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RESEARCH ARTICLE

EFFECT OF COPPER ON GROWTH, STRUCTURAL, OPTICAL, AND THERMAL STUDIES OF LITHIUM AMMONIUM SULPHATE CRYSTALS GROWN BY SLOW EVAPORATION METHOD

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ABSTRACT

Effects of the addition of 1.5 mol% CuSO4 on the growth and the various properties of Lithium Ammonium Sulphate (LAS) single crystals grown by the slow evaporation solution growth technique have been studied. The grown crystals were characterized by single crystal X- Ray Diffraction analysis (XRD), Fourier Transform Infrared spectral studies (FT-IR), UV-Vis- NIR, Atomic Absorption Study (AAS), Thermal analysis and Micro hardness studies. It is observed that the intensity of the plane (111) in pure LAS increases with that of CuSO4-doped LAS increases than in the pure LAS crystal. The strong peak for both crystals in the region 1120 -1130 cm^{-1} in FTIR spectra corresponds to the SO_4^{2-} symmetric stretching modes. UV-Vis-NIR spectra revealed that absorption occurs at 205 nm. The metal contents in the doped LAS crystals were estimated as 662 ppm from the Atomic Absorption studies. Thermal studies indicate that the decomposition temperature of the crystal are decreased in $CuSO_4$ - doped LAS crystals. Vicker's micro hardness study reveals that the addition of $CuSO_4$ increases the hardness of the crystal.

INTRODUCTION

Lithium Ammonium Sulphate (LAS) is an excellent inorganic ferroelectric material. The interest in studying the crystal growth and ferroelectric properties of pure and doped LAS is due to their applications in sensors and actuators. Previous interest in Lithium-Ammonium Sulphate (LAS) crystals has been mainly associated with their unusual ferroelectric and ferroelastic properties (Dollase 1969; Itoh *et al.,* 1981). At room temperature LAS has an orthorhombic symmetry, space group P21cn. The lattice parameters are a = 5.280Å, b = 9.140Å, c = 8.786Å and z = 4, it undergoes two structural phase transitions at about 283 K and 459.5 K, respectively (Yuzwak *et al*., 1975). Between 283 K and 459.5 K LAS is ferroelectric along the a-axis. In the low temperature phase, below 283 K, this crystal belongs to the monoclinic structure with space group P21/a (Shimizu *et al*., 1978). Many papers have been reported the characteristics of phase transition exhibited by this crystal below room temperature and mechanism of transition observed at 459.5K. Recently, it is observed that another transition is reported at 328 K (Krishnan *et al*., 2008; Kleemann *et al*., 1987 ; Tanasaki *et al*., 1980) in the space group P21cn, exhibiting ferroelectric behavior.

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The growth of pure and CuSO4 doped TGS is already reported (Balasubramanian *et al*., 2010). The present work is to investigate the influence of copper on growth, structural, optical, and thermal studies of lithium ammonium sulphate crystals.

Experimental Procedure

Sample preparation

LAS salt was synthesized by stoichiometric incorporation of lithium sulphate (AR grade) and ammonium sulphate (AR grade) in the molar ratio 1:1 and dissolved in the double distilled water. The homogeneity of the mother solution was achieved by constant stirring for 36h. The saturated solution was kept in a constant temperature bath maintained at 303 K in order to obtain the super saturation. 1.5 mol% CuSO4 doped LAS crystals were grown from aqueous solutions using the slow evaporation technique. The untwined and transparent single crystals pure (colourless) of size 35 mm x 8 mm x 5mm shown in Fig (1a) and CuSO4-doped (slightly bluish) crystal of size 17mm x13 mm x 5mm shown in Fig (1b) have been grown successfully in a period of 30 days.

Solubility

The solubility of the material in a solvent decides the amount of the material, which is available for the growth and hence,

defines the size of the crystal. The solubility of pure LAS in double distilled water was assessed as a function of temperature in the range 30-55˚C. The saturated solution was allowed to reach the equilibrium in about 1 day at a chosen temperature and then the solubility was gravimetrically analyzed. The same process was repeated from 30- 55˚C solubility curve was obtained. 1.5 mol% $CuSO_4$ is dissolved fully in 100 ml distilled water and the solubility of LAS is analyzed. The solubility of $CuSO_4$ doped LAS crystals increases with temperature compared with pure sample (Fig.2). In both the cases the solubility increases with the temperature.

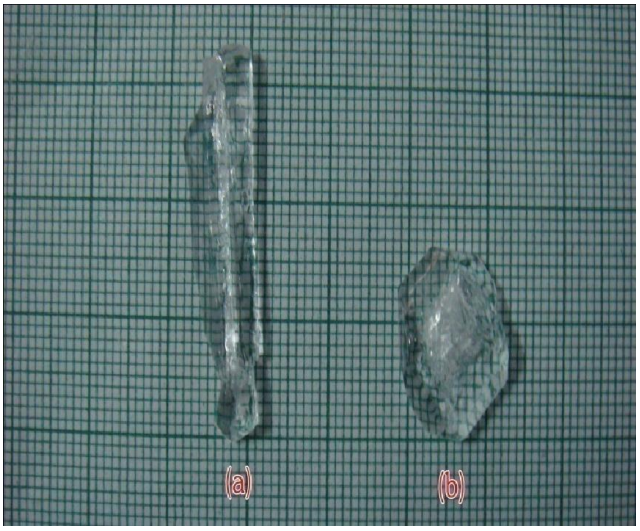

Fig. 1(a). Grown crystals of Pure LAS. 1(b). Grown crystals of CuSO4-doped LAS

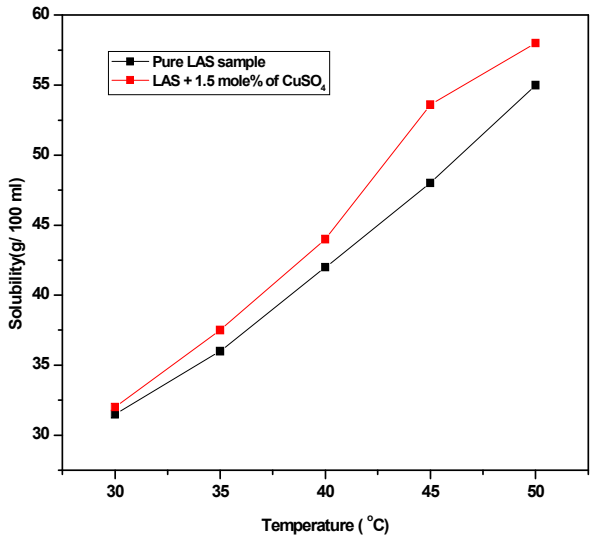

Fig. 2. Solubility diagram for pure and CuSO4-doped LAS salts

Characterization

Single crystal X-ray diffraction analysis for the grown crystals has been carried out using an ENRAF NONIUS CAD4 automatic X-ray diffractometer. Powered XRD for the pure and doped LAS crystals were studied using Ritz-170 powder X-ray diffractometer with Nickel filtered CuKα radiations (λ=1.5406 Å). The specimen in the form of powder was scanned in the reflection mode in the 2θ range 10-60° at the rate of 1° / minute. The infrared spectra were taken in the range 400–4000 cm^{-1} using JASCO FTIR-410 spectrophotometer using KBr pellet. UV- Visible transmittance spectra of the samples were recorded using a Varian Cary 5E UV-Vis-IR spectrophotometer in the range 200-1300 nm. A crystal of thickness 3 mm has been used in this UV study. Atomic absorption studies of 1.5 mole % CuSO4-doped LAS crystals were carried out using an atomic absorption spectrometer (Model: AA 6300). DTA and TG studies on the grown crystals have been carried out using SDTQ 600 V 8.2 (Universal V4.2 ETA) thermal analyser in the temperature range 35 – 600 oC. The mechanical strength of the grown crystals was estimated using Leitz Weitzler hardness tester fitted with a diamond indenter attached to Leitz incident light microscope. Indentations were made for various loads from 5 g to 25 g. Several trials of indentation were carried out on the prominent face and the average diagonal lengths were measured for an indentation time of 10 seconds.

RESULTS AND DISCUSSION

Single crystal X-Ray Diffraction

The grown crystals crystallize in the orthorhombic system with the space group P21cn which agrees with the reported values (Dollase 1969; Itoh *et al.,* 1981; Abul Hossain *et al.,* 1994). The observed lattice parameters (Table 1) for pure LAS compared with the standard pattern (Krishnan *et al.,* 2008; Madhu Mohan 2005) and it agrees.

Table 1. Lattice parameters for pure LAS and $CuSO_4$ - doped LAS crystals

	a (Å)	b (Å)	c (Å)	Volume $(Å)^3$
Std. Values	5.280	9.140	8.786	424.01
Pure LAS	5.276	9.129	8.768	422.30
LAS+1.5mole% $CuSO_4$	5.282	9.118	8.734	420.32

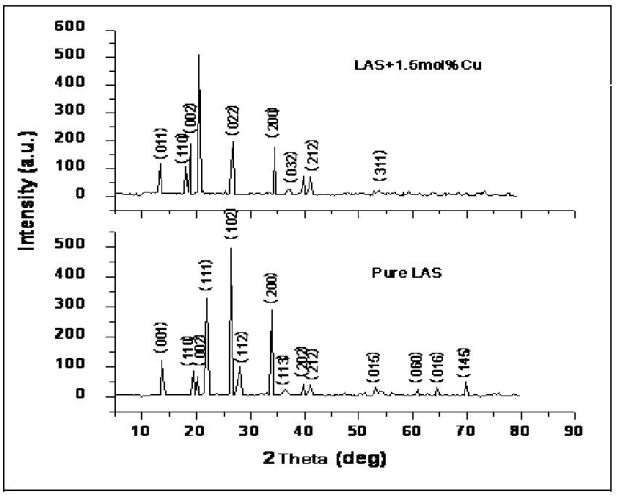

Fig. 3. XRD pattern of Pure LAS and CuSO4-doped LAS

The planes (113), (112), (015), (060), (016), (145) in the pure LAS disappeared in CuSO4-doped LAS pattern. The intensity of planes (102) and (200) in pure LAS decreases compared

with that ofCuSO4-doped LAS pattern. It is observed that the intensity of the plane (111) in pure LAS increases with that of CuSO4-doped LAS increases than in the pure LAS pattern. Additional planes (032), (311) are observed in doped LAS. Similar behaviour was observed for TGS crystal doped with CuSO4 (Balasubramanian *et al.,* 2010).

FTIR studies

The FTIR spectrum of pure and doped LAS are shown in Fig.(4). The broad band covering at 3500-1650 cm^{-1} indicates the asymmetric stretching of NH3+ modes. The peak at 1633.42 cm^{-1} in pure LAS corresponds to NH^{3+} scissor bending. The peaks around 1400 cm^{-1} can be assigned to NH^{3+} asymmetric rocking mode for both crystals. The strong peak for both crystals in the region 1120 -1130 cm^{-1} in FTIR spectra corresponds to the $SO4^{2-}$ symmetric stretching modes. The peak observed in pure and doped LAS crystal around 630 cm^{-1} belongs to $SO4^{2-}$ scissor bending. Li-N stretching modes are observed around 470 cm^{-1} in pure and doped samples. The observed changes in pure LAS and doped LAS crystals are mostly around $SO4^{2-}$ scissor bending and NH^{3+} scissor bending there by suggesting strong coupling/interactions of pure LAS crystals with the copper metal ion (Gauglitz 2003; Kalsi 1985; Kumar *et al.,* 2007; Muthene *et al.,* 2009; Balakrishnan *et al.,* 2006).

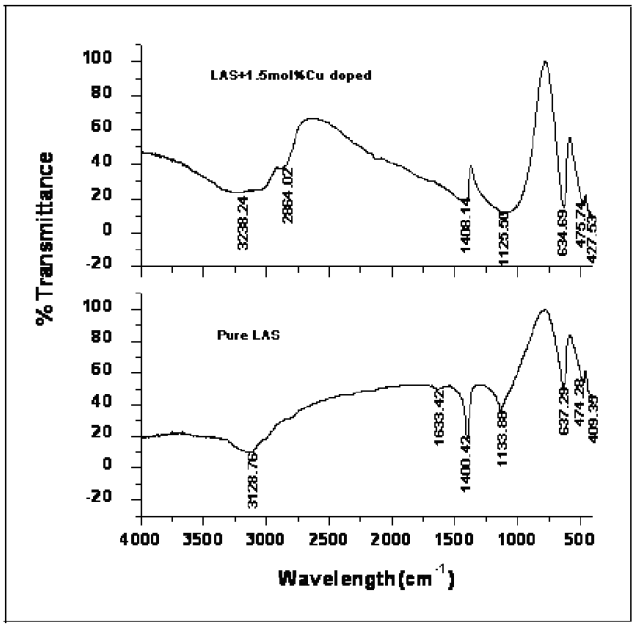

Fig. 4. FTIR spectra for pure LAS and CuSO4-doped LAS

UV-Vis-NIR studies

The recorded UV-Visible transmittance spectra of pure and CuSO4-doped LAS crystals in the wavelength range 200-1300 nm are shown in Fig. (5). From the transmittance spectra, it is noticed that pure LAS crystal has a transmittance of more than 85 % in the visible region. The transmittance of the 1.5 mole % CuSO4-doped crystal decreases when compared with pure LAS. From the UV spectra it is observed that a absorption occurs at 205 nm. The band gap is calculated using the formula Eg = 1240 / λ (nm) and the value is found to be 6.048 eV. Absorption in the near ultraviolet region arises from electronic transitions associated within the samples.

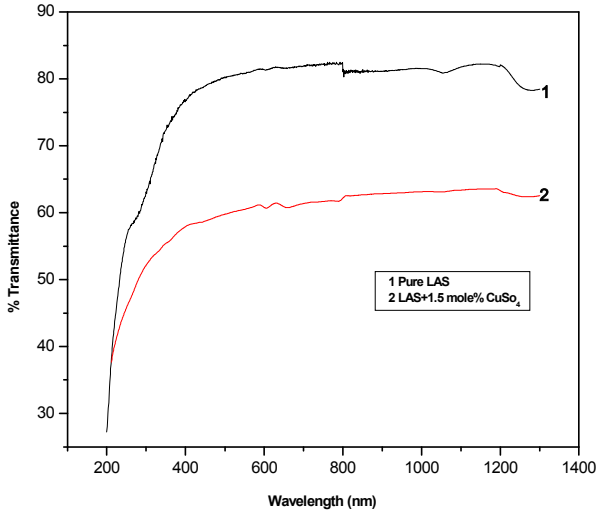

Fig. 5. Transmittance spectra for pure LAS and CuSO4-doped LAS

Atomic Absorption Studies (AAS)

The metal contents in the grown doped crystal are estimated as 662 ppm by atomic absorption studies. This study confirms the presence of dopants in the CuSO4-doped LAS crystals.

Thermal Analysis

TG/DTA thermograms for pure and CuSO4 doped LAS crystals are shown in Fig. (6) and Fig. (7) respectively. From TG curves, it is noticed that there is a negligible weight loss upto 300˚C for pure and doped and there is a maximum weight loss in the temperature range 300˚C - 425˚C. The thermograms show three major weight loss occurring at 295˚C, 385˚C and 445˚C in the case of pure LAS and at 290˚C, 382˚C and 437˚C in the case of CuSO4doped LAS.

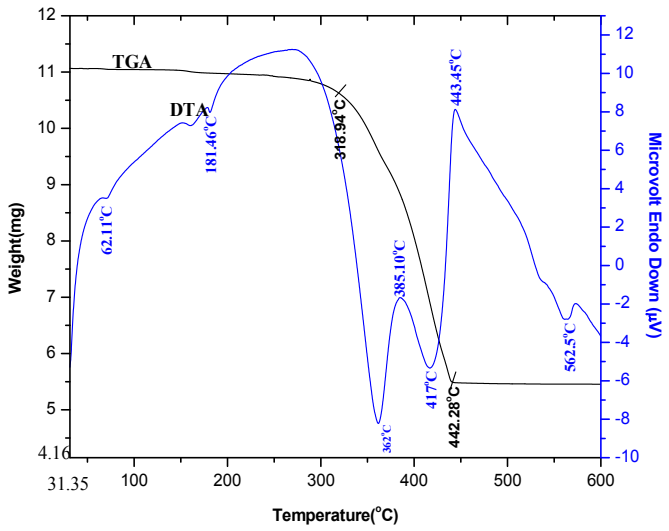

Fig. 6. TG/DTA thermograms for pure LAS crystals

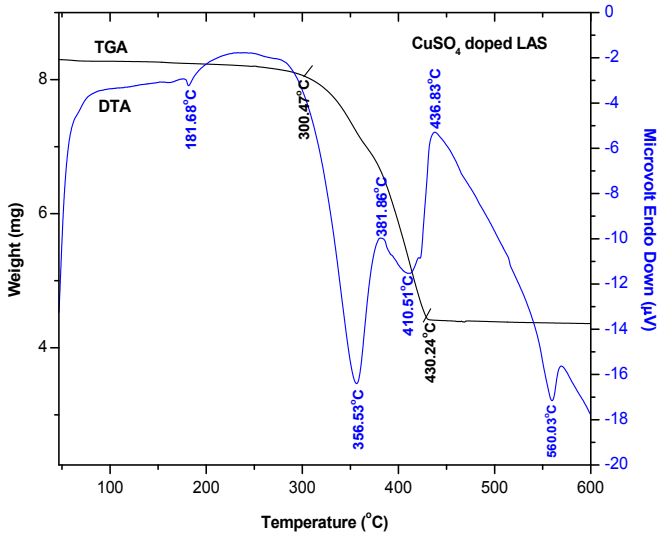

Fig.7. TG/DTA thermograms of CuSO4-doped LAS crystals

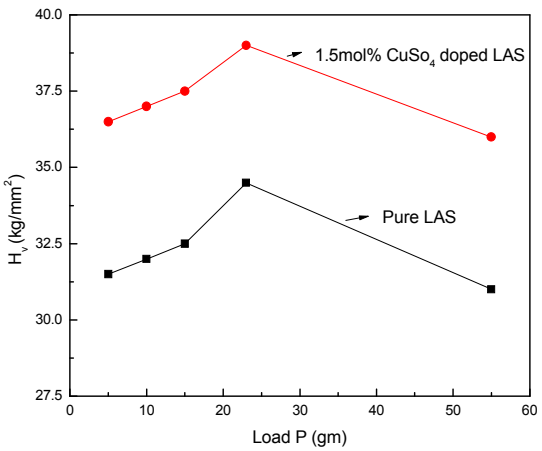

Fig.8. Dependence of hardness number (H_v) with loads in grams for pure and CuSO4-doped LAS crystals

From DTA curve it is observed that the pure LAS is stable up to 295˚C after that it starts to decompose. The endothermic peak at 362˚C is due to decomposition of the sample. In CuSO4doped LAS crystal, the sample is stable up to 290˚C and then it decomposes. The endothermic peak at 357˚C in CuSO4 doped LAS corresponds to the decomposition of the sample. There is a gradual and significant weight loss as the temperature increases above the melting point (Manikandan 2007; Manivannan *et al.,* 2004; Senthil Pandian *et al.,* 2008; Nallamuthu *et al.,* 2010; Hameed *et al.,* 2005). TG/DTA thermograms revealed that the decomposition point of the doped LAS crystal decreases when compared to pure LAS. It is seen that at different stages, various gaseous fractions are liberated leading to a significant decomposition of the compound. Two pure transitions, above 58˚C and 184˚C were observed in DTA thermogram which is in good agreement with the reported values (Krishnan *et al.,* 2008; Madhu Mohan *et al.,* 2005). The irreversible endothermic peaks observed in DTA thermograms denote the stepwise decomposition (Dhanuskodi *et al.,* 2008; Vijayakumar 2010).

Vicker's Microhardness Studies

Vickers microhardness studies, revealed that the hardness number for the pure crystals increases with the load and then decreases for higher load and is in good agreement with values of microhardness of LAS crystals reported by others (Krishnan *et al.,* 2008). It is also observed that the hardness of the doped LAS crystal increase with pure LAS. Similar behavior was observed for TGS doped crystals (Balasubramanian *et al.,* 2010). This increase in the hardness of doped LAS crystal can be attributed due to the incorporation of impurities in the lattice of the crystals. The Vickers micro hardness number was calculated using the relation (1) $HV = 1.8544\ P/d^2\ kg/mm^2$, (1) where P is the applied load and d is the diagonal length of the indentation impression. The increase in Hv for increasing load (P) is shown in Fig. (8). It is in good agreement with theoretical prediction and the grown pure and CuSO4-doped LAS crystals belong to the group of soft materials (Hanneman 1941; Onitsch 1947). It is noted that CuSO4-doped LAS crystals are harder than pure LAS crystals.

Conclusion

Good quality optical single crystals of pure LAS and CuSO4-doped LAS were grown using slow evaporation technique within a period of 30 days. The lattice parameters of grown crystals have been identified from XRD studies. The shift and additional frequencies in the FTIR spectra of doped crystals establish the presence of dopant in the crystal lattice. The UV-Vis-NIR spectral study reveals that the material has a wide optical transparency window in the entire visible region with a cutoff at 205 nm. The presence of dopant in the lattice of doped LAS crystal was confirmed by atomic absorption studies. It is found that the decomposition point of the doped sample decreases slightly as compared to the pure sample. Microhardness studies reveal that the CuSO4doped LAS crystal is harder than pure LAS crystals. The increase in the hardness of divalent impurity-doped LAS crystals will have a significant effect on infrared detector's element fabrication and processing.

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