Examination on Bulk Growth, Thermal, Mechanical, Dielectric, and Optical Properties of $Li_2na_3(So_4)_2$ Single Crystal for Optoelectronic Applications

M. Krishna Kumar

Abstract: ***Nonlinear optical lithium sodium sulphate hexahydrate (LSS) crystal of 17 mm x 14 mm x 12 mm dimension was harvested by temperature reducing method. The single crystal and powder X-ray diffraction investigation studies reveal the crystal system and crystalline characters of grown LSS crystal. The FT-IR spectrum of LSS crystal was recorded to confirm its functional constituents present in the synthesized compound. Mechanical ability of the grown LSS crystal was studied by Vicker's hardness method. The etching pattern was recorded to identify the growth feature of the grown crystal. The parameters of dielectric constant and dielectric loss were calculated for the grown crystal. Thermal analysis was carried out on the crystal by employing thermogravimetric method. The cutoff wavelength and optical transmittance character and second harmonic generation efficiency of the LSS crystal were done by UV-Visible and Kurtz-Perry studies respectively.***

Keywords : Solution growth, X-ray diffraction, Thermo-gravimetric analysis, Second harmonic generation.

I. INTRODUCTION

The nonlinear optical (NLO) crystals plays a major role in fabrication of nonlinear optical device utility, such as laser devices, optical storage systems, optical switching applications, telecommunication, sensor devices, optical filter and its allied areas in the impact of information and technology developments [1-4]. The growth of crystals at lower temperature in solution growth method is to produce important crystals of different materials, when large volumes of single crystals are needed for certain applications and this induces the physicists, material scientists and crystal engineers to grow bulk size NLO crystals which should fulfil the above fields [5]. The growth of the inorganic NLO materials and its related properties are most interestedly investigated because of its good optical and mechanical properties [6]. The inorganic elements of lithium, sodium and its complexes are mostly investigated by various researchers for NLO applications [7-8]. The elastic properties of lithium sodium sulphate hydrate (LSS) crystal were reported [9]. However, there is no past studies on bulk growth of LSS and nonlinear optical properties. In this study, attempt has been made to grow good quality lithium sodium sulphate hexahydrate (LSS) single crystal in temperature reducing method and that was studied by various characterization techniques.

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II. EXPERIMENTAL

A. Synthesis and Crystal growth

Lithium sodium sulphate hexahydrate (LSS) compound was synthesized by calculated stoichiometric amounts of lithium sulphate and sodium sulphate were dissolved in de-ionized H_2O. After, stirring homogeneous mixture of solution was achieved by continuous stirring and excess of salt was dissolved by slightly increasing temperature to the solution. The growth solution was filtered and kept in a fixed temperature bath with an fluctuation standard of $\pm 0.01^oC$. The defect free quality seed LSS was used to develop bulk crystal from the saturated solution. The slow cooling method was adopted during the growth period and the temperature of mother solution was reduced by 0.2oC per day. The bulk crystal of the title compound, lithium sodium sulphate hexahydrate (LSS) was grown by 15 days (Fig.1).

$$Li_2SO_4 + Na_2SO_4 \longrightarrow Li_2Na_3(SO_4)_2.6H_2O$$

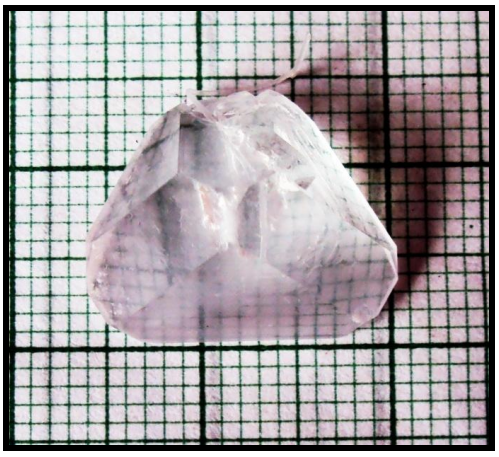

Fig.1 Photograph of lithium sodium sulfate hexahydrate crystal

B. Characterization

The starting materials were purchased from Merck India and used for synthesis. The FTIR spectrum was recorded for the LSS compound using JASCO FTIR 410 spectrometer. LSS single and powder X-ray diffraction studies were done by using Bruker Kappa APEX II diffractometer and Brucker AXSCAD4 diffractometer respectively.

III. RESULTS AND DISCUSSION

A. Single and powder X-ray diffraction analyses

The X-ray diffraction studies to know unit cell parameters by single crystal study was carried for LSS crystal. The single crystal XRD data dictates that, LSS crystal in rhombohedral system (R3c space group). The calculated unit cell dimension values of LSS crystal are a=b=8.451 Å, c=30.28 Å and β=111.95 Å, and the observed values are well agreed with past report [9-10]. The recorded powder X-ray diffraction spectrum is shown in Fig.2. The PXRD pattern reveals the crystalline planes of LSS crystal and corresponding hkl miller indices were indexed. The results of single and powder X-ray diffraction study declares that, synthesized compound is LSS and matched with JCPDS data (PDF No: 331258).

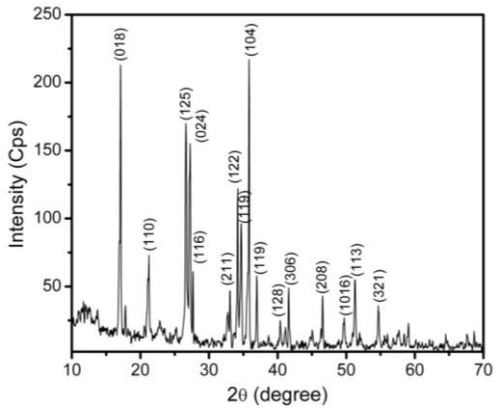

Fig.2 Powder X-ray diffraction pattern of LSS crystal

B. FT-IR spectral studies

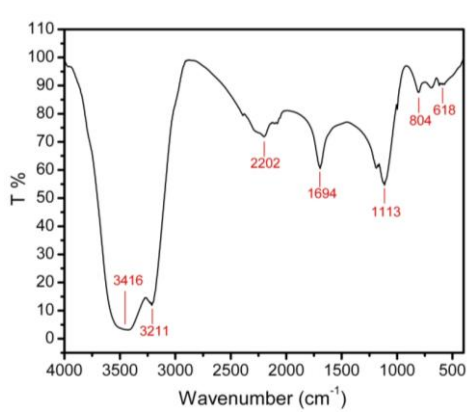

Fig.3 FT-IR spectrum of LSS crystal

The FT-IR spectral study was done to LSS compound between 4000-400 cm^{-1} wavelength range by using KBr pellet method. This spectral data gives the inorganic composition of LSS (Fig.3). Wavenumber at 1113 cm-1 stretching vibration at confirms the presence of SO4 group in the compound. The vibrations at 3416 and 3211 cm-1 are assigned to the H2O molecules present in LSS crystal. Hence, this FT-IR spectrum confirms the synthesized compound was lithium sodium sulphate hexahydrate.

C. Microhardness study

The damage, strength and other mechanical property of the LSS crystal was measured using Vickers hardness testing equipment. The indenter made by diamond in pyramid shape (square base) and its angle is 136o between the opposite faces. This was needle was applied to the surface of flattened LSS crystal sample. The load was applied on the crystal with the indentation time of 10 s, and the indentation of the two diagonal averages onto the crystal was measured [11-12]. This experiment was repeated for several loads and the hardness number Hv was calculated. The plot of calculated Vickers hardness number vs. applied load is shown in Fig.4.

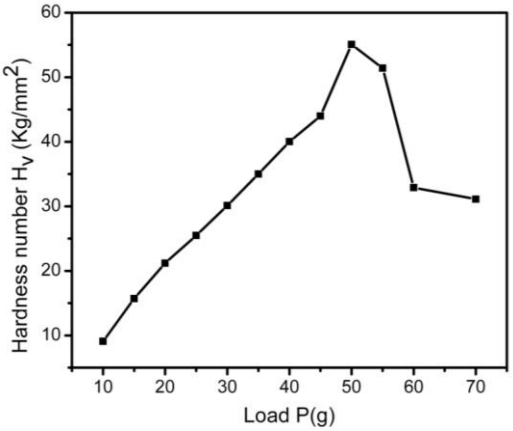

Fig.4 Plot of Hardness number (Hv) vs. Load (P) of LSS crystal

D. Etching studies

Fig.5 Etch pit pattern of LSS crystal

Nonlinear optical character is a ability of the grown crystal and it is purely based on the

structural arrangements. The microstructure analysis was investigated with optical microscope images which is recorded in reflective mode.A polished LSS crystal was etched by using water for few seconds and immediately its surface image was recoded. The internal atoms at the grain boundaries are active, and consequently dissolves more easily, which forms, the grain forming small grooves. This grooves becomes discernible, viewed over microscope due to reflected light (Fig.5).

E. Dielectric studies

Dielectric constant (ε′)and dielectric loss (ε′′) of LSS crystal were calculated. The LSS crystal sample was cut and polished about the dimension of 11.56 x 8.56 x 1.41 mm3 for the measurement. The smooth faces of LSS were coated by Ag paste to make good contact with copper electrodes. The capacitance (C) of LSS was evaluated at different temperatures by changing frequency from 50 Hz to 5 MHz. The dielectric constant (ε′) was calculated by,

$$\varepsilon' = Cd/\varepsilon_{\circ}A$$

where ε′ is relative permittivity, ε o is relative permittivity of free of space, C is the capacitance of the material, d is the thickness of the LSS crystal and A is the area of LSS crystal used for this study.

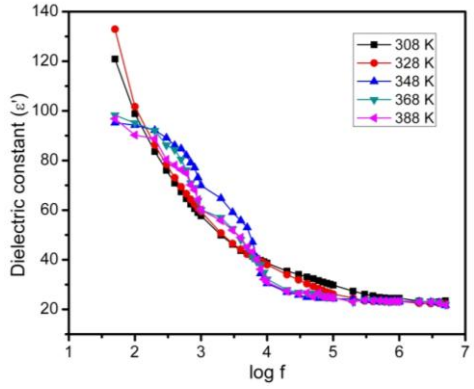

Fig.6 Plot of dielectric constant vs. frequency of LSS crystal

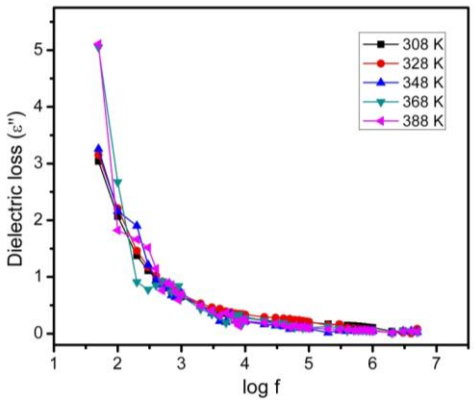

Fig.7 Plot of dielectric loss vs. log frequency of LSS crystal

The plots of dielectric constant (Fig.6) and dielectric loss (Fig.7) are shown and it reveals that the ε′ and (ε′′) are inversely proportional to the applied frequency. In the lower frequencies, dielectric constant showed higher value, when increasing the frequency the dielectric constant decreases gradually and it is constant at higher frequencies [13].

F. TGA/DTA thermal analyses

Thermogravimetric analysis of the compound was carried out to explore the thermal behaviour (Fig.8). From this thermogram, TGA revealed that, the decomposition stages of the sample in two steps. In the first step of the decomposition, it is observed that weight loss starts at 59.60oC and it ends at 72.47^{o}C, because of removal of water molecules from the sample. Its weight loss by dehydration is ~27.92% of weight. In the second step of the thermogram, it is observed that there is no decomposition in the compound up to the temperature of 986^{o}C. It describes the suitability of the title compound at high temperature. The residue percentile of the compound is ~68.76% weight at 986^{o}C. A deep endothermic peak is observed at 70.14^{o}C in the DTA analysis, because of the evaporation of the water molecules.

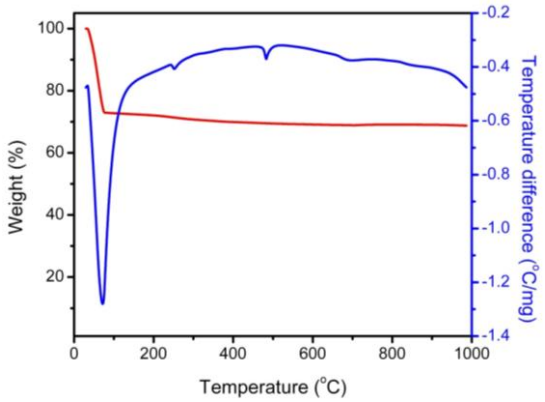

Fig.8 TGA/DTA thermogram of LSS crystal

G. Linear and nonlinear optical studies

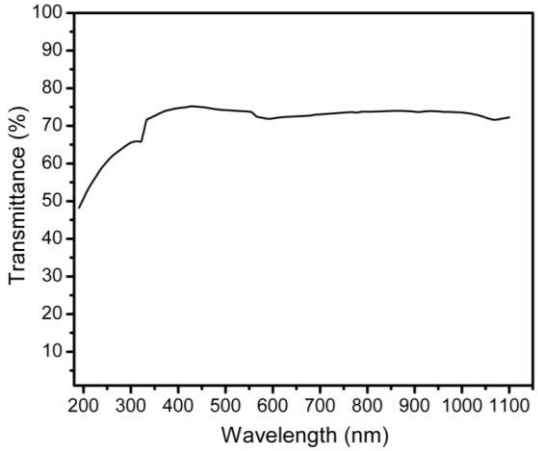

Fig.9 UV-Vis transmission spectrum of LSS crystal

The linear optical transmittance of grown LSS crystal was studied in 190-1100 nm range (Fig.9). The observed declares that, LSS has 75% transmittance ability in the entire range of spectrum and 195 nm was found to be as cut-off wavelength of LSS crystal, which is most desired for optical applications [14]. This NLO property of LSS crystal was analysed by using Kurtz-Perry SHG test [15]. 1064 nm Q-switched Nd:YAG laser which has modulated radiation as optical source. The input energy about 5.65 mJ/ pulse for that of laser beam with 8 ns pulse width was used and the repetition rate was 10 Hz.

The frequency doubling character of LSS crystal was confirmed by green light emission with wavelength of 532 nm. The observed output SHG signal voltages of LSS sample and KDP reference sample are 7 mV and 10 mV respectively. The SHG efficiency of LSS was estimated about 0.7 times with respect to KDP crystal.

IV. CONCLUSSION

Lithium sodium sulphate hexahydrate crystal was successfully grown by temperature reducing method. The single, powder X-ray diffraction techniques were carried out for the LSS crystal and found cell parameters. Mechanical ability and strength of LSS crystal was estimated to LSS crystal by using Vicker' s hardness indenter. The dielectric constant (ε′), dielectric loss (ε″) of LSS crystal were calculated. Thermal stability and behaviour of LSS was explored by employing TGA and DTA studies. The optical transparency ability and cut-off wavelength property of LSS crystal was found by UV-Vis spectral graph. NLO study of LSS crystal was made and compared with KDP reference crystal.

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