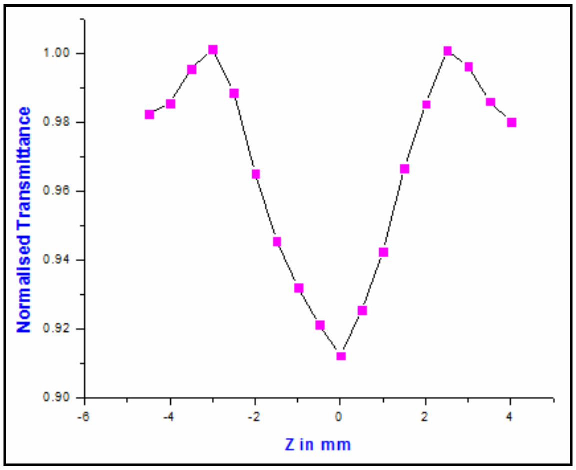

Figure 5. Division Curve of Ammonium Bromide

4 Conclusion

We have reported here the optical properties of Ammonium Bromide single crystal. The absence of SHG efficiency confirms the centro-symmetry nature of the crystal. The Z-scan measurement with 632.8 nm laser pulses revealed that non-linear refractive index of the crystal is in the range of $10^{-8}\,cm^2/W$. The measured third order non-linear properties confirm its suitability for non-linear optical devices such as optical limiting and switching.

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