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Third order Non - Linear optical properties of Aluminium Sulphate Single Crystals by Z-Scan Technique

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Abstract: Single crystals of Aluminium Sulphate were grown by the solution growth method using de-ionized water as a solvent. Crystals up to the size of $1\times1.2\times1.4\,cm^3$ were grown for optical characterization. Optical quality of crystal was observed to be good. Aluminium Sulphate has a higher figure of merit when compared to other crystals suitable for non-linear optical applications in the visible to near-infrared region. The crystal structure was studied by X-ray diffraction. The UV–Visual absorption spectra indicate a good transparency between 200 and 800 nm. The nonlinear refractive index n_2 and susceptibility $\chi^{(3)}$ have been measured through the Z-scan technique. Aluminium Sulphate exhibits reverse saturation absorption and self de-focusing performance. Non-linear absorption Co-efficient β is determined as $2.5113\times10^{-6}\,cm/W$ .Non-linear refractive index n_2 measured at the wavelength of 632.8 nm is calculated as $3.482\times10^{-8}\,cm^2/W$. The real and imaginary parts of $\chi^{(3)}$ have been measured at 632.8 nm and were found to be $9.5645\times10^{-7}\,esu$ and $6.3867\times10^{-6}\,esu$ respectively. Also, the absolute value of the third order Non-linear optical susceptibility $\chi^{(3)}$ is $6.4579\times10^{-6}\,esu$.

Keywords: Growth from solution, Aluminium Sulphate, 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 Aluminium Sulphate single crystals by the solution growth method using de-ionized water as a solvent. Single X-ray diffraction, optical absorption spectrum 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]. The experimental setup used to measure the nonlinear refractive index and absorption of our crystal sample in this work as depicted in the Figure 1.

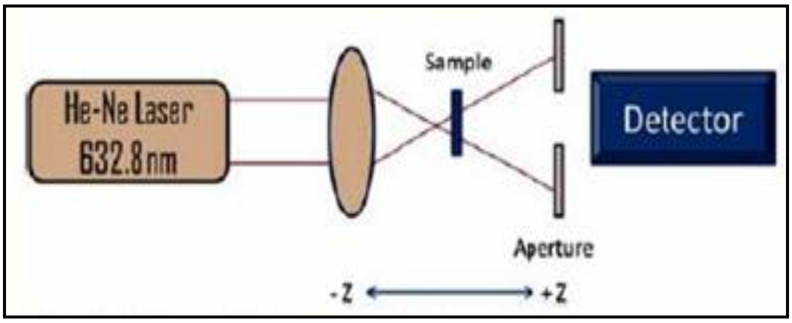

Figure 1 Schematic diagram of Z-scan technique

2. Experiments and Crystal Growth

Aluminium Sulphate 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 $1\times1.2\times1.4\,cm^3$ are obtained within 20 days. The grown crystals present good optical transparency. Grown crystals were as shown in the figure 2.

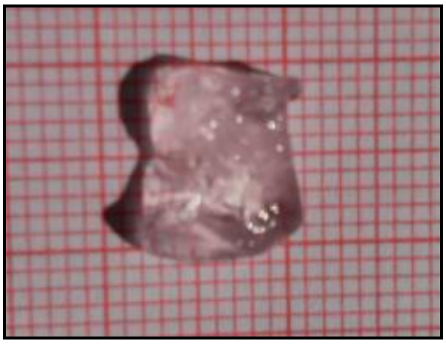

Figure 2 Grown Crystal of Aluminium Sulphate.

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 Aluminium Sulphate. The single crystal data of Aluminium Sulphate is given in Table 1.

Table 1. The single crystal X-ray data for Aluminium Sulphate single crystal

System	**Cubic**		
Lattice parameter	$a =$ 12.283 $\AA$	$b =$ 12.283 $\AA$	$c =$ 12.283 $\AA$
	$\alpha = 90°$	$\beta = 90°$	$\gamma = 90°$
Volume (V)	1853.16 $\AA^3$		
Space group	$Pa3$		

3.2 UV –Vis-NIR Spectra of Aluminium Sulphate

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 Aluminium Sulphate were recorded using Varian Cary 5E UV spectrophotometer in the range 200-800 nm. The spectra reveal a low UV cut off value at 381 nm for Aluminium Sulphate. The absorption is found to be low in range 380 to 800 nm for Aluminium Sulphate. Figure 3 shows the UV-Vis-NIR spectra of Aluminium Sulphate.

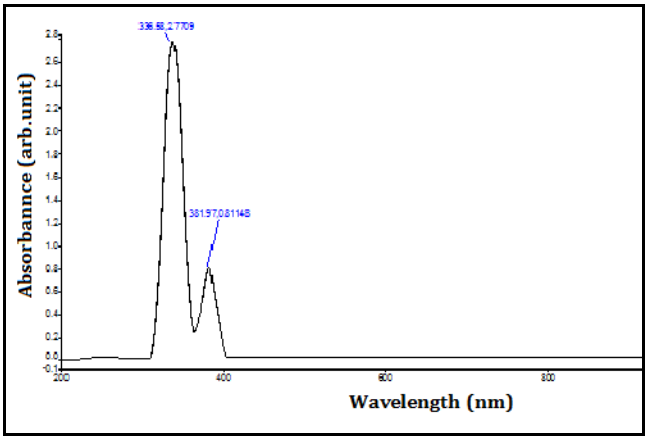

Figure 3. UV-Vis-NIR Spectra of Aluminium Sulphate

3.3 NLO Measurements

3.3.1. SHG Measurement

Powder SHG studies for Aluminium Sulphate single crystal has been carried out in accordance with the classical powder method developed by Kurtz and Perry [14]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm and pulse width of 8 ns with a repetition rate 10 Hz was used. The Aluminium Sulphate single crystals were powdered with a particle size of around 150 µm and placed in a micro capillary tube and exposed to laser radiation. The second harmonic signal was absent for this sample and it confirms the centro-symmetric nature of the crystals.

3.3.2. Refractive Index Measurement

The refractive index of the Aluminium Sulphate Single crystal was determined by Brewster's angle method using He-Ne laser of wavelength 632.8 nm. A polished flattened single crystal is mounted on a rotating mount at an angle varied from 0 to 90 degrees. The angular reading on the rotary stage was observed, when the crystal is perfectly perpendicular to the intra-cavity beam. The crystal was rotated until the laser oscillates and the angle has been set for maximum power output.Brewster's angle (θ_P) for Aluminium Sulphate single crystal is measured to be 55.93 degrees. The refractive index has been calculated using the equation $n = \tan\theta_P$, where θ_P is the polarizing angle and it is found to be 1.4786.

3.3.3. Third Order Non-Linear Optical Measurement

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 (ΔT_{P-V}) is written in terms of the on axis phase shift at the focus as,

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}|\Delta\Phi_0| \quad \text{………………..} (1)$$

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

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

The nonlinear refractive index is given by

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

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 $= \frac{(1-e^{-\alpha L})}{\alpha}$ '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

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

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

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

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

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

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

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

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

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

Figure 4 shows the normalized transmittance for the Open Aperture (OA) curve of Aluminium Sulphate. The transmission is symmetric with respect to the focus (Z = 0), where it has a minimum transmission. This indicates that the materials exhibit Reverse Saturation Absorption (RSA).

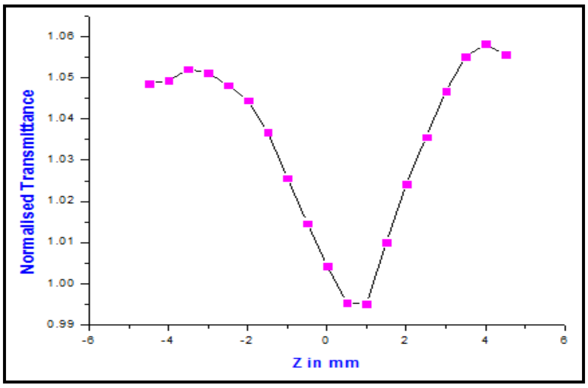

Figure 4 Open Aperture curve of Aluminium Sulphate

Figure 5 shows the normalized transmittance for the Closed Aperture (CA) curve of Aluminium Sulphate. The peak to valley configuration of the curve (figure 5) suggests that the refractive index change is negative, exhibiting a self de-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 peak is followed by the post focal valley which is the signature of negative nonlinearity [15].

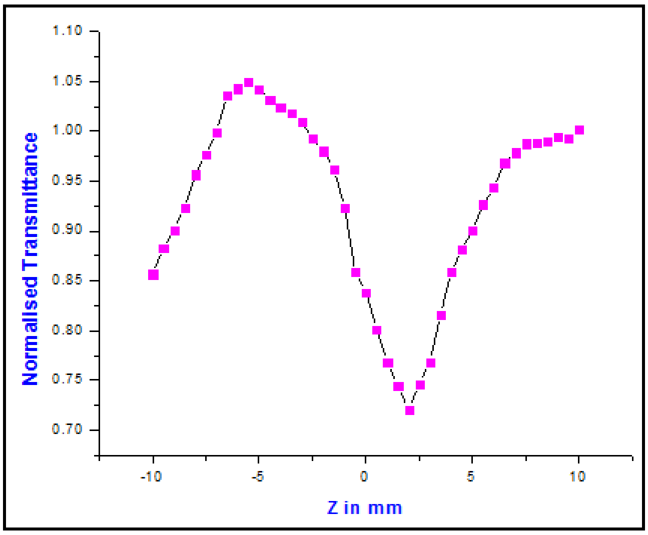

Figure 5 Closed Aperture Curve of Aluminium Sulphate

Figure 6 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.

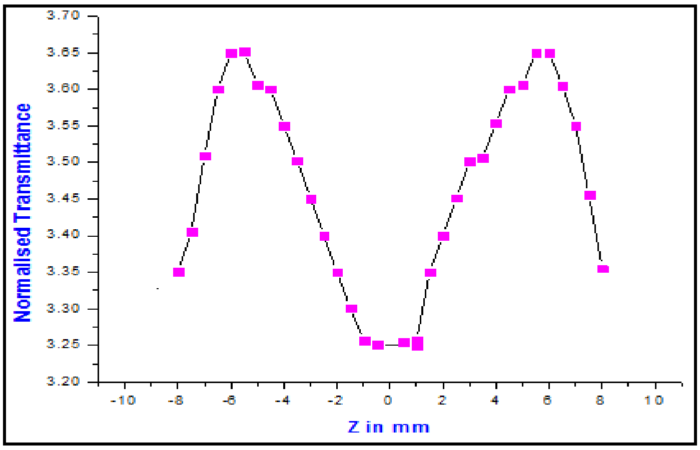

Figure 6 Division Curve of Ammonium sulphate

The calculated value of the nonlinear refractive index n_2 is found to be $3.482 \times 10^{-8}\,cm^2/W$. 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 reverse saturation absorption. The nonlinear absorption coefficient (β) is found to be $2.5113{\times}10^{-6}\,cm/W$. The real and imaginary parts of $\chi^{(3)}$ have been measured at 632.8 nm and were found to be $9.5646 \times 10^{-7}\,esu$ and $6.3867 \times 10^{-6}\,esu$ respectively. Also, the absolute value of the third order Non-linear optical susceptibility $\chi^{(3)}$ is $6.4579 \times 10^{-6}\,esu$. 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 Aluminium sulphate single crystals reported here is of the same order of the magnitude of the materials such as Chaclogenide glasses [17] and C60 [18] etc.

4. Conclusion

We have reported here the optical properties of Aluminium sulphate 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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References

1. Sheik – Bahe M, Said A A, Wei T H, Hagan D J and Van Stryland E W (1990) IEEE J.Quantum Electron. 26 760.
2. Zhao W and Palffy-Muhoray P (1993) Appl.Phys.Lett. 63, 1613. And Zhao W and Palffy-uhoray P (1994) Appl.Phys.Lett. 65, 673.
3. Yin M, Li H P, Tang S H and Ji W (2000) Appl. Phys. B 70, 587 - Annals of Optics 2006.
4. Sheik-BaheM.,Wang J. and Van stryland E.W. IEEE J. Quantum Electron 30 (1990), 249.
5. Krauss T. D. andWise F.W. Appl. Phys. Lett. 65 (1994), 1739.
6. Ma H. Gomes A. S. L. and de Araujo G. B. Opt. Commun. 87 (1992), 19.
7. Rangel-Rojo R.,Kosa T,Hajito E.,Ewen P.J.S., OwenA.E. KarA.K. and Whereett B.S.Opt. Commun. 09 (1994), 145.
8. Wei T. H., Hagan D. J., Sence M. J. Van Stryland E.W. Perry J.W. and Coulter D. R. Appl.Phys. B 54 (1992), 46.
9. Gu G.,ZhangW.,Zen H., Du Y., Han Y., Dong F.and Xia Y. J. Phys. B 26 (1993), L 451.
10. PAparo D., Maddalena P., Abbade G., Santamato E. and Jannossy. Mol. Cryst. Liq. Cryst.251 (1994), 73.
11. Li L., Yuan H. J., Hu G. H., and Palffy-Muthoray P. Liq. Cryst. 16 (1994), 703.
12. LeeW. Tutt, Thomas F. Boggess. Prog. Quant. Elecr. 17 (1993), 299.
13. Fryad Z. Henari, Shane MacNamara, Orla Stevenson, Joesph Callagham, Declan Weldon,Werner J. Blau. Adv. Mater 5 (1993), 930.
14. S K Kurtz, T T Perry (1968), J. Appl. Phys. 39,3798.
15. Wei T H , Hagan D J Sence M J Van Stryland E.W. Perry J.W. and Coulter D R (1992) Appl.Phys. B 54 46.
16. Gu G, Zhang W, Zen H, Du Y, Han Y, Dong F and Xia Y (1993) J. Phys. B 26 L 451.
17. F. Michelotti, E. Fazio, F. Sensi, Bretolotti (1993) Opt. Comm. 101, 74 1993) Adv.Mater. 5, 930
18. Fryad Z. Henari, Shane MacNamara, Orla Stevenson, Joesph Callagham, Declan Weldon, Werner J. Blau,

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