Growth and characterization of compound crystal of magnesium sulphate heptahydrate and threonine

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Abstract— In the present study, growth and various characterizations of compound crystal of magnesium sulphate heptahydrate (MSH) and threonine (THR) are reported. The crystal is grown by a slow solvent evaporation technique. This technique was taken up at the room temperature. After nearly 5 weeks, good quality, transparent and rod shape crystal is obtained.The crystal is characterized by elemental, FTIR, thermal, SHG and UV-Vis analysis. The various properties of the compound crystal are compared with the pure crystal of MSH and THR. The elemental analysis confirms the presence of atoms of pure MSH and THR in the grown compound crystal. The spectra generated from the FTIR dataset confirmed the presence of expected functional groups of MSH and THR in current compound crystal. The thermal analysis of compound crystal shows changes in the thermal profile of pure crystal of MSH and/or THR in terms of different hydrated phases and anhydrous phases. The SHG analysis shows an increase in the efficiency of compound crystal compared to pure THR crystal. The UV-Vis analysis shows the effect of formation of compound crystal in terms of decrease and increase in transparency % of pure crystal of MSH and THR, respectively. The bandgap energy is calculated from the Tauc's plot, wherein, value of the same was found to increase, as compared to pure THR crystal. All the results are discussed.

Keywords— MSH, THR, FTIR, thermal analysis, SHG, UV-Vis

I.   INTRODUCTION

L-Threonine is a vital member in the family of amino acids and possesses significantly good NLO property. The study of the formation of its compound with metal sulphate, though, in the present paper, with magnesium sulphate heptahydrate, has technological importance because of the enhanced SHG conversion efficiency relative to pure KDP. The formation of a compound crystal of threonine with magnesium sulphate heptahydrate is known as a semi-organic compound crystal. In the literature, various semi-organic compound crystals are reported with their various characterizations. For example, Kumar et al. [1] have reported growth and optical as well as thermal properties of Dl-Norleucine magnesium sulphate crystal,Nalini Jayanthi et al. [2] have reported growth and optical properties of glycine copper sulphate crystal, Nithya et al. [3] have reported the optical and physical properties of the crystals of glycine zinc sulphate and Pabitha et al. [4] have reported synthesis and characterization of l-alanine magnesium sulphate crystal. Sagunthala et al. [5] have used metal sulphate as a dopant and synthesized zinc sulphate monohydrate doped glycine crystal and reported UV-Vis and thermal properties. In most of the literature, neither the comparison of various properties of semi-organic compound crystal with the pure metal sulphate crystal and pure organic crystal is reported nor is the positive and/or negative effect of formation of compound crystal on pure metal sulphate crystal and pure organic crystal discussed. In this paper, we have attempted to discuss the effects related to formation of a compound crystal of magnesium sulphate heptahydrate and threonine with the comparison of its various properties with a pure crystal of magnesium sulphate heptahydrate and threonine.

II.   EXPERIMENTAL TECHNIQUE

For the growth of pure crystals of magnesium sulphate heptahydrate (MSH), threonine (THR) and its compound crystal MSH-THR, slow solvent evaporation technique is adopted. To grow the pure crystals of MSH and THR, the saturated solution of MSH and THR is prepared by dissolving the necessary amount of both the chemicals in distilled water, stirred to achieve a homogeneous solution and covered by filter paper for the controlled evaporation. To grow compound crystals of MSH and THR, both the saturated solutions are mixed at a definite volume, stirred to achieve the homogeneous solution of this mixture and covered by filter paper for the controlled evaporation. After nearly 5 weeks, the colorless and transparent crystals are harvested. Figure 1 shows the photograph of the grown crystals.
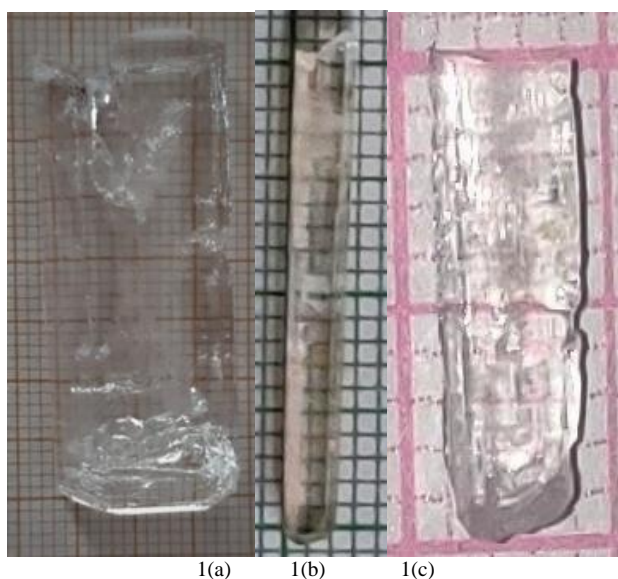
Figure 1: (a) Pure magnesium sulphate heptahydrate (MSH) crystal (b) Pure threonine (THR) crystal and (c) compound crystal of MSH and THR

Figure 2: FTIR spectra of crystals of (a) sample – 1 (b) sample – 2 and (c) sample – 3

III. RESULT AND DISCUSSION

To find out the presence of related atoms in the grown compound crystal of MSH and THR, elemental analysis is carried out by using Philips XI-30 and by using CHNS/O Analyzer, model unicube, make Elementar. The result of this analysis shows the presence of magnesium (Mg), sulphur (S) and oxygen (O) in the wt% of 18.27, 27.94 and 53.79, respectively and nitrogen (N), hydrogen (H), carbon (C), having wt% 4.84, 5.28 and, 10.24 respectively.

The chemical formula of magnesium sulphate heptahydrate (MSH) and threonine (THR) is $MgSO_4 \cdot 7H_2O$ and $C_4H_9NO_3$, respectively. Hence, in the compound crystal of MSH and THR, the presence of magnesium (Mg), carbon (C), hydrogen (H), oxygen (O), sulfur (S), and nitrogen (N) confirms that the formed crystal is a compound crystal of magnesium sulphate heptahydrate (MSH) and threonine (THR).

Further, the calculated wt% of sulfur (S), magnesium (Mg) and oxygen (O) match well with the $MgSO4$, while the calculated wt% of hydrogen (H), carbon (C), and nitrogen (N) match with nearly 1% variation for hydrogen (H) and nitrogen (N) with the compound crystal.

IV. FTIR SPECTROSCOPY STUDY

FTIR spectra of pure MSH crystal (sample – 1), pure THR crystal (sample – 2) and compound crystal of MSH and THR (sample – 3) are generated at room temperature, wherein, the frequency range for the same is 400 to 4000 cm^{-1} and are presented in figure 2.
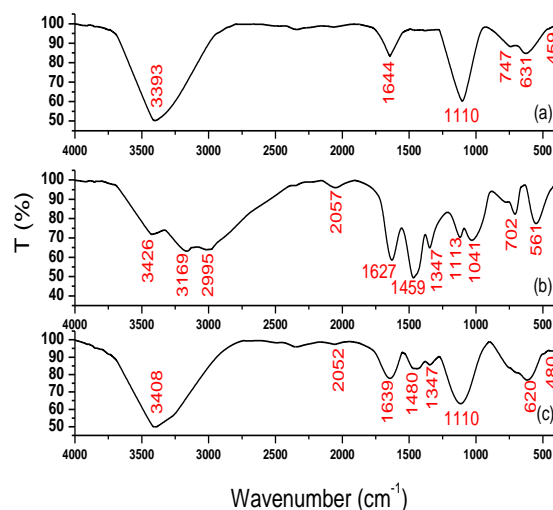
The observation of the FTIR spectrum of compound crystal (sample – 3) shown in figure 2c shows abrupt changes in the appearance when compared with the FTIR spectrum of pure MSH crystal shown in figure 2a and pure THR crystal shown in figure 2b. The FTIR spectrum of figure 2a shows that there is no absorption observed for the crystals of sample – 1 within wavenumber 1644 to 1110 cm^{-1}, while within the same range of wavenumber, the FTIR spectrum of the threonine crystal of figure 2b shows its characteristics vibrations and the same are present in the FTIR spectrum of compound crystal of figure 2c, indicating the formation of the compound crystal. The discussion of each assignment of the bands shown in the figure for all the three crystals is as under.

The pure MSH crystal of sample – 1 shows a band at 3393 cm^{-1}, i.e., within the range 3000 to 3700 cm^{-1}, which corresponds to O-H stretching vibration [6]. Various metal sulphate crystal possesses the O-H stretching vibrations of the HSO4 group around 3400 cm^{-1} [7], having slight variation in absorption frequency depending upon the metal. The band obtained at 1644 cm^{-1} is attributed to H-O-H banding vibration [8], i.e., the bending modes of different water molecules of crystallization [6,9], indicating the hydrated nature of the MSH crystal. The frequency corresponding to the bending mode H-O-H ranges from nearly 1590 cm^{-1} (gas phase) to nearly 1650 cm^{-1} (liquid phase) because of the formation of the hydrogen bond. Upon increase in H-O-H bending frequency, the O-H stretching frequency decreases [10]. In the present case, the frequency corresponding to O-H stretching obtained is correlated with H-O-H bending frequency. The characteristic absorption of sulphate ion is observed within wavenumber 1130-1080 cm^{-1}, 680-610 cm^{-1} [11], 971-993 cm^{-1} and 445-490 cm^{-1} [12], which are known as triply degenerate asymmetric stretching vibration mode of sulphate, triply degenerate asymmetric bending vibration mode of sulphate, non-degenerate symmetric

stretching vibration mode of sulphate and double degenerate vibration mode of sulphate, respectively [12]. In the present case, the strong and broadband observed at 1110 cm^{-1} and 631 cm^{-1} could be assigned to triply degenerate asymmetric stretching vibration of sulphate [6] and triply degenerate asymmetric bending vibration of sulphate [7], while the band observed at 459 cm^{-1} could be assigned to double degenerate vibration mode of sulphate [13]. The band observed at wavenumber 747 cm^{-1} could be assigned to the liberation mode of water molecules [13].

In the FTIR spectrum of threonine crystal (sample – 2), the band observed at 3426 cm^{-1}can be attributed to the O-H stretching vibration [11]. The band observed at wavenumber 3169 cm^{-1} and 2995 cm^{-1} can be attributed to the NH asymmetric stretching vibration of aliphatic primary amine [14] and CH asymmetric stretching vibration of side chain methyl group [11]. The absorption at wavenumber 2057 cm^{-1} indicates the presence of degenerative deformation and torsional vibration of NH$_3$ [15]. The asymmetric bending vibration of primary amine NH is observed at 1627 cm^{-1} [14, 11]. The absorption at wavenumber 1459 cm^{-1} and 1347 cm^{-1}indicate the presence of CH asymmetric and symmetric bending vibration of CH$_3$ [14, 11]. The absorption at wavenumber 1347 cm^{-1} can also be attributed to the primary or secondary O-H in-plane bending vibration of the carboxyl group of amino acids [11]. The absorption at wavenumber 1113 and 1041 cm^{-1} can be assigned to the CN stretching vibration of aliphatic amine [16]. Further, the side chain of Threonine contains CH$_3$CHOH. Therefore, within wavenumber 1000 to 1420 cm$^{-1,}$ the absorption due to stretching vibration of CO and bending vibration of COH was also observed [17]. The absorption band observed at 702 cm^{-1}can be assigned to of plane wagging vibration of NH [16]. The band observed at 561 cm^{-1}can be assigned as rocking vibration of CO$_2^-$, as the same is confirmed in Raman spectra by other researchers also [14,15].

In the FTIR spectrum of compound crystal of sample – 3, the band observed at 3408 cm^{-1}can be attributed to the O-H stretching vibration [11]. The shifting of O-H absorption frequency of compound crystal towards lower frequency side with significant bond broadening indicates that the formed crystal possesses strong hydrogen bonding [11]. The non-appearance of NH and CH stretching vibrations, which are present in pure threonine, may be due to the broadness of the band. The deformation of degenerative kind and torsional vibration of NH$_3$ of pure threonine shifts slightly towards the lower frequency side and appear at 2052 cm^{-1} in the compound crystal. The asymmetric bending vibration of primary amine NH of pure threonine shifts slightly towards the higher frequency side and appears at 1639 cm^{-1} in the compound crystal. The asymmetric bending vibration of CH of the CH$_3$ group shifts towards the higher frequency side and appears at wavenumber 1480 cm^{-1} in the compound crystal, while the symmetric bending vibration of CH of the CH$_3$ group remains as it is and appears at the same wavenumber. The appearance of characteristic absorption of sulphate ion at

the same position as it is observed in the crystals of sample – 1, i.e., at 1110 cm^{-1}, dominating the CN stretching vibration of the amine group, at a slightly lower frequency, i.e., at 620 cm^{-1}, dominating the out of plane wagging vibration of NH and at a higher frequency, i.e., at 480 cm^{-1} strongly indicates that the grown crystal is a compound crystal.

V. THERMAL ANALYSIS

The investigation of thermal strength of the pure MSH crystal (sample – 1), pure THR crystal (sample – 2) and compound crystal of MSH and THR (sample – 3) is done through different scanning Calorimetry (DSC) and thermogravimetric analysis (TG). The combined DSC and TG plots of samples 1, 2 and 3 are shown in diagrams 3(a), 3(b) and 3(c), respectively.
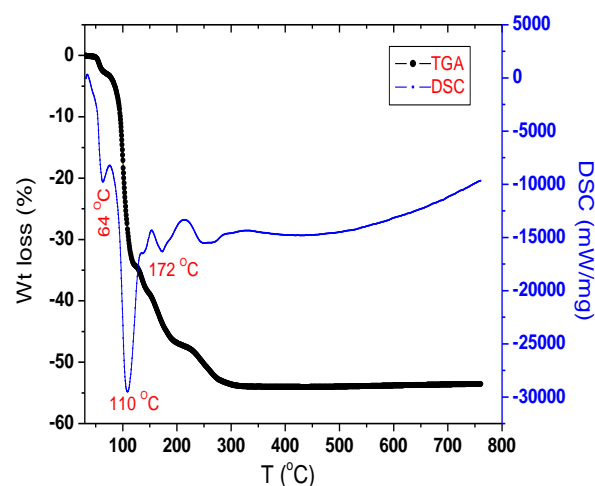

Figure 3(a): Combine TG and DSC plots of pure MSH crystal (sample – 1)

From the weight loss plot, it is observed that no decomposition of the MSH crystal is observed up to temperature 50 ^{o}C from the room temperature. It indicates that the MSH crystal remains stable up to 50 ^{o}C. Then weight loss process starts and ends at a temperature of 300 ^{o}C. It is observed that within the temperature range 50 to 300 ^{o}C, the crystal of MSH loses weight only due to loss of water molecules. The weight of the residue at temperature 300 ^{o}C is the anhydrous phase of MgSO$_4$, which remains as it is, i.e., without decomposition, up to the upper limit of temperature, i.e., 760 ^{o}C. Within the temperature range of 50 to 300 ^{o}C, the different hydrated phases are observed due to the weight loss of the sample MSH. When MSH is heated, stepwise dehydration can produce hydrates with 1, 1.25, 2, 3, 4 and 6 moles of crystal water [18] and different temperatures, such as 300 ^{o}C [19], 320 ^{o}C [20], 330-380 ^{o}C[21] and 400-500 ^{o}C [18] are also observed for complete dehydration to anhydrous magnesium sulphate. In the present case, the different hydrated phases are observed by the TG curve lines having different slops within a temperature range of 50 to 80 ^{o}C, 80 to 130 ^{o}C, 130 to 190

^{o}C and 190 to 300 ^{o}C. The final anhydrous phase of MgSO$_4$ is observed at 300 ^{o}C with the remaining 46% weight of the sample.

Three sharp endothermic peaks at 64 ^{o}C, 110 ^{o}C and 172 ^{o}C temperature in three DSC plots.

The final product, i.e., the anhydrous phase of MgSO$_4$ remains without decomposition up to the upper limit of the temperature, i.e., 760 ^{o}C, because the decomposition of MgSO$_4$ starts within the temperature range 900 to 1100 ^{o}C in the absence of any reducing agent [22].

The decomposition process of the threonine (THR) crystal of sample 2 is shown in figure 3b along with the DSC plot.
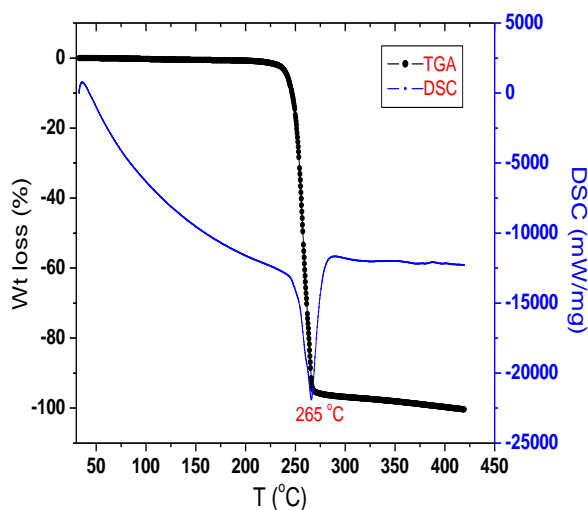

Figure 3(c): Combine TG and DSC plot of compound crystal of MSH and THR (sample – 3)

When the TG plot of compound crystal of MSH and THR, shown in figure 3c, is compared with the TG plot of pure MSH (figure 3a) and pure THR (figure 3b), the change in the thermal profile of MSH is observed. First, the stability of the pure MSH increases from 50 to 60 ^{o}C. Second, the compound crystal also loses weight only due to water but the different hydrated phases are observed with long and small temperature intervals compared to pure MSH. The different hydrated phases of compound crystal are observed within temperature ranges 60 to 110 ^{o}C(corresponding to 50 to 80 ^{o}C of pure MSH), 110 to 240 ^{o}C (corresponding to 80 to 130°C and 130 to 190 ^{o}C of pure MSH), 240 to 260 ^{o}C (corresponding to 230 to 267 ^{o}C of pure THR) and 260 to 550 ^{o}C (corresponding to 190 to 300 ^{o}C of pure MSH). The final anhydrous phase of MgSO$_4$ of compound crystal is observed at 550 ^{o}C with the remaining 36% weight of the sample. As the use of reductant reduces the decomposition temperature of the MSH, the coordination of THR with MSH shows the change in the different hydrated phases of MSH.

The DSC plot of the compound crystal shows three sharp endothermic peaks at 108 ^{o}C (corresponding to 110 ^{o}C of pure MSH), 185 ^{o}C (corresponding to 172 ^{o}C of pure MSH) and 251 ^{o}C (corresponding to 265 ^{o}C of pure THR) temperatures.

Figure 3(b): Combine TG and DSC plot of pure THR crystal (sample – 2)

From the TG plot of THR, shown in figure 3b, it is observed that the THR crystal shows no wt loss up to temperature 230 ^{o}C from room temperature, indicating that it remains stable up to temperature 230 ^{o}C. Then within a temperature range of 230 to 267 ^{o}C, it shows decomposition and then remains stable up to the upper limit of temperature, i.e., 420 ^{o}C.

From the DSC curve, it can be said that no phase transition of pure THR crystal is observed because the DSC curve shows only a single endothermic peak at 265 ^{o}C, the onset and offset temperature of which are 245 ^{o}C and 282 ^{o}C, respectively.

The formation of compound crystals of MSH and THR may reflect in terms of either change in the thermal profile of MSH or THR. The TG plot of the compound crystal of MSH and THR is shown in figure 3c.
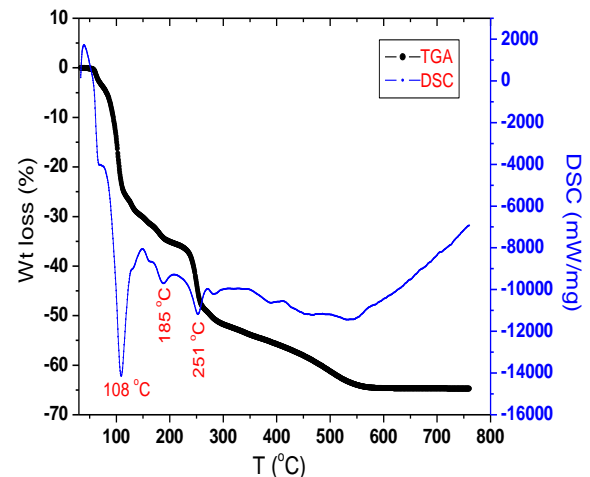
VI. SHG ANALYSIS:

For the confirmation of NLO property, the grown crystals pure MSH, pure THR and compound crystal are subjected to Kurtz powder test using Q switched High Energy Nd: YAG Laser with modulated radiation of wavelength 1064 nm, having repetition rate 10 Hz and pulse width 6 ns on the powder of crystals through a visible blocking filter. The input laser beam is directed at the crystal powder to get maximum powder SHG. The generation of a second harmonic signal in the crystals of wavelength 532 nm is confirmed by the emission of green radiation. This leads to

the confirmation of NLO behavior of the crystals. The NLO SHG efficiency is calculated by taking the monocrystalline powder of KDP as reference material using the equation:

SHG Efficiency = Output Energy (sample)/Output Energy (KDP)

The SHG efficiency of all the three crystals is presented in the following table 1.

Table 1: SHG efficiency

Sample Specifications	Output Energy (mJ)	Input Energy (mJ)	SHG Efficiency
Pure KDP	8.94	0.70	1
MSH Crystal	NIL	0.70	NIL
THR Crystal	3.63	0.70	0.40
Compound Crystal	15.4	0.70	1.72

From table 1, it is observed that the pure crystal of MSH does not possess the NLO property, while the value of SHG efficiency of threonine crystal is observed to be less than that of KDP. On the contrary, the SHG value for the same is found to be higher than that of many organic NLO crystals, such as L-alanine, L-proline, L-asparagine and L-leucine [15]. At the same time, the compound crystal shows enhanced efficiency compared to KDP. It is well-known fact that the organic molecules with conjugated donor-acceptor substitution give rise to the nonlinear effects. The addition of a strong electron donor or acceptor compound can enhance the NLO property of the precursor organic compound. In the present case, the presence of sulphate (SO_4) group, i.e., strong electron acceptor group in the compound crystal may be responsible for the enhancement of SHG efficiency of threonine without affecting the non-centrosymmetric packing of the molecular structure of threonine [23].

VII. UV-Vis ANALYSIS

For the use of crystals in optical applications, the study of optical transmittance window is a very important parameter. The transparent nature of a crystal in the visible region is a required property for NLO applications. The optical transmission spectra of pure MSH crystal (sample 1), pure THR crystal (sample 2) and compound crystal of MSH and THR (sample 3) are observed in the wavelength range of 190 to 800 nm and are shown in figure 4.
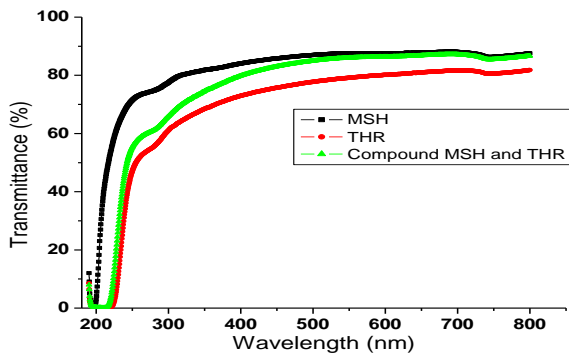

Figure 4: Transmission spectra of pure MSH, pure THR and compound of MSH and THR

Within the wavelength range 179 to 256 nm and 256 to 466 nm, pure MSH crystal shows an increase in transparency from 53 to 69% and 69 to 88%, respectively. Then, the crystal retains the maximum value of transparency of 88% up to the upper limit of wavelength, i.e., 800 nm. Particularly, within the visible range of 380 to 700 nm, the pure MSH crystal shows % transmittance from 83% to 88%.

Pure THR crystal shows an increase in transparency from 49 to 81.65% within wavelength range 247 to 641 nm and then retains the maximum value of transparency of 81.65% up to the upper limit of wavelength, i.e., 800 nm. Particularly, within the visible range of 380 to 700 nm, the pure THR crystal shows % transmittance from 71.36% to 81.65%.

The compound crystal MSH and THR showan increase in transparency from 56 to 87.12% within the wavelength range 244 to 512 nm and then the compound crystal retains the maximum value of transparency of 87.12% up to the upper limit of wavelength, i.e., 800 nm. So, the effect of the formation of the compound crystals of MSH and THR is observed in terms of a decrease and increase in transparency % of pure MSH and pure THR, respectively. Elaborately, the formation of compound crystal raises the % of transparency of pure THR from 81.65% to 87.12% and also widens the wavelength range of transmittance from 641 to 800 nm to 512 to 800 nm, while a slight decrease in % transmittance from 88% to 87.12% and shorten of the wavelength range of transmittance from 466 to 800 nm to 641 to 800 nm is observed in the case of pure MSH crystal. Particularly, within the visible range of 380 to 700 nm, the compound crystal shows % transmittance from 77.88% to 87.12%. The transparency% of threonine has been reported as nearly 85% [24]. The present research showed an increase in transparency% up to 87.12% when the compound of threonine (THR) is formed with magnesium sulphate heptahydrate (MSH).

The transmittance% within the optical region of all the three crystals is shown in table 2.

Table 2: Transmittance % and bandgap energy

Sample	Transmittance% within visible range	Bandgap energy (eV)
Pure MSH (Sample 1)	83% to 88%	6.09
Pure THR (Sample 2)	71.36% to 81.85%	5.39
The compound of MSH and THR (Sample 3)	77.88% to 87.12%	5.47

A. Determination of optical energy bandgap

The optical energy band gap is a fundamental quantity to investigate the optical properties possessed by a material. In the present study, the optical energy bandgap (E_g) has been evaluated for the pure crystal of MSH (sample 1), a pure crystal of THR (sample 2) and a compound crystal of MSH and THR (sample 3) from the Tauc relation [25]:

$$\alpha h\nu = A(h\nu - E_g)^n,$$

Where h is the Planck constant, ν is the frequency of the incident photon, A is constant, E_g is the average bandgap

of the material and n is an index that depends on the types of transition. The coefficient of optical absorption (α) is calculated by using a standard formula [26]

Tauc's plot is shown in figure 5 for all three crystals.
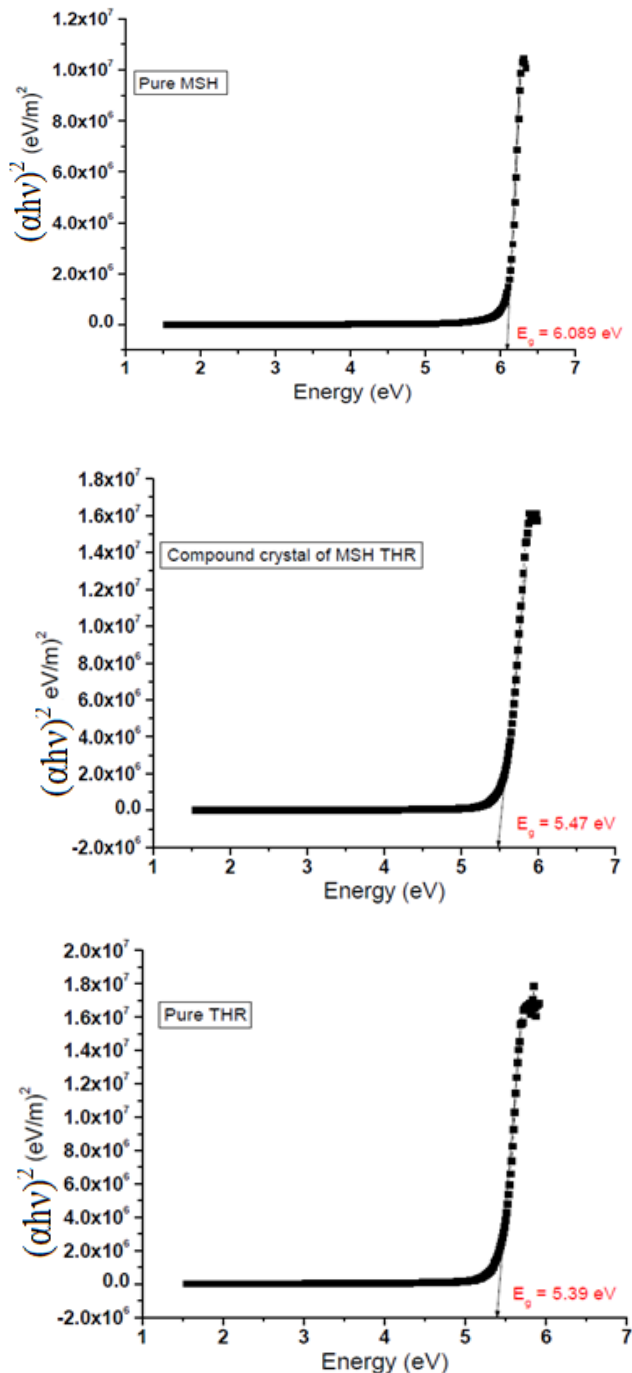

Figure 5: Tauc's plot

In figure 5, the graphs are plotted between energy (hν) on X-axis and $(\alpha h\nu)^2$ on Y-axis. Upon extrapolation of the tangent of the linear part of the graph to the X-axis, i.e., $(\alpha h\nu)^2 = 0$, we get the value of optical energy bandgap (E_g) of the grown crystals. The value of the optical energy bandgap (E_g) is listed in table 2.

From table 2, it is observed that the formation of the compound of MSH and THR raises the energy band gap value of pure THR crystal and reduces the same of pure MSH crystal. Though, all three crystals possess a large value of energy bandgap and hence, are useful in optoelectronic device applications [27,28]. The energy band gap values obtained in the present case for all the three crystals are found to be quite superior to the metal sulphate crystals formed with glycine, nickel doped magnesium sulphate heptahydrate crystals, pure threonine crystals and a novel organic single crystal 2-Amino-5-Chloropyridinium-4-hydroxybenzoate [2, 3, 8, 29, 30, 31].

VIII. CONCLUSION

To grow the pure crystals of MSH, THR and compound crystal of MSH-THR, slow solvent evaporation technique at room temperature was adopted. The elemental analysis confirms the presence of Mg, S, O, C, H and N in the compound crystal. By FTIR analysis, the confirmation of the presence of characteristic functional groups of MSH and THR are confirmed in the compound crystal. The thermal analysis of compound crystals shows the change in the thermal profile of pure MSH and THR crystals. The SHG analysis confirms the NLO property of the compound crystal. The formation of a compound of THR with MSH raises the SHG efficiency of pure THR crystal. The UV-Vis analysis shows an increase in transmittance% and bandgap energy of pure THR after the formation of a compound of THR with MSH.

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