The Effects of Mn^{2+}, Mg^{2+} Dopants in Structural, Optical, Mechanical and Dielectric Properties of L-Alanine Sodium Sulphate Single Crystals

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Abstract **:** Single crystals of manganese and magnesium doped L-Alanine sodium sulphate(LASS) crystal has been synthesized by slow evaporation technique.The effects of Mn^{2+},Mg^{2+} ions on the Structural property of LASS crystal was analysed by powder X-ray diffraction(PXRD) method . The optical property of the grown crystals were measured by ultraviolet-visible (UV-VIS) absorption spectroscopy. The absorption of electromagnetic radiation is analysed through UV-VIS spectrum. The second harmonic generation efficiency (SHG) was measured by Kurtz-Perry powder technique. Microhardness was measured at different applied load to understand the mechanical stability of the crystal. Dielectric constant and dielectric loss for various frequencies were carried out in the different temperatures to the grown crystals.

Key words: **LASS,Slow Evaporation Technique ,PXRD,UV-VIS,SHG.**

I.INTRODUCTION

Innovation of NLO crystals plays a vital role in recent decades for their potential applications in emerging opto-electronic technology, frequency conversion devices and parametric oscillator etc. Amino acids are interesting materials for NLO application as they contain proton donar carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group in them [1].The amino acid L-alanine is an efficient organic NLO material under the amino acid family. L-alanine is an isomer of alanine with the chemical formula CH_3CHNH_2COOH and forms novel nonlinear optical (NLO) compounds [2].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. Several new complexes incorporating the amino acid L-alanine have been crystallized and their structural, optical and thermal properties have been investigated .Recently also optical, spectral and second harmonic generation studies were carried out on L-Alanine based materials .A typical semi-organic NLO material is formed by combining an organic ion and an inorganic counter ion to have a favorable high optical nonlinearity, low damage threshold, excellent mechanical and thermal properties[3]-[8] .

Presence of small amount of bimetallic dopants (Mn^{2+} and Mg^{2+}) plays a vital role on the growth, chemical and physical properties of the material. It is also reported that the addition of transition metal as dopant enhances the NLO property of the organic material [9]-[11]. The present paper describes Mn^{2+} and Mg^{2+}doped L-Alanine sodium sulphate crystals as synthesized by slow evaporation method. Characterization studies such as powder XRD, UV-VIS method were done. Kurtz and Perry SHG test confirms the NLO property of the grown crystals. Hardness values are found out by Vicker's hardness test. Dielectric studies were done for analysis of its electrical properties of the crystal.

II.SYNTHESIS AND GROWTH OF THE CRYSTAL

Analytical reagent (AR) grade L-alanine and sodium sulphate (Na_2SO_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 were dissolved in double distilled water and stirred for four hours to obtain a homogeneous solution. The solution was filtered and kept in a dust free environment. Transparent and colorless single crystals of L-alanine sodium sulphate (LASS) with dimenions13.5x11x6 mm^3 were formed at room temperature in a period of about 30 days as per the reaction. LASS was added with the different dopants $MgSo_4.7H_2O$ and $MnSO_4$ in the same molar ratio 1:0.01. Mn^{2+}, Mg^{2+} doped LASS crystals of 11x8x4 mm^3 and 8x7x3mm^3 were grown respectively under identical conditions with the pure LASS crystal growth. The photographs of pure and doped LASS crystals are shown in figure1.

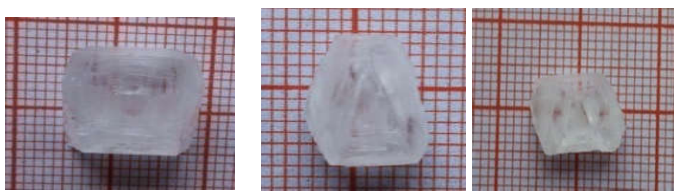

Figure1:photographs of grown crystals of pure LASS,Mn^{2+}doped ,Mg^{2+} doped LASS respectively

III.RESULTS AND DISCUSSION

A.Structural Analysis

(i)Powder XRD

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 LASS,Mn^{2+} doped LASS and Mg^{2+} doped LASS crystals.The position of the peaks are slightly shifted and the intensity varied due to the dopants . The XRD pattern of the grown LASS crystal and (Mn^{2+} , Mg^{2+}) doped LASS crystals are shown in fiures 2-4.

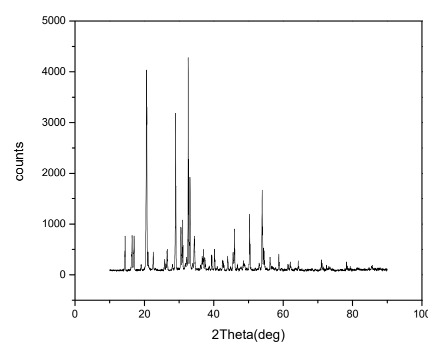

Figure 2: powder XRD pattern of pure LASS

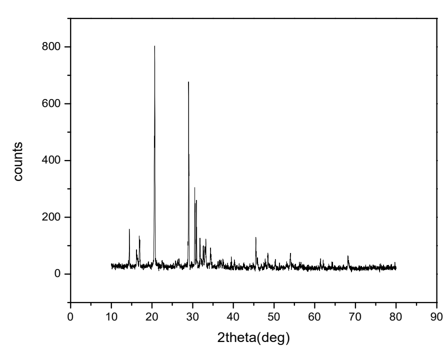

Figure 3: powder XRD pattern of Mn^{2+}doped LASS

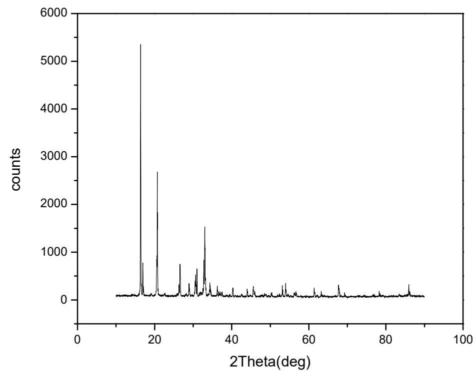

Figure 4: powder XRD pattern of Mg^{2+}doped LASS

B.Optical Analysis

(i)Non Linear Optical Analysis

The NLO property of the crystal is confirmed by the Kurtz and Perry technique. The fundamental beam of 1064nm from Qswitched Nd:YAG laser is used to test the second harmonic generation (SHG) property of the undoped and doped L-alanine sodium sulphate cryst als. The output power from LASS and doped LASS crystals were compared to that of KDP crystal and the results are presented in table1.It is observed that the SHG efficiency increases when pure LASS doped with manganese ions and 1.28 times greater than the reference KDP crystal. 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.

Table1: SHG efficiency of Pure ,Mn^{2+} and Mg^{2+} doped LASS

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	Mn^{2+} dopedLASS	10.01	0.68	1.28
3	Mg^{2+} dopedLASS	18.84	0.68	2.40

(ii)UV-VIS method

The optical absorption spectrum of grown pure LASS, Mn^{2+} doped LASS and Mg^{2+} doped LASS was recorded in the wave region 200-1100. The recorded optical absorption spectrum of the grown single crystals are shown in fig.5. It is observed from the spectrum that the grown crystals has a wide transparency in the entire visible region and the lower cut-off wavelength is230nmfor pure LASS. After being doped with manganese the cut off wavelength is shifted to 224nm. When magnesium ions are added to the pure LASS the cut off wavelength is turned to 215 nm. It is also shows that the effect of dopants has blue –shiifted the absorption edge of pure LASS crystal.

Using the formula,

$$Eg = hc/\lambda \text{ ………………………………..(1)}$$

The optical band gap (Eg) was determined to be5.3,5.5,5.7 eV for the pure LASS,Mn^{2+} doped LASS and Mg^{2+} doped LASS respectively.Thus the cut off wavelength is shifted to lower wavelengths when the dopants are added to the pure L-Alanine Sodium Sulphate .

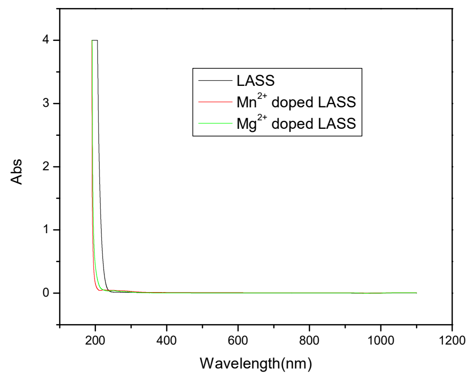

Fig.5: UV_VIS spectrum of undoped and doped LASS

C.Mechanical Analysis

i) Vicker's Micro hardness study

The mechanical property of grown crystals were studied by Vickers 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,

$$H_v = 1.8544\ P\ /\ d^2 \text{ …………………………………(2)}$$

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

Fig.6. shows that the plots of the load p and H_v values.It is observed that the Vicker's hardness number increases with increasing load. Above 100gm cracks developed on the surface of the crystals due to the to increase the hardness value. Fig.7. shows that the plots of log d against log P for the pure and 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, 3.07and 2.7 respectively for pure and Mn^{2+} and $Mg2^{+}$ 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 belong to soft material category [12]-[13].

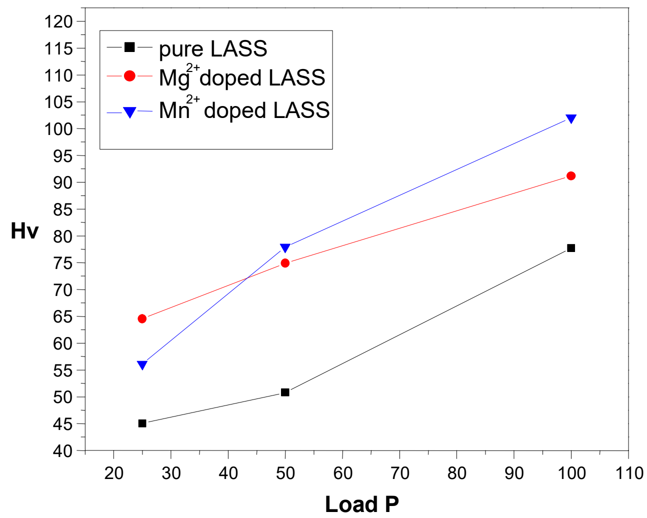

Fig. 6. Hardness behavior of pure and doped LASS

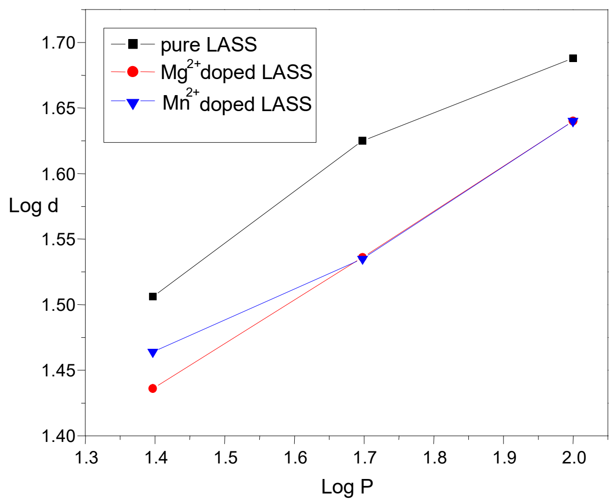

Fig.7. plots of log d verses log P of pure and doped LASS

D.Electrical Studies

Dielectric And Conductivity Analysis

Polished section of the samples with known dimensions were subjected to dielectric measurement using a Dielectric-LCRZ meter TH2816A with a conventional two terminal sample holder.The dielectric properties are correlated with electro-optical properties of the crystals. The dielectric constant ε was calculated using the relation,

$$\varepsilon_r = (Cp\ d) / (A\ \varepsilon o) \quad \text{.........................(3)}$$

The dielectric constant and the dielectric loss factor are measured at different frequencies for various temperatures using a multi-frequency LCR meter. The frequency dependence of the dielectric constant and loss factor at the frequency 1 KHz for undoped and doped LASS crystals are presented in Figs. 8 and 9.The dielectric constant and loss factor have high values at lower frequencies and and are low at higher frequencies. The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar or orientation and a space charge polarization which is high relay upon on the frequencies.

The space charge polarization is generally active at lower frequencies and high temperatures. dielectric constant and loss factor have high values at high temperature and are low at lower temperature.

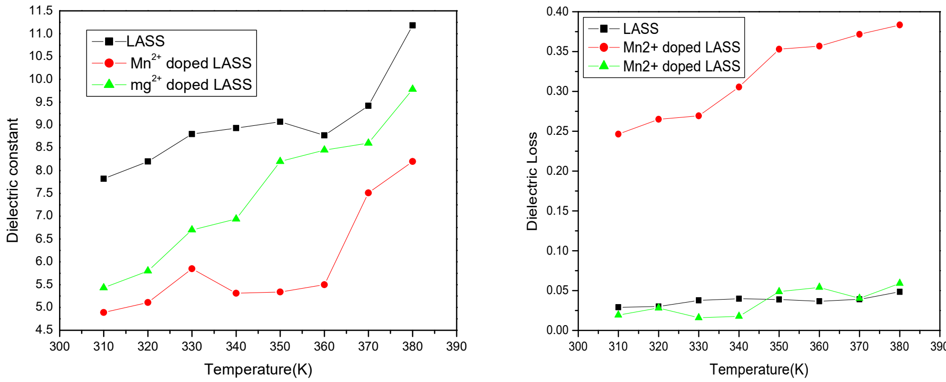

Fig.8: Dielectric constant Vs temperature for 10^3 KHz Fig.9: Dielectric Loss Vs temperature for 10^3K Hz

IV.CONCLUSIONS

In this paper, we have described the synthesis, structural, optical, mechanical and electrical characterization of pure, Mn^{2+} doped and Mg^{2+} doped LASS crystals. Good optical quantity of NLO transparent crystals of undoped and doped L-Alanine sodium sulphate are successfully grown by slow evaporation technique. Structural Characterization was carried out by Powder X-ray diffraction method. From Optical absorption studies the value of bandgap is determined as 5.3eV for Mn^{2+} doped LASS. For Mg $^{2+}$ doped LASS it is found to be 5.7. From SHG test, it is clear that the efficiency of the crystal is increased when manganese and magnesium doped with pure crystal. The SHG efficiency of Mn^{2+} doped L-Alanine sodium sulphate was found to be 1.2 times greater than that of KDP crystal. In case of $Mg2^{+}$ doped L-Alanine sodium sulphate, 2.4 times greater than KDP. The good second harmonic generation efficiency indicates that the 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, 3.07 and 2.7 respectively for pure L-Alanine sodium sulphate , Mn^{2+} doped LASSand Mg^{2+} doped LASS crystals. Since the value of 'n' is greater than 1.6, the grown crystals belongs to soft material. The dielectric constant and loss factor have high values at lower frequencies and are low at higher frequencies. The dielectric constant and loss factor are found to be increasing with increase in temperature. The low values of dielectric loss of the sample confirms the good quality of dielectric sample.

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