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Investigations on optical, theoretical, mechanical and dielectric properties of newly synthesised optical single crystal - trisglycine epsomite

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Abstract : A novel, semi-organic peculiar optical crystal trisglycine epsomite (TGE) has been synthesized from aqueous solution by conventional solution growth method at room temperature. Single crystal XRD study has been carried out to categorize the crystal system and lattice parameters. PXRD study reveals the crystalline nature of the crystal. Optical spectral studies have been conducted to locate the cut-off wavelength, absorption coefficient, extinction coefficient and optical band gap of the material. The dielectric constant and dielectric loss as a function of frequency were measured. The solid state parameters of the title compound such as valence electron, plasma energy, Penn gap and Fermi energy were calculated theoretically using the empirical relation and deduced their electronic polarizability, found to be better-quality than KDP. The mechanical behaviors of TGE were studied by utilizing Vickers micro hardness tester.

Key Words : Solution growth, Optical Properties, dielectric constant, Penn analysis Vickers's hardness number.

1. Introduction

Many research groups have swiftly prompted to hunt for novel promising amino acid complexes with inorganic salts showing superior properties in many opto electonic applications like signal transmission, data storage, optical switching, laser printing, infloresescence, photolithography, remote sensing, chemical and biological species detection, high resolution spectroscopy, medical diagnosis and underwater monitoring and.

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communication[1]. Simplest among the amino acids is glycine existing in zwitterionic form having two or more types of coordination atoms to act as bridging ligands, tendency to form complexes with anionic, cationic and neutral chemical compounds. It has been subjected to extensive research for their efficient NLO properties.[2] The glycine molecule is found to form many compounds with metal sulfates, metal halogenides and acids. The epsomite (MgSO4:7H2O), as a source of Mg2+ ions has wide applications in medicine (acute management of cardiac arrhythmia) and agriculture (fertilizer)[3]. This material, when doped with selected activators yields efficient for nonlinear optical (NLO) applications. In the same manner it was found that the optical quality of the Epsomite crystal improves on doping with KCl. From technological and application point of view, in the present study, an attempt has been made to grow high quality optically efficient semiorganic amino acid complex triglycine magnesium sulphate single crystal by solution growth method, and reported their optical theoretical, mechanical and dielectric properties in detail.

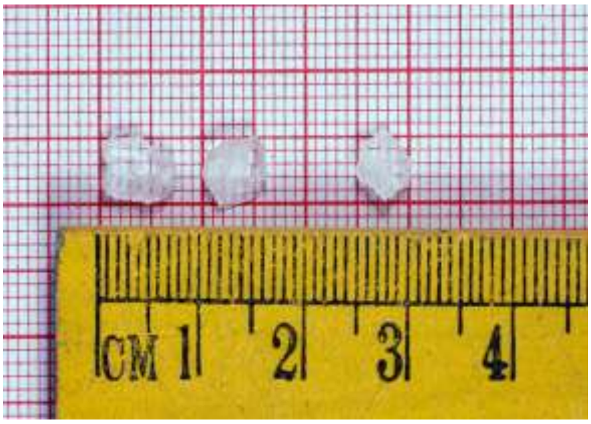
2. Experimental

2.1 Growth and synthesis

Glycine complex optical crystal TGE was synthesised by taking Analar grade Glycine and magnesium sulphate in 3:1 stoichiometric ratio, and dissolved in double distilled water. The

resultant growth solution was stirred perpetually for 8 hrs to achieve the homogenous equilibrium and filtered for purity. A white crystalline TGE salt was obtained after consummate evaporation of solvent at room temperature. The purity of the synthesized salt was further increased by repeated re-crystallization. After growth period of 20 days, good quality single crystal were harvested and is as shown Figure 1.

Figure 1-Photograph of as grown crystal TGE



3. Results and discussions

3.1 Single X-ray diffraction study

The single crystal X-ray diffraction (XRD) analysis was carried out using Bruker X8 Kappa APEXII spectrometer (USA) to study its unit cell dimensions. Single crystal XRD substantiate that the TGE crystallizes in triclinic with noncentrosymmetric space group $P\bar{1}$ and which are in very good agreement with the reported values[4], as listed in Table 1, thus satisfying one of the indispensable requirement for NLO activity of the crystal.

Table 1-Single crystal x-ray diffraction data of TGE crystal

Parameters	**Lattice parameters (Å)**			**Interfacial angles**			**V ($Å^3$)**	**Crystal system**	**Space group**
	a	**b**	**c**	**α**	**β**	**γ**			
Present study	5.96	8.47	13.38	88.8°	82.9°	52.9°	534.7	triclinic	$P\bar{1}$
Reported values [4]	5.98	6.78	13.39	85.3 °	82.8°	82.8°	534.7	triclinic	$P\bar{1}$

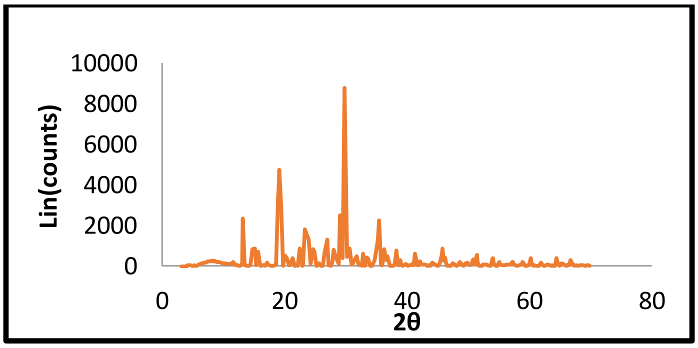
3.2. Powder X-ray diffraction studies

The synthesised mateaial were subjected to powder XRD using D8 advance and Bruker X-ray diffract meter with $CuK_{\alpha}1$ radiation (λ=1.5406Å) studies, to analyze whether the synthesized material is crystalline or amorphous. The powder X-ray diffraction pattern of TGE is as shown in Figure 2. It shows many diffraction peaks confirms the crystalline nature of the synthesised compoud. The average grain of the OMH were calculated using Scherer's equation

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

β is the half high width of the diffraction peak of the sample then β=0.217 and θ=14.51° is the Braggs' angle (deg.) Then the average size of the particle is 39.59.nm.

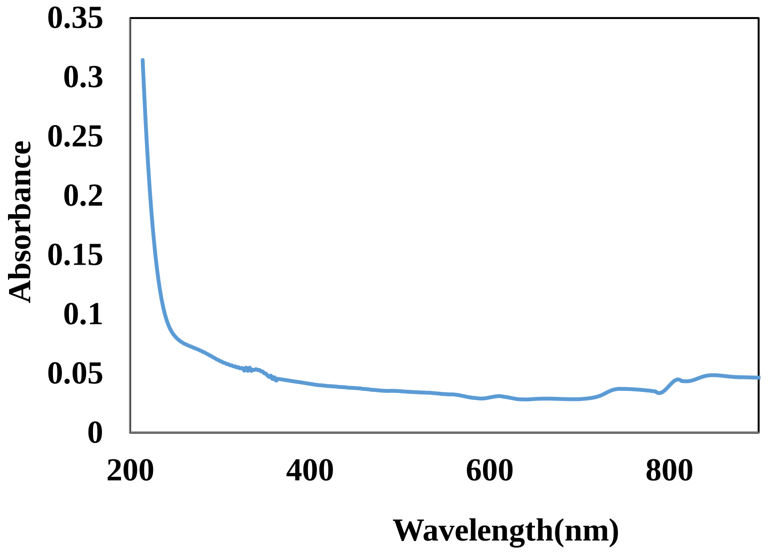
Figure 2 -Powder XRD spectrum of the TGE single crystal



3.3 UV-Vis-NIR spectral analysis

The UV-VIS-NIR absorbance spectrum was assessed using Varian, Cary 5000 with the wavelength range of 200-1000 nm to determine its optical transmittance and band gap. The recorded UV-Visible absorbance spectrum of the grown crystal is as shown in the Figure 3. Optical band gap and extinction coefficient were two important optical properties of materials to determine its usage in optoelectronic devices[5].

Figure 3 - UV-Vis-NIR absorbance spectrum of TGE crystal



Using the formula Eg = hc / λ, optical band gap of TKHP single crystals were determined to be Eg = 5.04 eV. The optical absorption coefficient (α) was premeditated from transmittance using the following relation,

$$\alpha = \frac{2.303}{d}\log\left(\frac{1}{T}\right) \qquad (2)$$

where T is the transmittance and d is the thickness of the crystal. The absorption coefficient was found to be α = 0.019 at 632 nm. The extinction coefficient (K) can be obtained from the following equation (4) and estimated to be 9.659×10^{-10} at λ = 632 nm.

$$K = \frac{\lambda\alpha}{4\pi} \qquad (3)$$

3.4 Dielectric studies

Transparent and good quality were selected for dielectric studies in the frequency range 50 Hz- 5 MHz using HIOKI 352-50 LCR HITESTER at different temperatures. It is significant and essential to study about the dielectric activities of materials in various fields such as optics, solid state, electronics and photonic device fabrications. Defect free, optically transparent TGE crystal of uniform cross sectional area 7.07×7.59 mm^2 and thickness 3.78 mm was chosen, and its outer coated with silver paint was placed between the two copper electrodes, which acts as parallel plate capacitor. The dielectric response of a material can be concisely described as a complex quantity made up of real and imaginary components, i.e., $\varepsilon = \varepsilon' + j\varepsilon''$ where ε' and ε'' are the real and imaginary components of dielectric constant respectively. The real part portrays the amount of energy stored by the material as a result of polarization, and imaginary component gives the energy loss by dielectric material placed in a varying electric field. Equations (3) and (4) are used to calculate the real and imaginary parts of dielectric constant of the grown crystal.

$$\varepsilon' = \frac{C\,d}{\varepsilon_0 A} \qquad (4)$$

$$\varepsilon'' = \varepsilon' \tan\delta \qquad (5)$$

where C is the capacitance (F), d is the thickness (m); A is the area (m^2) of the crystal, tanδ is the loss tangent and ε_0 is the absolute permittivity of the free space having the value 8.854×10^{-12} F/m.

The dielectric measurements at various frequencies are called dispersion[6]. The dielectric dispersion of the sample was noted for the applied frequency that ranging from 1 Hz to 5 MHz at different temperatures from 311 K to 401 K is shown in Figures 4 and 5 respectively, From Figure 3, it is observed that the dielectric constant shows normal behavior with frequency, i.e., real part of dielectric constant decreases with the increase in frequency. The low value of dielectric constant at high frequencies occurs due to the loss of these polarizations at low temperature[7]. The dielectric loss parameter characterizes the energy dissipation from the applied field into the dielectric materials shown in Figure 5. In the present study the low value of dielectric constant and dielectric loss with high frequency exhibits superior optical quality with fewer defects and this feature is specifically vital for employing this material probable for various nonlinear optical applications.

Figure 4 -Variation of dielectric constant with frequency

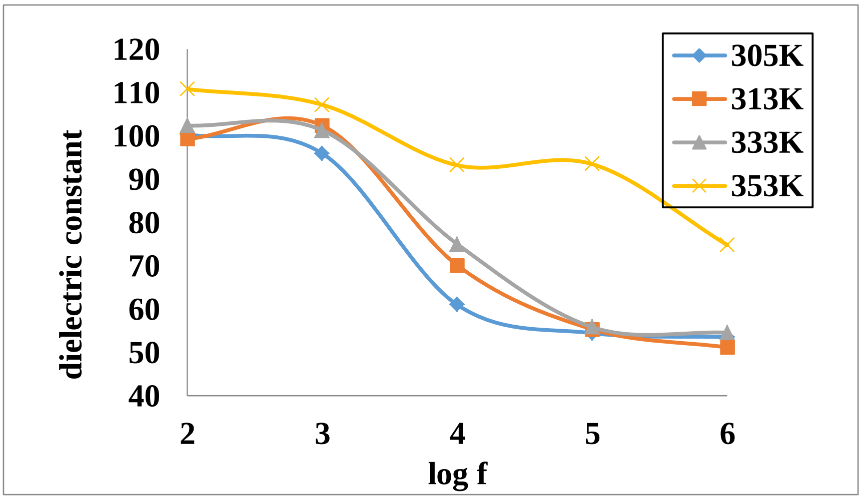
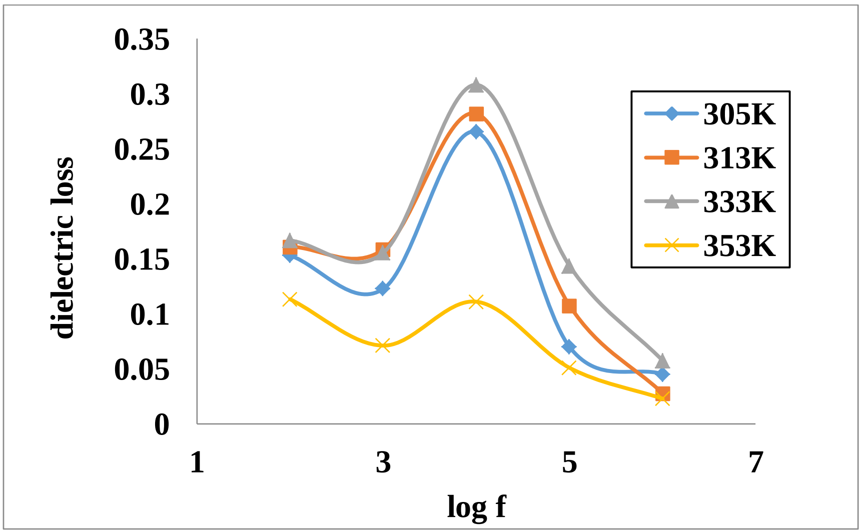


Figure 5 - Variation of dielectric constant with frequency



3.4.1. Determination of Electronic polarizability (α)

The dielectric measurement is a practical tool to work out the polarizability of the medium for evaluating NLO efficiency of TGE crystal. The dielectric constant at higher frequency (1MHz) is considered for these computations. According to the Penn model[8] the average Penn gap (E_p) and Fermi (E_F) were indented by subsequent equations.

$$E_p = \frac{\hbar\omega_p}{(\varepsilon_{r-}\ 1)^{\frac{1}{2}}} \qquad (6)$$

$$E_{F=}\ 0.2948\ (\hbar\omega_p)^{\frac{1}{2}} \qquad (7)$$

$$\hbar\omega_p = 28.8\left(\frac{Z\rho}{M}\right)^{\frac{1}{2}} \quad (8)$$

where Z=[$(9 \times Z_C) + (7 \times Z_H) + (3 \times Z_O) + (2 \times Z_N)$+$(1 \times Z_K) + (1 \times Z_S)$] =122. Z can be worked out by substituting respective valences electrons of elements existing in the sample.

The electronic polarizability (α) of the grown material is given by the relation[9],

$$\alpha = \left[\frac{(\hbar\omega_p)^2\ S_0}{(\hbar\omega_p)^2\ S_0 + 3\ (E_P)^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24}\ cm^3 \quad (9)$$

where S_0 is a constant for a particular material

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \quad (10)$$

The value of α is also inveterate by using Clausius-Mosotti equations.

$$\alpha = \left[\frac{3M}{4\pi N_A \rho}\right]\left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right] \quad (11)$$

where N_A is the Avagadro number.

Considering that the polarizability is highly sensitive to the band gap, the following empirical relationship is also used to calculate α using the optical band gap of TGE sample.

$$\alpha = \left[1 - \frac{\sqrt{E_g}}{4.06}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24}\ cm^3 \quad (12)$$

where E_g is the band gap, M is the molecular weight and ρ is the density of TGE crystal.

The calculated parameter of electronic polarizability (α) of TGE is higher than the standard KDP[10] and the values are scheduled in Table 2 proves that the polarizability enhances the optical properties of the material.

Table 2 -Solid state parameters of TGE crystal

Parameters	**Present study**	**Reported values of KDP[10]**
Plasma energy(eV)	22.94	17.29
Penn gap(eV)	3.041	0.3458
Fermi energy(eV)	19.22	13.18
Electronic polarisability by Penn gap analysis(cm^3)	7.214×10^{-23}	2.14×10^{-23}
Electronic polarizability by Clausius-Mosotti equation(cm^3)	7.219×10^{-23}	2.14×10^{-23}
Electronic polarizability by using band-gap(cm^3)	7.22×10^{-23}	-----

3.5. Mechanical studies

The fracture toughness, brittleness index and elastic stiffness constant were calculated using Microhardness Tester, MATSUZAWA MMTZ-7(Singapore) series. Hardness of the material gives information about resistance offers by the material to local deformation or damage under an applied stress[11] and it plays a significant role in device fabrication. A transparent, smooth and flat surface of the grown TGE crystal was subjected to hardness study at room temperature with the load ranging from 25-100g using Vicker's hardness. The indentation time was kept as 5s for all the loads. The Vickers microhardness number was calculated using the relation,

$$H_v = 1.8544 \left(\frac{P}{d^2}\right) kg/mm^2 \qquad (13)$$

where P is the indenter load and d is the diagonal length of the indentation marks in mm. A plot obtained between the hardness number (H_v) and the applied load (P) is depicted in

Figure 6. According to normal indentation size effect, the hardness of the crystal decreases with increasing load and but in present study the hardness of the grown TGE crystal shows reverse indentation effect(RISE)[12] indicates the behaviour of increase in hardness number with increasing load. In accordance with traditional Meyer's law, the relation connecting the applied load P and d, is given by [13],

$$P = K_1 d^n, \qquad (14)$$

and K_1 is the standard hardness value and n is the Meyers index or working hardening coefficient. The plot of log P versus log d for TGE crystal is shown in Figure 7, yields a straight line and from the slope, the work hardening exponent n is found to be 3.433. As per Onitsch[14] , the materials having workhardening exponent $1 \leq n \leq 1.6$ are hard materials and $n > 1.6$ are soft materials. Since in the present investigation the n value is 3.433, TGE belongs to soft category material.

In view of the fact, the material takes some time to revert to elastic mode, for every indentation a correction x is applied to the d value and Kick's law is related as

$$P = K_2 (d+x)^2 \qquad (15)$$

$$\text{(i.e) } d^{\frac{n}{2}} = \left(\frac{K_2}{K_1}\right)^{1/2} d + \left(\frac{K_2}{K_1}\right)^{1/2} x \qquad (16)$$

For the grown crystal, the plot $d^{\frac{n}{2}}$ versus d shown in Figure 8 gives slope $\left(\frac{K_2}{K_1}\right)^{1/2}$, the intercept is a measure of x. The striking factor x is positive only when $n < 2$ and negative for $n > 2$ and it is proved in our case.

The fracture toughness determines how much fracture stress is applied under uniform loading for a crystal with well-defined crack, resistance to fracture indicated the toughness of a material. The nature of crack system developed in TGE is radial-median and the fracture toughness (K_c) is given by

$$K_c = \frac{P}{\beta C^{3/2}} \qquad (17)$$

where P is the applied load and β the geometrical constant and the value is equal to 7 for Vickers indenter and the value of K_c is specified in Table 3. The another property which affects the mechanical behaviour is Brittleness index(B_i) which deals about the fracture induced in a material without any appreciable deformation. and is computed using the realation[15],

$$B_i = \frac{H_v}{K_c} \qquad (18)$$

For the hardness value, the yield strength(σ_v) was found out using

$$\sigma_v = \frac{Hv}{2.9}(1-(2-n))\left[\frac{12.5(n-2)}{1-(n-2)}\right]^{n-2} \qquad (19)$$

The elastic stiffness constant(C_{11}) were calculated for the title compound using Wooster's empirical relation is given by

$$C_{11} = H_v^{\frac{7}{4}} \qquad (20)$$

The mechanical parameters like K_1, K_2, H_v, K_c, B_i, σ_v and C_{11} were tabulated in Table 4 and it is verified from C_{11} (first order coefficient) that the binding forces between the ions are resonably tough and the mechanical strength of material was determined to be adequately large enough to withstand the stresses set up internally in the material.

Figure 6 - Plot of Vickers's hardness versus load of TGE

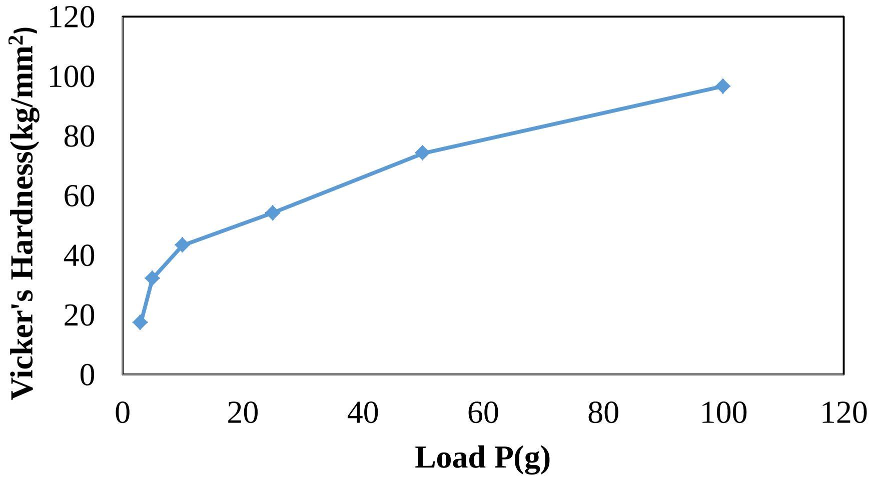


Figure 7 - Plot of log P versus log d

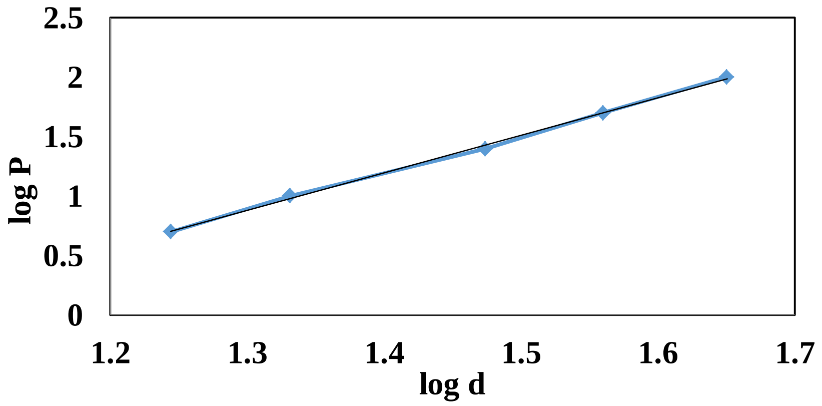


Table 3: Mechanical parameters of TGE crystal

Parameters	Work hardening index (n)	H_v (kg mm^{-2})	K_c (MN m$^{-3/2}$)	B_r (m$^{-1/2}$)	σ_v (M Pa)	C_{11} (10^{14}Pa)
TGE	3.433	53.04	0.15066	3713	26.34	17.9

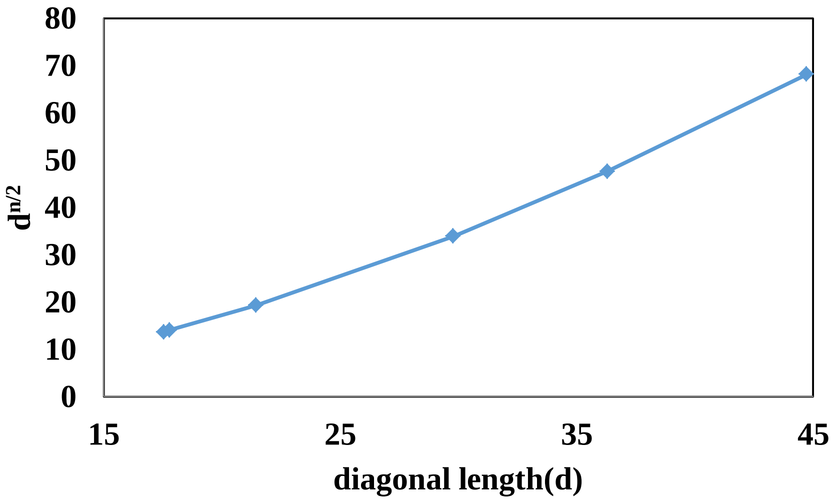


Figure 8 - Plot of (diagonal length)$^{n/2}$ versus diagonal length

3.6 Conclusions

Good optical quality single crystals of Trisglycine epsomite have been grown from aqueous solution by slow evaporation technique under room temperature. The title compound were characterized by single crystal X-ray diffraction and confirmed it crystal structure as triclinic system with space group $P\bar{1}$. PXRD study reveals the crystalline nature of the material and by using Scherer's formula the particle size was estimated to be 39.59nm. The optical transmission studies revealed that TGE crystal have low absorption in the visible region and cut-off wavelength was found to 246 nm with band gap value to be 5.04 eV. The variation of dielectric constant and dielectric loss was studied as a function of frequency. Mechanical behaviors studied using Vickers's hardness identifier discloses that it exhibits reverse indentation effect, soft in nature with good mechanical stability. All these studies reveal that TGE crystal can be considered as potential candidates for the fabrication of electro-optic, nonlinear optical and optoelectronic devices.

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