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INVESTIGATIONS ON GROWTH, OPTICAL, FTIR, HARDNESS AND SHG STUDIES OF LITHIUM SULFATE CRYSTALS DOPED WITH MAGNESIUM SULFATE OR RUBIDIUM CHLORIDE

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Abstract:

Undoped, magnesium sulfate doped and rubidium chloride doped lithium sulfate crystals were grown by solution method using lithium sulfate, magnesium sulfate and rubidium chloride as the reactants. Colourless, transparent and non-hygroscopic crystals were harvested after a growth period of 30-35 days. The grown crystals were subjected to various studies like FTIR studies, XRD studies, thermal studies, SHG studies, optical transmittance studies, EDAX studies and microhardness studies. XRD studies reveal that the crystals crystallize in monoclinic system and FTIR studies reveal the various functional groups present in the samples. Nonlinear optical property was studied by measurement of SHG efficiency. Transparency and band gap of the samples were studied by optical studies. Thermal stability and mechanical strength of the samples were analysed by TG/DSC and hardness studies.

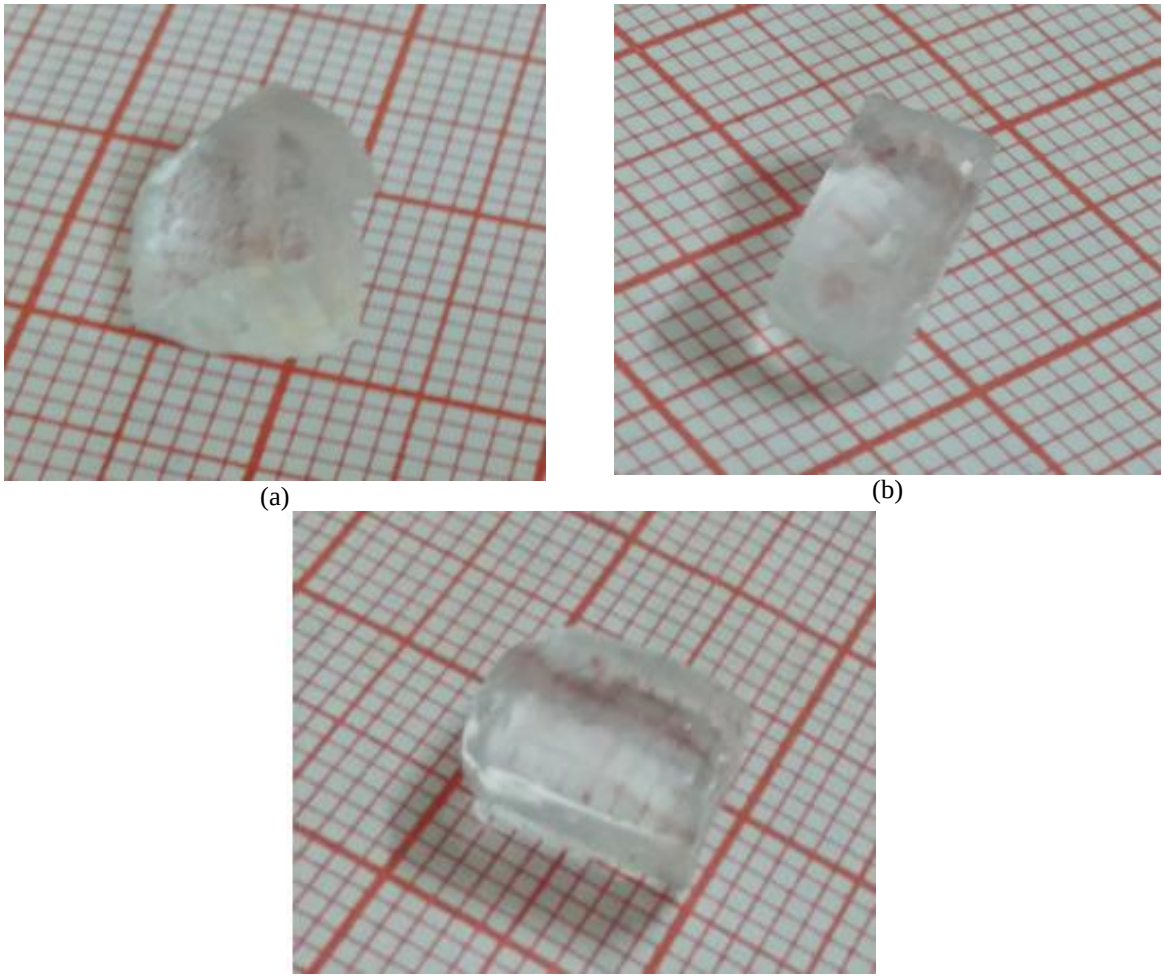
Key Words: Lithium Sulfate, Single Crystal, Solution Technique, Characterization, XRD, SHG, EDAX, TG/DSC, FTIR & Hardness

1. Introduction:

Inorganic NLO materials exhibit excellent mechanical and thermal properties. Especially, a great deal of interest has been focused on the exploration of NLO materials for the development of frequency doubling crystal [1-3]. For example, KH_2PO_4 (KDP) is among the most widely-used commercial NLO material, and it is commonly used for doubling, tripling and quadrupling of Nd: YAG laser at the room temperature. The design of optoelectronics and photonic devices realizes heavily in the development of nonlinear optical materials with higher efficiency. So the materials possessing large second order nonlinear susceptibility with favorable in thermal and mechanical stability are intensively used in many device applications [4-6]. Complex of sulfates are of great interest in industry, due to their outstanding physical properties and widely used as nonlinear optical (NLO), ceramic, ferroelectric, electric, and catalytic materials [7-11]. Lithium sulfate is one of the sulfates and it crystallizes in $P2_1$ space group with monoclinic structure. The structural analysis of lithium sulfate crystal was already reported [12, 13]. Many researchers studied on various properties of lithium sulfate crystals and reported in the literature [14-18]. In this work, single crystals of undoped, magnesium sulfate doped lithium sulfate (MSLS) and rubidium chloride doped lithium sulfate (RCLS) crystals have been synthesized and grown by the slow evaporation technique. The grown crystals were characterized by Fourier transform infrared spectroscopic (FTIR) analysis to find the different modes of vibration due to various functional groups present in the crystal. The optical transmission spectrum was investigated to study its linear optical properties using UV–vis-NIR spectrophotometer. The thermal behaviour of the samples has been analyzed using thermal curves. The mechanical property of the grown crystals has been studied using Vickers micro hardness tester. The nonlinear optical property was tested using Kurtz Perry powder technique and SHG efficiency was measured.

2. Methodology for Crystal Growth:

Commercially available lithium sulfate, magnesium sulfate and rubidium chloride were used as the starting materials for the growth of undoped, magnesium sulfate doped and rubidium chloride doped lithium sulfate crystals. Saturated solution of lithium sulfate was prepared using the double distilled water as the solvent and it was stirred well with a magnetic stirrer for about 2 hours. Then it was filtered into the growth vessel using the Whatmann filter papers. The growth vessel was covered with a perforated cover for occurring slow evaporation. Due to slow evaporation, the saturated solution was initially changed into supersaturated solution and small crystal nuclei were formed in the solution. As the slow evaporation was continued, the crystal nuclei were changed into big-sized crystals. After a growth period of 30 days, the lithium sulfate crystals were harvested and stored in a desiccator to avoid the adsorption of moisture from air. To grow the magnesium sulfate doped and rubidium chloride doped lithium sulfate crystals, 1 mol% of magnesium sulfate and 1 mol% of rubidium chloride were separately added into the aqueous solutions of lithium sulfate and solutions were separately stirred and filtered. The filtered solutions were taken in two different growth vessels and due to slow evaporation, the doped crystals were harvested after a growth period of about 35 days. The grown crystals of undoped, magnesium sulfate doped and rubidium chloride doped lithium sulfate crystals are shown in the figures 1 (a), (b) and (c).



(a) (b)

(c)

Figure 1: Photographs of (a) undoped, (b) magnesium sulfate doped and (c) rubidium chloride doped lithium sulfate crystals

3. Results and Discussion:

3.1 FTIR Spectral Analysis:

FTIR spectroscopic studies were effectively used to identify the functional groups present in the synthesized compounds. To analyze qualitatively the presence of the functional groups in the grown crystals, FTIR spectra were recorded using spectrometer in the range 400 - 4000 cm^{-1}. The recorded FTIR spectra of the samples are shown in Figs. 2, 3 and 4. The stretching vibrations of the water molecule are expected in 3000-3700 cm^{-1}. The broad vibrational band observed around 3490.40cm^{-1} is attributed to symmetric stretching mode of water molecule. The medium broad band noticed around 1616.13 cm^{-1} is assigned to the bending vibration of water molecules. In general free SO_4^{2-} ion has some fundamental vibrations. The peak at 1555.93 cm^{-1} is assigned to non-degenerate stretching mode (ν_1) of SO_4^{2-} ion .The peaks at 1106.54 and 1011.35 cm^{-1} are attributed to SO_4 stretching mode (ν_3). The functional group assignments are given in accordance with the reported data [19]. The assignments to the absorption frequencies are provided in the tables 1, 2 and 3.

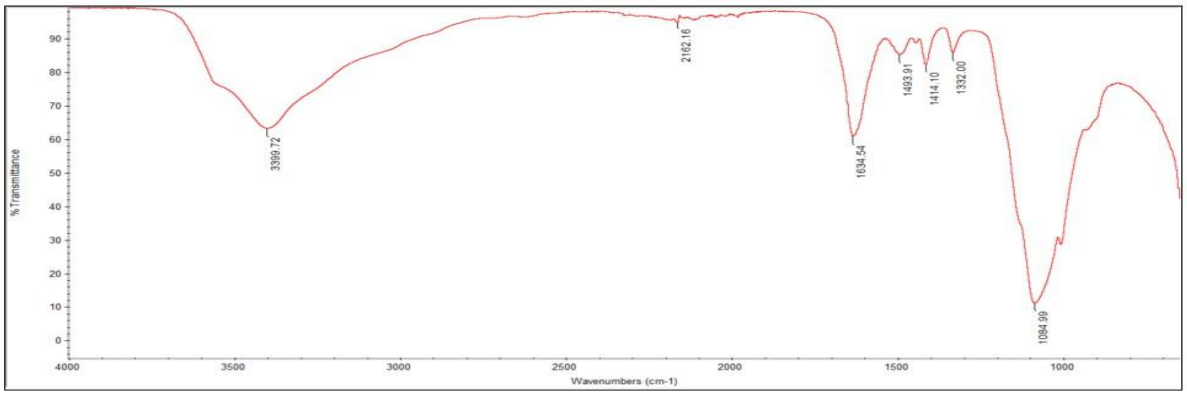


Fig.2: FTIR spectrum of undoped lithium sulfate crystal

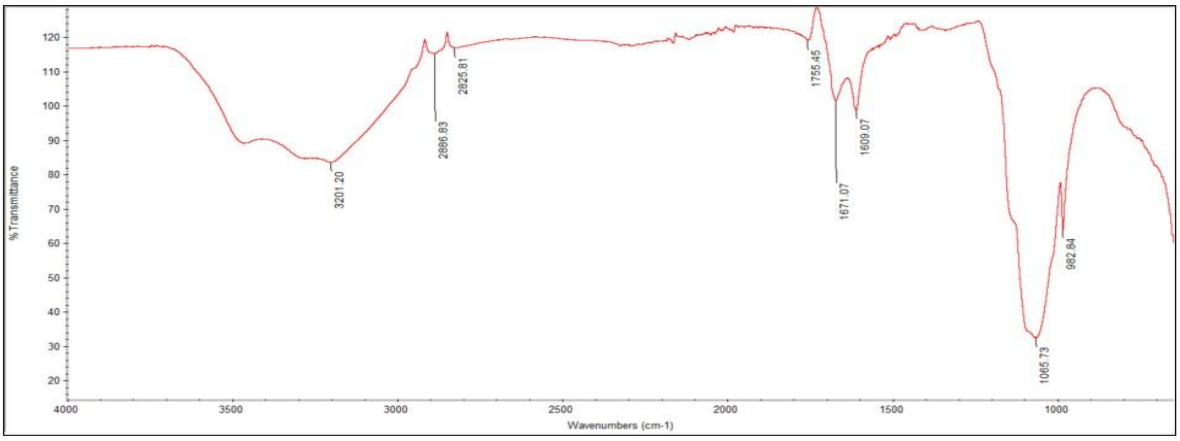


Figure 3: FTIR spectrum of magnesium sulfate doped lithium sulfate crystal

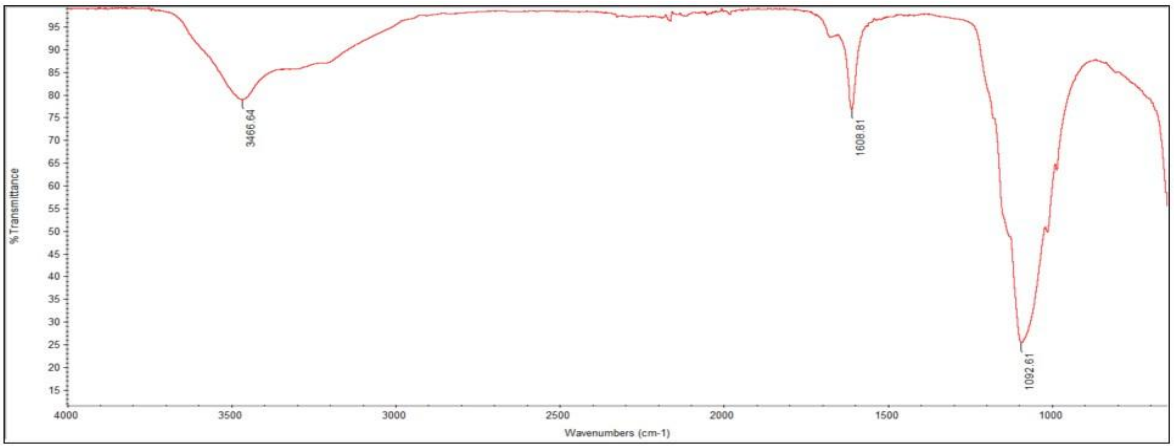


Figure 4: FTIR spectrum of rubidium chloride doped lithium sulfate crystal

Table 1: Spectral assignments for undoped lithium sulfate monohydrate crystal

Wave number in cm^{-1}	**Assignments**
3399	Symmetric stretching mode of water molecule
2162	Bending vibration of water molecules
1634	Stretching (ν_1) of S=O
1493	Stretching (ν_3) of SO_4
1414	Stretching (ν_3) of SO_4
1332	Triply degenerate vibrations (ν_4) of SO_4
1084	Doubly degenerate (ν_2) of SO_4^{2-} mode

Table 2: Spectral assignments for magnesium sulfate doped lithium sulfate monohydrate crystal

Wave number in cm^{-1}	**Assignments**
3350-3200	Symmetric stretching mode of water molecule
2825	Bending vibration of water molecules
1671	Stretching (ν_1) of S=O
1609	Stretching (ν_3) of SO_4
1065	Doubly degenerate (ν_2) of SO_4^{2-} mode

Table 3: Spectral assignments for rubidium chloride doped lithium sulfate monohydrate crystal

Wave number in cm^{-1}	**Assignments**
3466	Symmetric stretching mode of water molecule
1608	Stretching (ν_3) of SO_4
1092	Doubly degenerate (ν_2) of SO_4^{2-} mode

3.2 XRD Studies:

X-ray diffraction (XRD) is a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. It is an analytical technique which provides detailed information about the internal lattice of crystalline substances, including atomic coordinates, bond lengths, bond angles, molecular orientation and packing of molecules. Single crystal X-ray diffractometer collects intensity data required for structure determination. The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and

directed towards the sample. The monochromatic X-rays incident on a plane of single crystal at an angle θ are diffracted according to Bragg's relation nλ = 2d sin θ. This law relates the wavelength of electromagnetic radiation, the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. Using the computerized single crystal XRD method, the lattice parameters of the samples are obtained [20]. Here a Bruker-Nonius MACH3/CAD4 single crystal X-ray diffractometer with MoK_α radiation (λ=0.71069 Å) was used collect the XRD data of the samples. The obtained single crystal XRD data of the samples are provided in the table 4. It is observed that the crystal of lithium sulfate monohydrate, magnesium sulfate doped lithium sulfate (MSLS) crystal and rubidium chloride doped lithium sulfate (RCLS) crystal crystallize in the monoclinic crystal system. The data indicates that the grown crystals crystallize in the space group $P2_1$ which is a non-centrosymmetric space group and this is the essential condition for generating a SHG output.

Table 4: Single crystal XRD data for undoped, MSLS crystal and RCLS crystal

Sample	a (Å)	b (Å)	c (Å)	α	β	γ	Space group
Lithium sulfate monohydrate crystal	5.478(4)	4.875(2)	8.179(3)	90°	106.98(5)	90°	$P2_1$
MSLS crystal	5.502(5)	4.863(7)	8.191(2)	90°	106.47(4)	90°	$P2_1$
RCLS crystal	5.527(3)	4.892(2)	8.187(6)	90°	106.25(5)	90°	$P2_1$

3.3 EDAX Spectral Studies:

Energy dispersive analysis by X-rays (EDAX) is a technique used for identifying the elemental composition of sample and this system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own without the latter. During EDAX analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atom's own electrons, knocking some of them off in the process. The EDAX spectrum is a plot of intensity of X-rays versus energy of the emitted X-rays. An EDAX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays have been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. An EDAX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-rays to which it corresponds as well [21]. The presence of various elements in the grown crystals was checked by using JEOL Model JED – 2300 spectrometer and the recorded EDAX spectra of the samples are shown in the figures 5 and 6. From the results, it is observed that the elements such as O, S, Mg, Rb, Cl etc are present in the magnesium sulfate doped and rubidium chloride doped lithium sulfate monohydrate crystals and it seems that the elements such as C, Al are present as impurities in the purchased chemicals. Here it is to be mentioned that hydrogen and lithium cannot be identified by EDAX method as they are low mass elements.

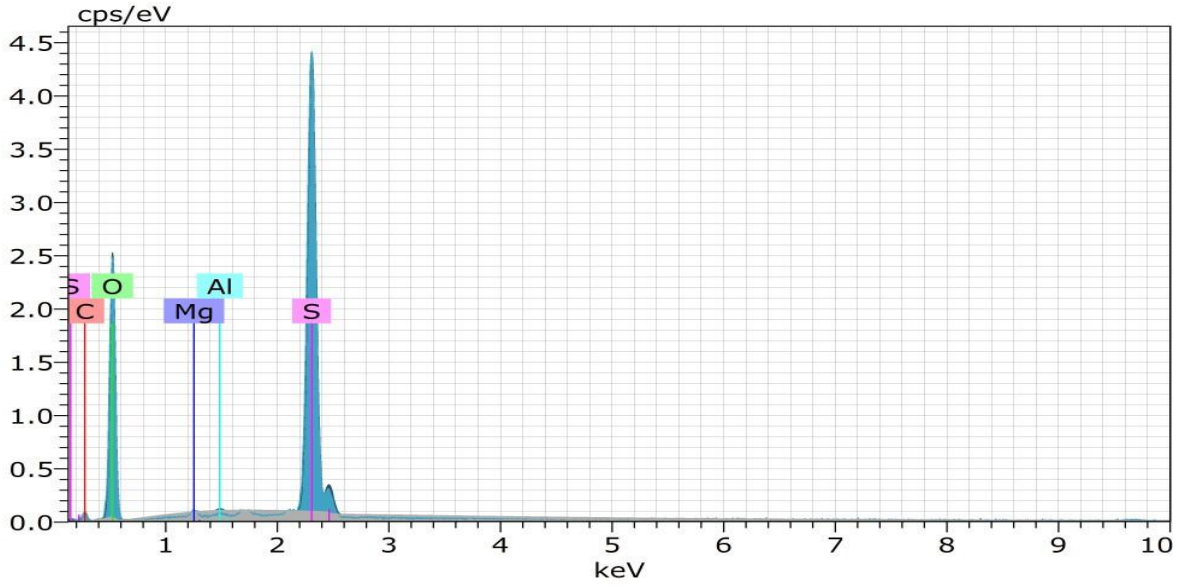


Fig.5: EDAX spectrum of magnesium sulfate doped lithium sulfate monohydrate crystal

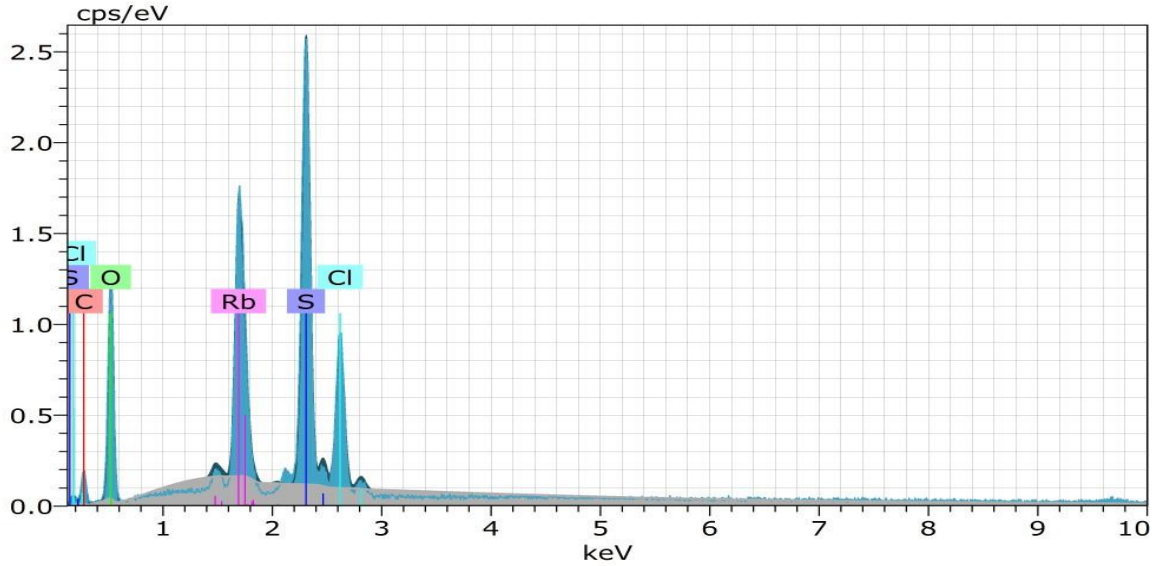


Figure 6: EDAX spectrum of rubidium chloride doped lithium sulfate monohydrate crystal

3.4 Thermal Studies:

Thermogravimetric (TG) analysis and differential scanning calorimetric (DSC) analysis of the grown samples were carried out in the temperature range of 25-700^{o}C in nitrogen atmosphere at a heating rate of 20 oC/min. The weight, particle size and the mode of preparation of a sample etc will govern the thermo gravimetric results and in practice, a small sample weight is desirable for thermo gravimetric analysis [22]. The recorded TG thermal curves for magnesium sulfate doped and rubidium chloride doped lithium sulfate monohydrate crystals are shown in the figures 7 and 9 and the DSC thermal curves for the samples are given in the figures 8 and 10. In the temperature region 25- 150^{o}C, the weight loss is corresponding to the removal of water molecules from the samples. The endothermic peak at 167.9^{o}C corresponds to decomposition point of magnesium sulfate doped lithium sulfate monohydrate (MSLS) crystal and the same at 163.5^{o}C corresponds to the decomposition point of the rubidium chloride doped lithium sulfate (RCLS) monohydrate crystal. From the literature it is found that the decomposition point of undoped lithium sulfate monohydrate crystal is at 142^{o}C [23] and hence MSLS and RCLS crystals have higher values of decomposition point. The residual mass left at 700^{o}C for MSLS crystal is 72.07% and that for RCLS crystal is 79.8%. Since the samples are inorganic crystals, residual mass left beyond 700^{o}C is observed to be high.

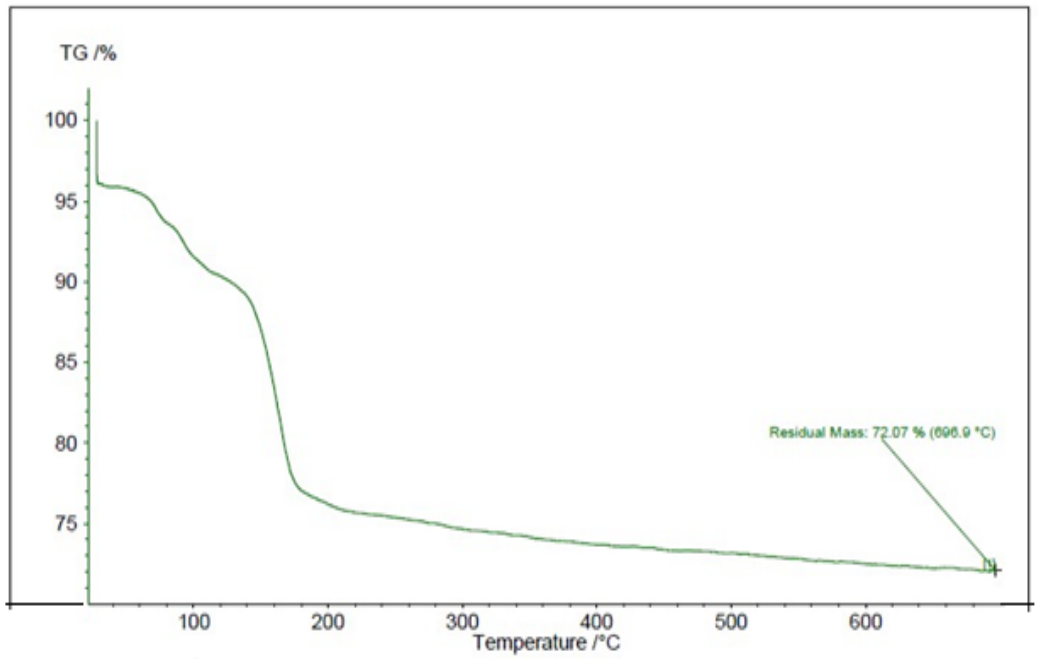


Figure 7: TG thermal curve of magnesium sulfate doped lithium sulfate monohydrate crystal

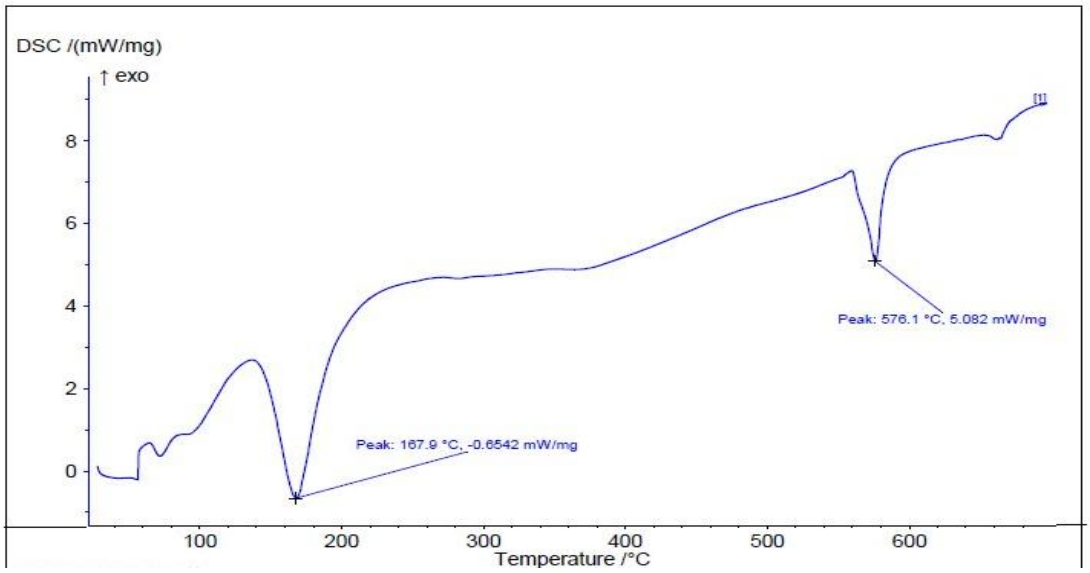


Figure 8: DSC thermal curve of magnesium sulfate doped lithium sulfate monohydrate crystal

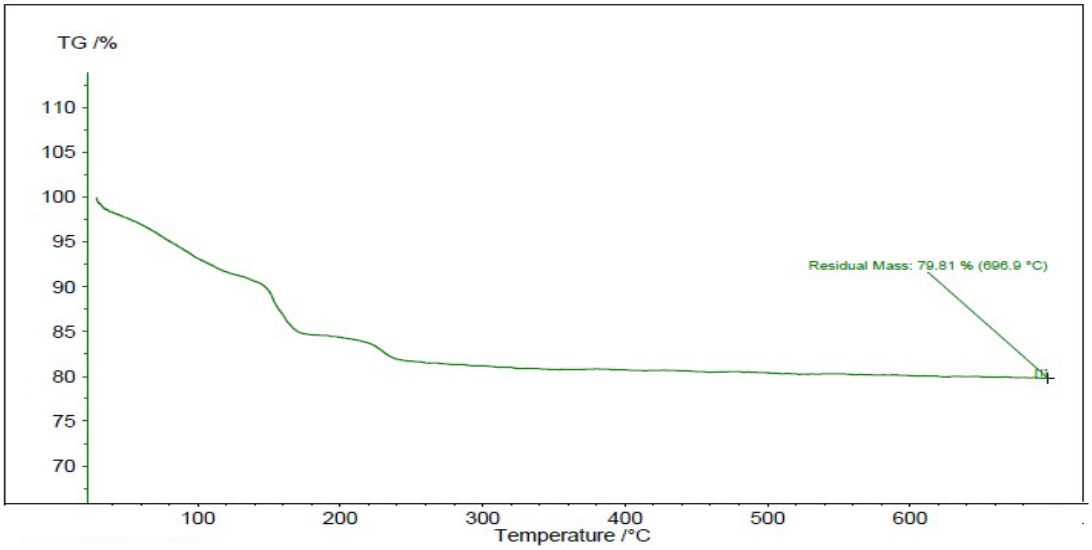


Figure 9: TG thermal curve of rubidium chloride doped lithium sulfate monohydrate crystal

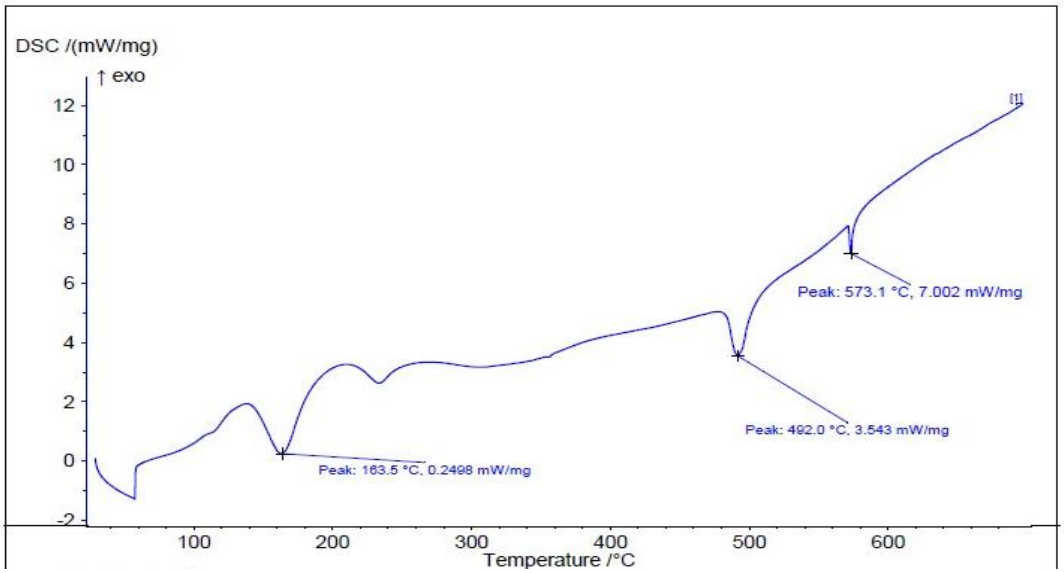


Figure 10: DSC thermal curve of rubidium chloride doped lithium sulfate monohydrate crystal

3.5 Measurement of Microhardness:

The structure and composition of the crystalline solids are related to the mechanical hardness. Microhardness testing is one of the best methods of understanding the mechanical properties of the materials such as fracture behavior, yield strength, brittleness index and temperature of cracking [24]. The grown samples of undoped lithium sulfate, MSLS crystal and RCLS crystal were subjected to hardness test by using a Vickers microhardness tester. Indentations were made on the faces of the crystals and loads applied onto the crystals vary from 25 g to 100 g. Vickers microhardness values have been calculated by using the formula

$$H_v = \frac{1.8544 \times P}{d^2} \text{ kg/mm2}$$

Where Hv is the Vickers microhardness number, P is the applied load in gram and d is the average diagonal length in mm of the indentation mark. The plots of hardness number and the applied load for the samples are shown in the figure 11. It is clear from the results that the hardness increases with increase of the applied load upto 75 g and then it decreases for all the samples. Thus the samples have both reverse indentation size (RISE) effect and direct indentation size effect. When lithium sulfate crystals are doped with magnesium sulfate or rubidium chloride as the dopants, the hardness seems to be increased.

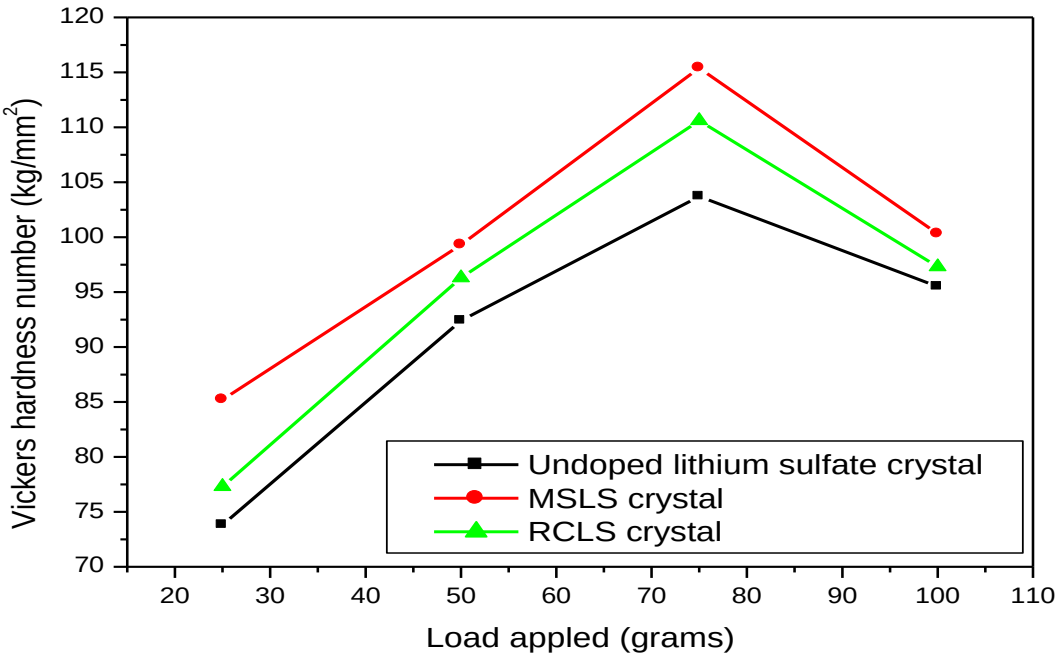


Figure 11: Plots of hardness number with the load applied for undoped, magnesium sulfate doped and rubidium chloride doped lithium sulfate crystals

3.6 Optical Transmittance Studies:

Molecules containing π-electrons or nonbonding electrons can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons, the longer the wavelength of light it can absorb. Absorption measures transitions from the ground state to the excited state [25]. The transmittance studies were carried out using a UV-visible spectrophotometer in the wavelength range 190-1100 nm. The recorded UV-visible transmittance spectra of undoped lithium sulfate, magnesium sulfate doped lithium sulfate (MSLS) and rubidium chloride doped lithium sulfate (RCLS) crystal are shown in Figure 12. This study helps us to find the suitability of materials in optical device applications. The optical property of the material gives information regarding the composition, nature and the quality of the crystals. From the results, it is noticed that the grown crystals have good transmittance in the visible region. The lower cut-off wavelength at 238 nm and greater transparency in the visible region make the samples as the suitable materials for optoelectronic applications. The results show that the transparency of MSLS and RCLS crystals has more compared to that of undoped lithium sulfate monohydrate crystal and the values of cut-off wavelength of the samples are the same at 238 nm. The optical band gap of the samples was determined using the formula $E_g = 1242 / \lambda$ (eV) where λ is the cut-off wavelength and the obtained value of band gap for the samples is to be 5.218 eV.

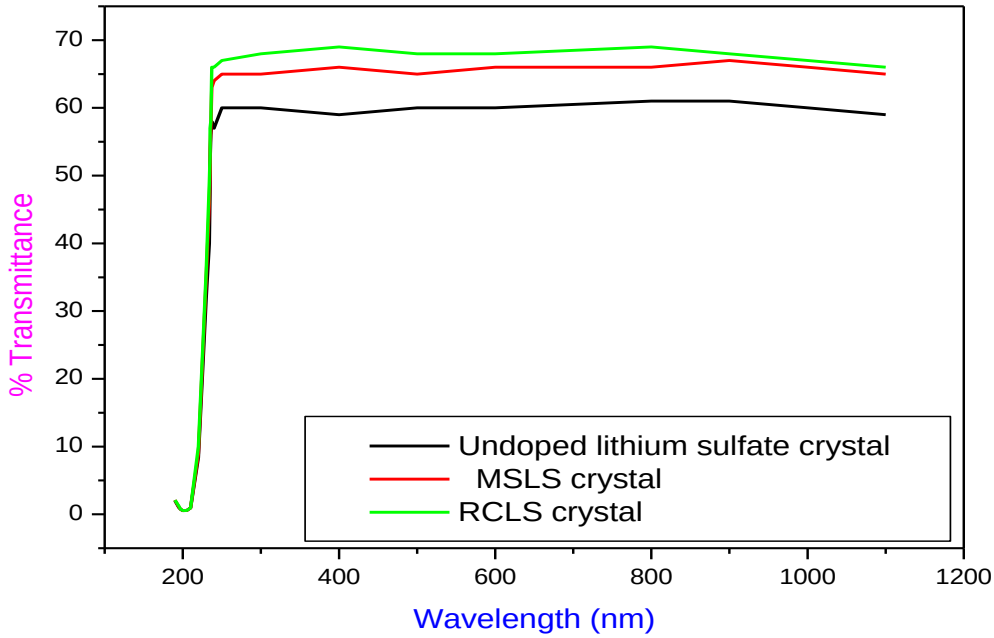


Figure 12: UV-visible transmittance spectra of undoped lithium sulfate, MSLS crystal and RCLS crystal

3.7 SHG Efficiency:

The first and the most widely used technique for confirming the second harmonic generation (SHG) from prospective second-order NLO material is the Kurtz and Perry powder technique [26]. Second harmonic generation efficiency of grown crystal lithium sulfate monohydrate crystal was estimated by Kurtz and Perry powder technique with the help of Nd:YAG laser beam of wavelength 1064 nm. The grown crystal was powdered to the particle size in the range 125-150 μm .The crystal was densely packed in a micro capillary tube. The first harmonic output of 1064 nm from Nd:YAG laser was made to fall normally on the sample. The SHG behavior of the crystal was confirmed from the emission of intense green radiation (λ =532 nm). The SHG efficiency of undoped lithium sulfate monohydrate crystal was found to be 0.97 times that of KDP crystal. Similarly, the SHG efficiency of MSLS crystal and RCLS crystal was found to be 1.13 and 1.26 respectively times that of the reference sample KDP. When lithium sulfate crystals are doped with magnesium sulfate or rubidium chloride as the dopants, the hardness is observed to be increased.

4. Conclusions:

Solution method with slow evaporation technique was adopted to grown undoped, magnesium sulfate doped and rubidium chloride doped lithium sulfate crystals. Undoped lithium sulfate monohydrate crystal crystallize in monoclinic system and the crystal structure was not altered when magnesium sulfate and rubidium chloride were added as the dopants into the host crystal. The absorption peaks/bands were slightly modified when lithium sulfate crystals were doped with the dopants of this work. Thermal studies reveal that the MSLS and RCLS crystals have higher values of decomposition point than that of undoped one. SHG efficiency of MSLS crystal and RCLS crystal was found to be 1.13 and 1.26 respectively times that of the reference KDP sample. The optical band gap of the samples was found to be 5.218 eV. The EDAX studies reveal the presence of various elements in the grown crystals.

5. Acknowledgement:

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