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GROWTH OF MAGNESIUM SULPHATE DOPED ZTS SINGLE CRYSTALS AND THEIR CHARACTERISATION

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ABSTRACT

Single crystals of magnesium sulphate doped ZTS were grown by the slow evaporation technique at room temperature. Unit cell parameters of the magnesium sulphate doped ZTS crystals were found by Powder XRD analysis.. The presence of various functional groups was confirmed by FT-IR analysis. UV-visible study shows that the grown crystal has cut off wavelength around 221.57nm.. The SHG efficiency was found to be 0.78 times that of KDP.

1 INTRODUCTION

Non-linear optical (NLO) materials play an important role in the field of tele-communication, optical switching and optical processing[1]. In the recent years, researchers working on NLO materials have been making an intense search for new NLO Organics with the high mechanical strength of inorganic materials. Zinc Thiourea sulphate (ZTS) is a good engineering material for second harmonic generation (SHG) device applications and Laser tuned experiments.[2,3] It is a novel metal organic crystal belongs to the orthorhombic system with space group $Pca2_1$ having potential application in electro-optic modulation. Have reported the properties of phosphate mixed ZTS single crystal the effect of sodium chloride on Communication. Effect of organic dopants on the properties of ZTS crystals has been reported by Subbiah Meenakshisundram also various studies have been carried out to study the modified properties of ZTS single crystal. The physical and chemical properties of ZTS have been improved by the addition Of various organic and inorganic materials. [4,5]. In the present work, ZTS has been doped with various molar percentage of Magnesium Sulphate to improve the SHG efficiency to find its suitability as better alternative to other NLO materials for optic-electronics application.. The grown crystal were characterized by various technique by powder X-ray diffraction, fourier transform infrared (FT-IR) studies, UV absorbance studies , SHG studies and the results were discussed detail.

II CRYSTAL GROWTH

The material of the ZTS compound was synthesized in the aqueous medium from zinc sulphate ($ZnSO_4$_ $7H_2O$) and thiourea [$CS(NH_2)_2$] taken in 1:3 stoichiometric ratio according to the following chemical reaction. To avoid decomposition, low temperature was maintained during preparation of the solution in the deionized water.

$$\mathbf{ZnSO_4 + 3CS(NH_2)_2 \rightarrow Zn[CS(NH_2)_2]_3SO4}$$

The calculated amount of the high purity analar grade zinc sulphate and thiourea were dissolved in de-ionised (DI) water in different beakers separately. The zinc sulphate and thiourea solutions were added in the molar ratio of 1:3 and continuously stirred using magnetic stirrer.
The homogeneous solution prepared at room temperature was and then filtered by Whattman filter paper to increase the purity of the solution. Then mole% of $MgSO_4$ solution was added to ZTS solution inorder to dope $MgSo_4$ in ZTS. The saturated homogeneous solution obtained was kept

in a glass vessel covered with perforated paper for slow evaporation in an undisturbed condition.

Seed crystals were obtained in a week period . Good quality crystal was obtained by successive recrystallization method. The successive recrystallization makes the product more purified. Perfect crystals were grown in the period of 2 weeks. The As grown transparent colourless crystals of Magnesium sulphate doped ZTS crystal of size 5x4x2 mm^3 is shown in Fig.3.1 the grown crystals were subjected to various characterization studies .

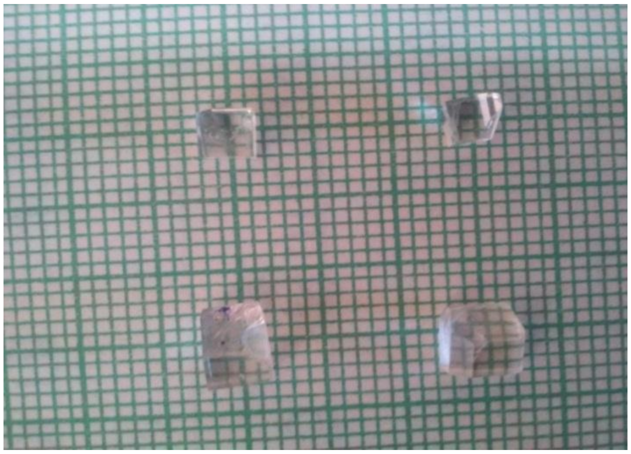

Fig.3.1 Photograph of grown $MgSo_4$ doped ZTS crystal

III CHARACTERIZATION

1. POWDER X-RAY DIFFRACTION STUDIES

The single crystals of $MgSO_4$ doped ZTS crystal were subjected to powder X-RAY diffraction studies using Rigaku diffractometer with cu kα radiation (λ=1.54056 Ǻ) to determine the lattice parameter and crystal structure [6]. The powder X-RAY diffraction pattern of $MgSO_4$ doped ZTS is shown in the figure 3.2. The result confirmed that the grown crystal belongs to the structure of orthorhombic system with space group $Pca2_1$.From the XRD pattern of $MgSO_4$ doped ZTS crystal it is found that the crystal structure does not alter much except that there is slightly variation in the unit cell volume due to addition of magnesium sulphate. The lattice parameter values are calculated and shown in the table.1 Lattice parameter values obtained in this work agrees well with the values repoted by Selvapandian el at [7] for $MgSO_4$ ZTS crystals grown with different mole% of $MgSo_4$

Table.1
Lattice parameters of $Mgso_4$ doped ZTS crystal

Lattice parameters	**$Mgso_4$ doped ZTS**
a(Å)	11.147
b(Å)	7.799
c(Å)	15.471
Volume $(Å)^3$	1345
Crystal system	Orthorhombic
Space group	$Pca2_1$

2 FT-IR SPECTRAL ANALYSIS

The FT-IR spectral analysis of $MgSO_4$ doped ZTS crystals were carried out in the frequency region of 450-4000 cm^{-1} by using PERKIN ELMER Two FTIR/ATR Spectrometer. The FT-IR spectrum provides more information about molecular structure of the compound, mode of vibration and the presence of functional groups. The FI-TR spectrum of $MgSO_4$ doped ZTS is shown in Fig 3.3 & 3.4. The peak present at 3360.06 & 3448.4 cm^{-1} is due to N-H stretching vibration of the NH_2 group of thiourea. The C=S stretching vibration occurs at 1629.92cm^{-1}. The peaks at 1515.71 and 1401.48cm^{-1} are due to NH_2 bending vibrations. The band observed at 1030.63 cm^{-1} can be assigned to CH_2 bending vibration and the peak observed at around 1140.21 cm^{-1} corresponds to C-N stretching vibration. The peaks 715.84 and 471.66cm^{-1} are assigned to Zn-S vibration [8]. The observed wave numbers and the assignments made from the recorded spectra for $MgSO_4$ doped ZTS crystal are given in table 2.

WAVE NUMBER IN CM^{-1}	ASSIGNMENTS
3360.06	N-H (stretching)
3449.4	N-H (stretching)
1401.48	S=O (stretching)
1629.92	C=S (stretching)
1030.65	NH_2 bending
1140.21	C-N stretching
715.84,471.66	Zn-S vibration

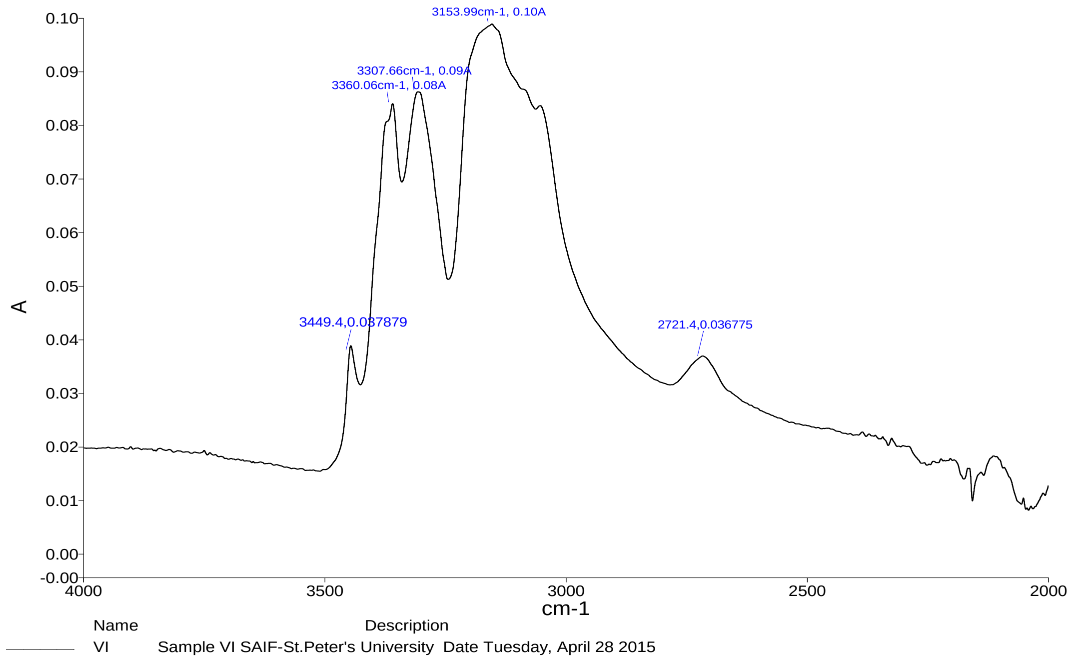

Fig 3.3 FT-IR spectra of $MgSO_4$ doped ZTS crystal

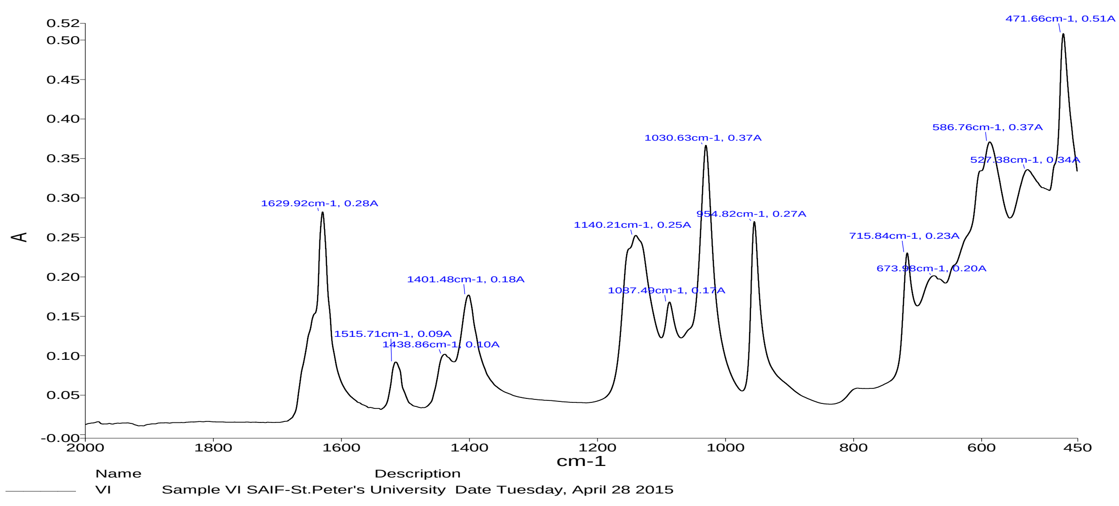

Fig.3.4. FT-IR spectra of $MgSO_4$ doped ZTS crystal.

3 ULTRAVIOLET VISIBLE SPECTROSCOPY ANALYSIS

The single crystals are mainly used for optical application. Thus the study of optical absorbtion range of grown crystal is important. Optical absorption spectra of 1 mole% $Mgso_4$ doped ZTS crystal were recorded in the range 200-1100 nm. The cut-off wavelength of the crystal is taken as the point at which absorbance falls to zero. The study indicates that u-v cut off wavelength of $MgSO_4$ doped ZTS crystal has 221.57nm. The forbidden energy gap of the grown crystal was estimated from the value of λ_{max} using the relation $E_g = hc/\lambda$ where 'h' is the planck's constant , 'c' is the velocity of light and and λ is the cut-off wavelength .The value of forbidden energy gap for the grown crystal was found to be 5.6eV. The grown magnesium sulphate doped ZTS crystals has good absorption in UV as well as in visible region, it is shown in fig.3.4.

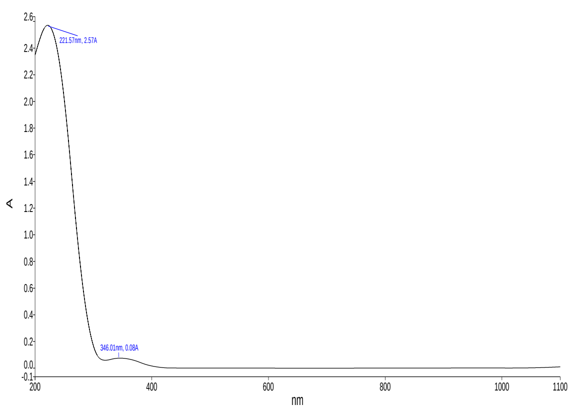

Fig 3.4 UV Absorption spectra of magnesium sulphate doped ZTS.

4. SECOND HARMONIC GENERATION (SHG) EFFICIENCY TEST:

The Kurtz powder technique is a standard method to evaluate the relative efficiency of nonlinear optical materials. The crystal was grounded into a fine powder and densely packed between two transparent slides. A Q switched ND: YAG laser emitting a fundamental wavelength of 1064 nm (pulse width 8 ns) was allowed to strike the same cell. The SHG output 532 nm (green light) was finally detected by the photomultiplier tube. The powdered material of potassium di hydrogen phosphate (KDP) was used in the same experiment as a reference material. The relative conversion efficiency was calculated from the output power of Magnesium sulphate doped ZTS crystals with reference to KDP crystals. The powder SHG efficiency output of pure ZTS was found to be 0.78 times greater with respect to KDP. The Kurtz powder SHG test confirms the NLO property of the grown Magnesium sulphate doped ZTS crystals.

IV.CONCLUSION

Single crystals of size 5 ×4 × 2 mm^3 magnesium sulphate doped ZTS were grown by the slow evaporation technique at room temperature. Unit cell parameters of the magnesium sulphate doped ZTS crystals were found by Powder XRD analysis. Sharp peaks of powder XRD spectrum of the crystal show good crystalline nature of the compound. The presence of various functional groups was confirmed by FT-IR analysis. UV-visible study shows that the grown crystal has cut off wavelength around 221.57nm. The magnesium sulphate doped ZTS going to play a vital role in the optic-electronics and laser technology. The SHG efficiency was found to be 0.78 times that of KDP.

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