Effects of Mg^{2+} ions on Structural, Optical and Mechanical properties of L-Alanine Sodium Sulphate Crystals

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Abstract – Single crystals of magnesium sulphate doped L-Alanine sodium sulphate (LASS) has been synthesized with different concentrations by slow evaporation technique.The effect of Mg^{2+} ions on the Structural property of LASS crystal was analysed by single crystal and powder X-ray diffraction methods. The second harmonic generation efficiency (SHG) was measured by Kurtz-Perry powder technique. The transmission of electromagnetic radiation is analysed through UV-VIS spectrum. Microhardness was measured at different applied load to understand the mechanical stability of the crystal.

Index Terms – LASS,PXRD,UV-VIS,SHG.

1. INTRODUCTION

New Non-linear Optical materials have been attracting in the research world for their potential applications in emerging opto-electronic technology,parametric oscillator and frequency conversion devices etc.Moreover the invention of semi-organic NLO crystals has been given more attention in recent decades as they share the advantages of both organic and inorganic materials[1-4]. Alanine is an amino acid which is an important source of energy for the brain, muscle tissues and central nervous system . L-alanine is an isomer of alanine with the chemical formula CH_3CHNH_2COOH and forms novel nonlinear optical (NLO) compounds[5].It is an ideal candidate for a wide range of applications in electron paramagnetic resonance (EPR) dosimetry due to the particular properties of the associated radiation-induced radicals such as the linear signal response over a wide dose range, good dose yield factors, tissue equivalence and stability of the EPR signal.

Presence of small amount of bimetallic dopant (Mg^{2+}) plays a vital role on the growth,chemical and physical properties of the material. Many responsible studies were carried out on L-Alanine based materials [6-9].It is also reported that the addition of transition metal as dopant enhances the NLO property of the organic material[10-13].

In this work, L-Alanine sodium sulphate(LASS) crystals codoped with different concentrations of Mg^{2+} ion (1 mol%,2 mol%) were grown using the slow evaporation technique. Powder XRD is used to investigate the effect of Mg^{2+} ion on structural property of LASS crystal. Characterization studies such as Kurtz-Perry powder technique and UV-VIS spectrum confirms the NLO property of the grown crystals. Hardness values are found out by Vicker's hardness test.

2. SYNTHESIS AND GROWTH OF THE CRYSTAL

Analytical reagent (AR) grade L-alanine, sodium sulphate(Na_2SO_4)and magnesium sulphate ($MgSO_4$) were used along with double distilled water (as a solvent) for the growth of single crystals by the slow evaporation method. L-alanine and Sodium sulphate mixed in 1:1 molar ratio and the doping concentrations of $MgSO_4$ were chosen to be 1 mol% and 2 mol%,They were dissolved in double distilled water and stirred for four hours to obtain a homogeneous solution.

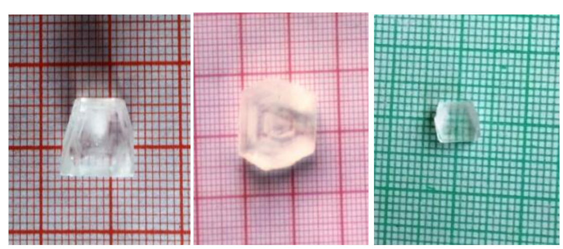

Figure 1:Grown crystals of pure,1% and 2% Mg^{2+} doped LASS

The solution was filtered and kept in a dust free environment.Transparent and colourless crystals of Mg^{2+} doped L-alanine sodium sulphate (LASS) with dimenions10x10.5x4mm^3, 15x14.5x4.38 mm^3 and 6.5X6X3.5mm^3 were formed at room temperature in a period of about 21 days as per the reaction. Figure.1 shows that the photographs of grown pure and Mg^{2+}doped LASS crystals with 1 mol%, 2 mol% respectively.

3. RESULTS & DISCUSSION

Single crystal X-ray diffraction studies

Pure and magnesium sulphate-doped LASS crystals were analyzed by single crystal XRD method and it is observed that the grown crystals crystallized in orthorhombic structure with space group P212121. The unit cell parameters of pure and magnesium sulphate doped LASS crystals were shown in table1.The slight changes of lattice parameters have been noticed for the magnesium doped LASS compared to pure LASS crystal. The changes in the lattice parameters are due to the incorporation of magnesium ions in the lattice of LASS crystal.

Name of the crystal	Parameter (Å)			Unit cell Volume $Å^3$	α°	β°	γ°
	a	b	c				
LASS	5.786	6.041	12.353	431.75	90	90	90
1% Mg^{2+} doped LASS	5.801	6.049	12.294	431.43	90	90	90
2% Mg^{2+}doped LASS	5.898	6.052	12.328	440.13	90	90	90

Table1:SCXRD data of pure and Mg^{2+} doped LASS

Powder XRD Analysis

The purified samples of grown crystals are crushed to a uniform powder and subjected to a powder X-ray diffraction using a XPERT-PRO advance powder X-ray Diffractometer. The Kα-radiations (=1.5406 Å) from a copper target are used for the diffraction studies. The powdered sample is scanned in the range 10–70°C at a scan rate of 2° /min.The well defined sharp peaks reveals the good crystalline nature of pure and doped LASS crystals.The position of the peaks are slightly shifted and the intensity varied due to the dopant . The XRD pattern of the grown LASS crystal and Mg^{2+} doped LASS crytals are shown in figures 2 - 4.

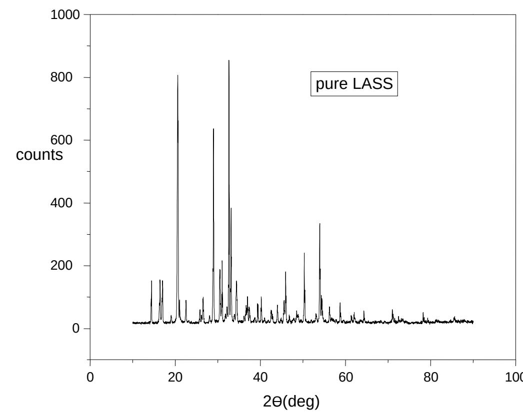

Figure 2: PXRD pattern of pure LASS

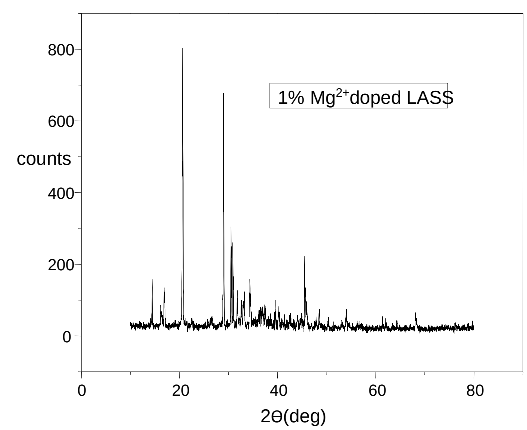

Figure3:PXRD pattern of 1Mg^{2+}doped LASS

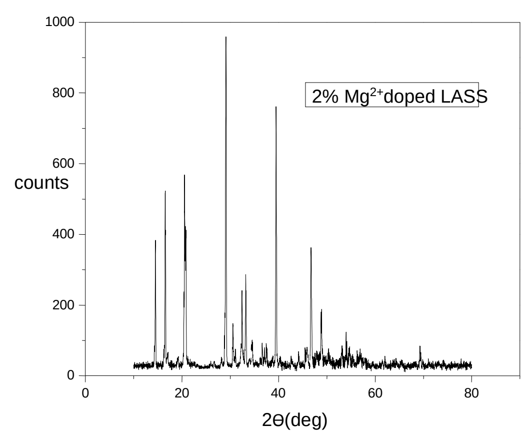

Figure4:PXRD pattern of 2%Mg^{2+}doped LASS

Nonlinear optical analysis

The NLO property of the crystal is confirmed by the Kurtz and Perry technique.The fundamental beam of 1064nm from Q-switched Nd:YAG laser is used to test the second harmonic generation (SHG) property of the doped L-alanine sodium sulphate crystals. The output power from pure and Mg^{2+} Doped LASS crystals were compared to that of KDP crystal and the results are presented in table2.

Sl. No.	Name of the crystal	Output Energy (milli joule)	Input Energy (joule)	SHG efficiency (compared with KDP)
1	LASS	6.81	0.68	0.87
2	1% Mg^{2+} dopedLASS	18.84	0.68	2.4
3	2% Mg^{2+} dopedLASS	8.49	0.68	1.0

Table2:SHG efficiency of Pure and Mg^{2+}doped LASS

The results obtained for Mg^{2+} doped LASS shows that SHG efficiency is about 2.4 times that of KDP crystal and more greater than pure LASS.Thus the crystals can be used for the applications in non-linear optical devices.

UV-VIS analysis

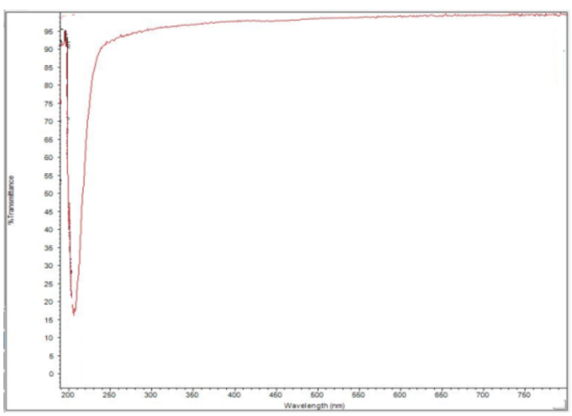

Figure5 pure L-Alanine sodium sulphate

Single crystals are mainly used in optical applications and hence the optical transmission studies plays a vital role in identifying the potential of crystal to be a NLO material. It can be concluded that only when the optical transmission spectrum of the crystal has a wide range of transparency window, without any absorption at the fundamental and second harmonic wavelengths, preferably when the lower limit of the transparency window is well below the 300 nm limits and it becomes a suitable NLO material. The UV - visible spectrum was recorded for the powdered sample of the crystals.This study was carried out in the spectral range 190-800 nm for the grown pure LASS and $MgSO_4$ doped LASS crystals.

UV-VIS transmittance spectrum of pure L-Alanine sodium sulphate and Mg^{2+}(1%,2%,3%) doped L-Alanine sodium sulphate are shown in the Figures 5-7.

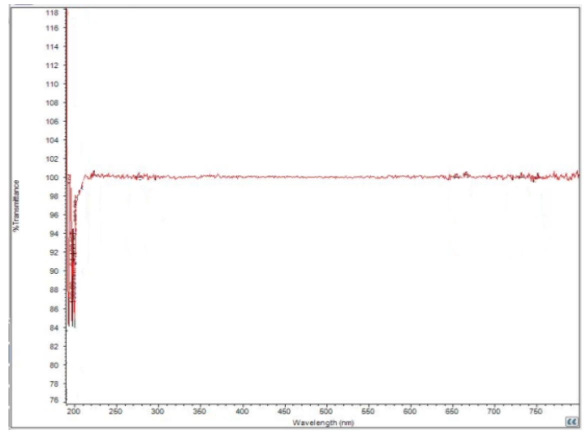

Figure 6: 1% Mg^{2+} doped LASS

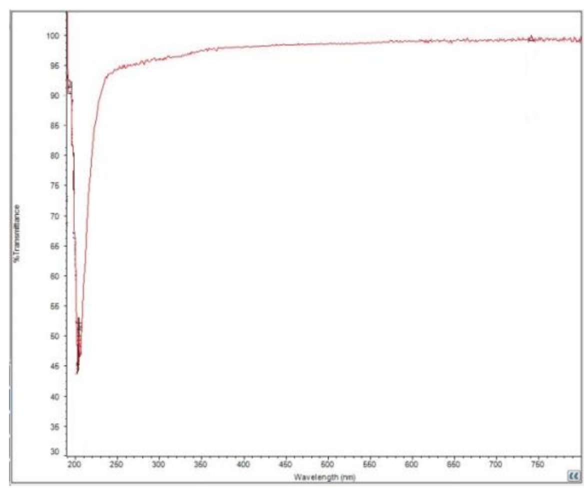

Figure 7: 2% Mg^{2+} doped LASS

From above studies, the grown crystals have good optical transparency between 200 to 800 nm. The effect of magnesium sulphate on LASS crystal is that the optical transparency has enhances to 100%.The percentage of transmittance is high for Mg^{2+} doped LASS than pure crystal. It can be used in opto-electronics applications.

Vicker's Micro hardness study

The mechanical property of grown crystals were studied by Vicker's hardness test. The applied loads were 25, 50 and 100 grams. The measurement was done at different points on the crystal surface and the average value was taken as H_v for a given load.The Vicker's micro hardness was calculated using the relation,

$$H_v = 1.8544\ P / d^2 \qquad \ldots\ldots\ldots\ldots(1)$$

Where, P - is the applied load and d- is the diagonal length of the indentation impression.

The plots of the load p and H_v values are shown in figure 8.It is observed that the Vicker's hardness number increases with increasing load. Above 100g cracks developed on the surface of the crystals due to the to increase the hardness value. Figure.9 shows that the plots of log d against log P for the pure and Mg^{2+} doped LASS crystals. The work hardening exponents were calculated from the slopes of the straight lines. The work hardening coefficients are found to be 4.4, 2.7 and 3.3 respectively for pure and Mg^{2+} doped LASS crystals. According to Onitsch, $1.0 \leq n \leq 1.6$ for hard materials and $n > 1.6$ for soft materials .Since the value of 'n' is greater than 1.6, the grown crystals belongs to soft material category [13-14].

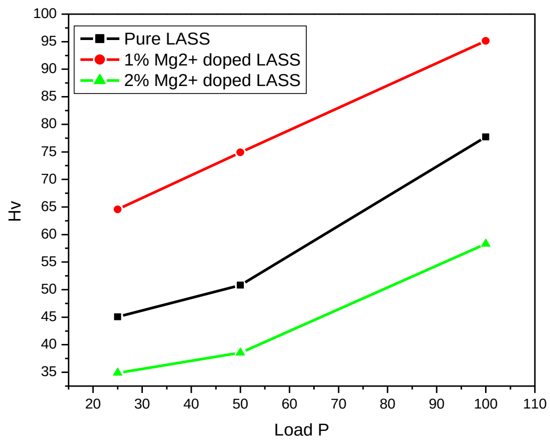

Figure 8: Hardness behavior of pure and doped LASS

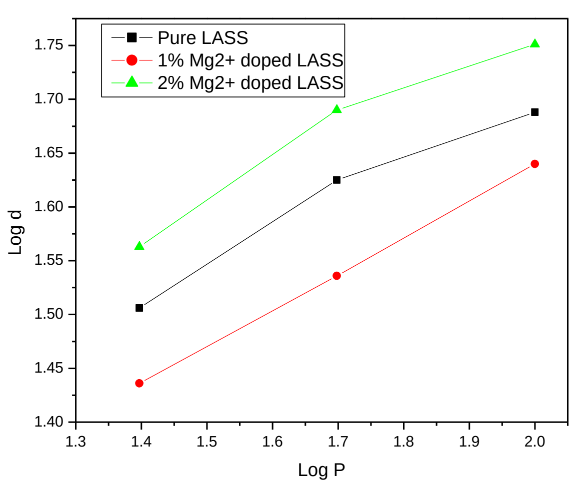

Figure9: plots of log d verses log P of pure and doped LASS

4. CONCLUSION

Good optical quantity of NLO transparent crystals of pure and Mg^{2+} doped L-Alanine sodium sulphate are successfully grown by slow evaporation technique. In this paper,we have described the structural,optical and mechanical properties of pure and Mg^{2+} doped L-Alanine sodium Sulphate crystals.

Structural Characterization was carried out by Powder X-ray diffraction and the cell parameters are found by single crystal X-ray diffraction method. studies From SHG test, it is clear that the efficiency of the crystal is increased when Mg^{2+} is doped with pure crystal.The SHG efficiency of doped L-Alanine sodium sulphate was found to be 2.4 times greater than that of KDP crystal. The good second harmonic generation efficiency indicates that the magnesium doped L-Alanine sodium sulphate crystals can be used for various applications in nonlinear optical devices..The Vicker's hardness number of the grown crystals increases with load and the work hardening coefficients are found to be 4.4,2.7 and 3.3 respectively for pure,1% Mg^{2+} and 2% Mg^{2+} doped LASS crystals. Since the value of 'n' is greater than 1.6, the grown crystals belongs to soft material.

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