

Third order non-linear optical properties of potassium aluminium sulphate single crystals by Z-scan technique

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Abstract

Potassium aluminum sulphate dodeca hydrate crystals were grown from aqueous solution and studied by X-ray diffraction. The UV - Visual IR transmission spectra indicate a better transparency between 200 and 800 nm. The non-linear refractive index n_2 and susceptibility $\chi^{(3)}$ have been measured through the Z-scan technique. The results indicate that the compound exhibits saturation absorption and self-focusing performance. Non-linear absorption Co-efficient β is determined as $7.6746 \times 10^{-4} \text{ cm/W}$. Non-linear refractive index n_2 measured at the wavelength of 632.8 nm is calculated as $1.46412 \times 10^{-8} \text{ cm}^2/\text{W}$. The real and imaginary parts of $\chi^{(3)}$ have been measured at 632.8 nm and found to be $7.84088 \times 10^{-07} \text{ esu}$ and $2.07218 \times 10^{-08} \text{ esu}$, respectively. The measured 3rd order non-linear properties confirm its suitability for non-linear optical devices such as optical limiting and switching.

Keywords: Growth from solution, single XRD, UV spectrum, Z-scan.

Introduction

The Z-scan technique is a popular method for the measurement of optical non-linearity of the material. It has the advantage of high sensitivity and simplicity (Sheik-Bahe *et al.*, 1990; Zhao *et al.*, 1993; Yin *et al.*, 2000). 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 third order non-linear optical properties of semiconductors (Sheik-Bahe *et al.*, 1990; Krauss *et al.*, 1994), dielectrics (Gomes *et al.*, 1992; Rangel-Rojo *et al.*, 1994) organic or carbon-based molecules (Wei *et al.*, 1992; Zhang *et al.*, 1993) and liquid crystals (Paro *et al.*, 1994; Li *et al.*, 1994). In this work we present the growth of alum crystal (inorganic crystal type), "Potassium aluminium sulphate dodeca hydrate single crystals" from aqueous solution. Recent discoveries of efficient stimulated Raman scattering (SRS) with a large frequency shift ($\approx 1000 \text{ cm}^{-1}$) in inorganic crystals containing SO_4^{2-} ion groups in their structure (Li *et al.*, 1994) have again focused the attention of researchers. The use of SRS on potassium aluminium sulphate dodeca hydrate crystals made it possible to consider crystals as practical $\chi^{(3)}$ active nonlinear optical materials for Raman laser frequency converters. 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 optical switching (Lee *et al.*, 1993) and optical limiting (Fryad *et al.*, 1993).

Crystal growth

Potassium aluminum sulphate dodeca hydrate single crystals were grown from aqueous solution by slow evaporation method using AR grade chemicals. By repeated re crystallization, beautiful water-clear cubic crystals of size $6 \times 5 \times 3 \text{ mm}^3$ are obtained in 25 days. The grown crystals present good optical transparency. It is grounded to 2 mm thickness and shaped as shown in Fig 1.

Results and discussion

Molecular formula: $\text{KAl}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$

Molecular Weight = 474.39 gm.

Refractive index $n=1.453$

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. The values are $a=12.195 \text{ \AA}$, $b=12.217 \text{ \AA}$, $c=12.313 \text{ \AA}$ and the unit cell volume $V=1834.43 \text{ \AA}^3$. The crystal belongs to the cubic crystal system with the point group symmetry $2/m^3$ and space group $\text{Pa}3$.

Optical transmission spectrum

The optical transmission spectrum analysis of the grown crystal was carried out between 200 nm to 800 nm using Perkin Elmer UV-Visual spectrophotometer. The recorded spectrum is as shown in Fig. 2. The crystal is transparent in the entire visible region and shows maximum UV transmission.

Fig. 1. Potassium aluminium sulphate dodecahydrate single crystal

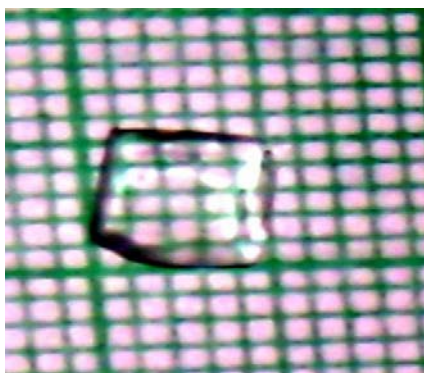


Fig. 2. UV-Visual IR transmission spectra of potassium aluminum sulphate

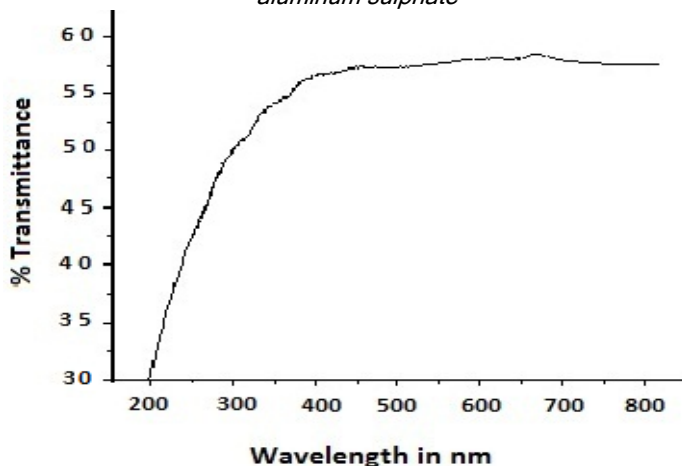


Fig. 3. Normalized transmission for the open aperture (OA)

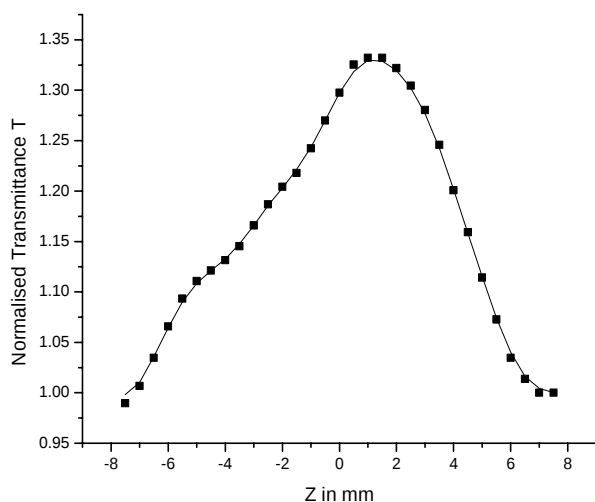
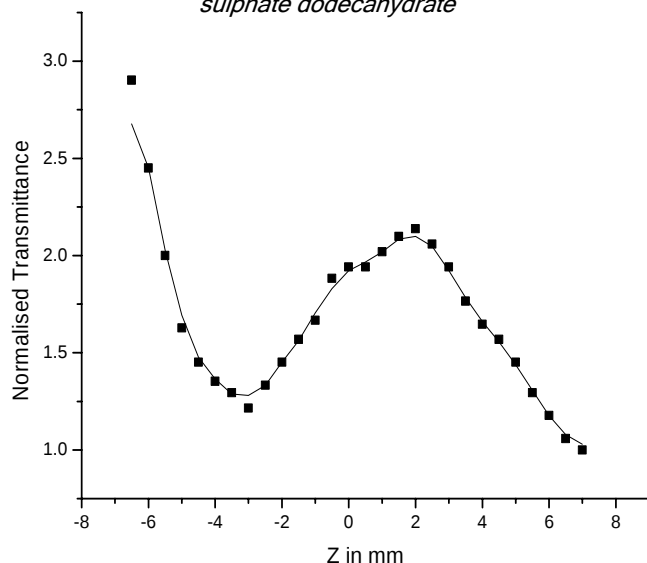


Fig. 4 Closed Aperture curve of potassium aluminum sulphate dodecahydrate



NLO measurements

SHG measurements: Powder SHG studies for Potassium aluminium sulphate dodecahydrate single crystal has been carried out in accordance with the classical powder method developed by Kurtz and Perry (1968). A Q-switched Nd: YAG laser beam of wavelength 1064 nm and pulse width of 8ns with a repetition rate of 10 Hz was used. The potassium aluminium sulphate dodecahydrate was powdered with a particle size of 100-150 μm and then placed in a micro capillary and exposed to laser radiation. The second harmonic signal was absent for this sample and it confirms the centro-symmetry nature of this crystal.

Refractive index measurement: The refractive index of the potassium aluminium sulphate dodecahydrate crystal was determined by Brewster's angle method using He-Ne laser of wavelength 632.8 nm. A polished flattened single crystal of Potassium aluminum sulphate dodecahydrate single crystal is mounted on a rotating mount at an angle varied from 0 to 90°. 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 potassium aluminium sulphate dodecahydrate is measured to be 55.46°. The refractive index has been calculated using the equation $n = \tan \theta_p$; where " θ_p " is the polarizing angle. The refractive index is found to be 1.453.

Z-scan method: The third order nonlinearities of potassium aluminum sulphate dodecahydrate were investigated with the Z-scan method. Schematic diagram of Z-scan setup is as shown by us elsewhere (Sivanesan *et al.*, 2010). A CW He-Ne laser of wavelength of 632.8 nm was used in the experiment. The laser beam was focused to a waist of 45 μm with the help of a convex lens of focal length 12 cm to give the intensity at the focus $6.25 \times 10^7 \text{ W/m}^2$. The sample is moved along the (beam direction) optic axis (Z-direction) through the focus of the lens. The energy transmitted through an aperture is recorded as a function of the sample position. The Rayleigh length of Z_0 calculated is lesser than the thickness of the sample. Fig. 3 shows the normalized transmission for the open aperture (OA). The transmission is symmetric with respect to the focus ($Z=0$), where it has a minimum transmission. This indicates that the sample exhibits Saturation Absorption (SA). Phase shift at the focus is calculated using the relation

$$\Delta\Phi_0 = \beta I_0 L_{\text{eff}} / Z \quad (1)$$

$L_{\text{eff}} = [1 - \exp(-\alpha d)] / \alpha$ where α is the linear absorption coefficient at 632.8 nm and " d " is the thickness of the sample. L_{eff} is the effective thickness of the sample I_0 is the intensity of the beam focused at the focus and β is Non-linear absorption co-efficient β is calculated from the formula

$$\beta = 2\sqrt{2}\Delta T / I_0 L_{\text{eff}} \quad (2)$$

The calculated value of $\beta = -8.88863 \times 10^{-5} \text{ cm/W}$. The imaginary part of the third order non-linearity $\chi_I^{(3)}$ is related to the non-linear absorption co-efficient β by the relation:

$$\chi_I^{(3)} = 10^{-2} \epsilon_0 c^2 n_0^2 \lambda \beta / 4 \pi^2 \quad (3)$$

Where n is the linear refractive index ($n=1.453$ at $\lambda = 632.8 \text{ nm}$) ϵ_0 is the permittivity of free space and c is the velocity of light. The experimentally determined value of $\chi_I^{(3)}$ at 632 nm was found to be $2.707218 \times 10^{-05} \text{ cm}^2/\text{W}$. The normalized transmittance for closed aperture (CA) is observed in Fig. 4.

The non-linear refractive index of the said crystal is calculated using the relation:

$$'n_2'' = \Delta\Phi_0 / K I_0 L_{\text{eff}} \quad (4)$$

The valley to peak configuration of the curve (fig. 4) suggests that the refractive index change is positive, exhibiting a self focusing effect. The value for non-linear refractive index " n_2 " calculated by Z-scan method is found to be $1.46412 \times 10^{-8} \text{ cm}^2/\text{W}$.

The real part of the third order non-linear susceptibility is calculated from the relation

$$\chi_R^{(3)} = 10^{-4} \epsilon_0 c^2 n_0^2 n_2 / \pi \text{ cm}^2/\text{W} \quad (5)$$

The value of $\chi_R^{(3)}$ at 632 nm was found to be $7.84088 \times 10^{-07} \text{ cm}^2/\text{W}$. By comparing the values of imaginary and real non-linearities, one can come to the conclusion that the $\chi_I^{(3)} > \chi_R^{(3)}$, i.e. $\chi_I^{(3)}$ which gives rise to the absorption change is dominant and this can be seen from Fig. 4 where the valley is much larger than the peak. The absolute value of $|\chi^{(3)}|$ was calculated from the formula:

$|\chi_R^{(3)}| = \sqrt{(\chi_I^{(3)})^2 + (\chi_R^{(3)})^2}$ gives $6.21083 \times 10^{-06} \text{ esu}$. The value of the $\chi_I^{(3)}$ and $\chi_R^{(3)}$ of potassium aluminium sulphate dodeca hydrate reported here is of the same order of the magnitude of the material such as carbon di sulphide (Sheik-Bahe *et al.*, 1990) and C_{60} (Fryad *et al.*, 1993) etc.

Conclusion

We have reported here the optical properties of potassium aluminium sulphate dodeca hydrate 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 $10^{-8} \text{ cm}^2/\text{W}$. The measured 3rd order non-linear properties confirm its suitability for non-linear optical devices such as optical limiting (Lee *et al.*, 1993) and switching (Fryad *et al.*, 1993).

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