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Growth, structural, mechanical and dielectric studies of undoped and urea doped L-alaninium maleate (LAM) crystals

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Abstract Undoped and urea doped L-alaninium maleate crystals were grown by solution method with slow evaporation technique. Solubility studies were carried out for the grown crystals and it is found that solubility increases with temperature for both the samples. XRD studies were performed to find the crystal structure of the samples. NLO activity of the grown crystals was studied using a Nd:YAG laser and SHG efficiency was found for both the samples. Microhardness studies were performed to understand the mechanical strength of the samples. Measurements of values of dielectric constant and dielectric loss were carried out and the electrical processes that are taking place in the samples are discussed.

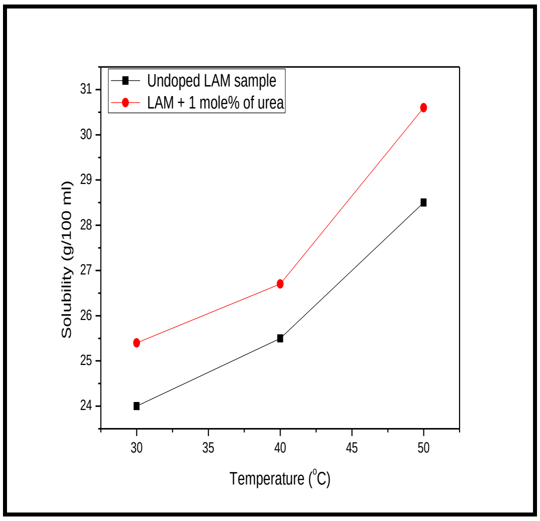
Keywords: Amino acid complex; NLO; doping; single crystal; solution growth; spectroscopy; SHG; hardness

1. INTRODUCTION

Nonlinear Optical (NLO) materials have potential applications in Second Harmonic Generation (SHG), optical storage, optical communication, photonics, .electro-optic modulation, optical parametric amplifiers , optical image processing etc [1,2]. L-alanine is an alpha amino acid with NLO activity and it has the chemical formula CH_3CHNH_2COOH. It is a white odorless crystal powder and easily dissolves in water, slightly dissolves in alcohol and undissolves in ether. L-alanine is a conditionally essential amino acid and it is an important source of energy for muscle tissue, the brain and central nervous system. L-alanine strengthens the immune system by producing antibodies, helps in the metabolism of organic acids and sugars and is used by protein synthesis and immune system regulation [3,4]. Considering the importance of L-alanine, it is combined with maleic acid to form L-alaninium maleate (LAM). To improve the NLO activity and other properties of LAM crystal, urea was added as the dopant into LAM in this work. The aim of this work is to report on the growth of undoped and urea doped LAM crystals and to discuss the results obtained from various studies such as solubility studies, XRD, hardness studies, SHG studies and dielectric studies.

2. GROWTH AND SOLUBILITY

L-alaninium maleate (LAM) sample was prepared from aqueous solutions of AR grade L-alanine and maleic acid taken in 1:1 molar ratio. The evaporation of the solution yielded LAM crystals. To obtain urea doped LAM, 1 mole% of urea was added the solution of LAM. The key factor for successful growth of any crystal is the proper selection of solvents. To find out the suitable solvent, the solubility test was carried out by gravimetrical method [5] and here water was found to be the suitable solvent for growing crystals. The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, equilibrium concentration of the solute can be determined. The solubility curves for undoped and urea doped LAM samples were plotted and they are shown in figure 1. It is observed that solubility increases with temperature for both the samples. When urea was doped into LAM crystal, it is noticed that the solubility increases leading to dissolution of more solute in the same amount of solvent.



Figuere 1. Solubility curves for undoped and urea doped LAM samples.

3. CHARACTERIZATION OF THE GROWN CRYSTALS

Single crystal XRD data of undoped and urea doped LAM crystals were collected from a single crystal X-ray diffractometer with graphite mono chromated MoK_a

radiation. The obtained crystallographic data for undoped LAM and urea doped LAM crystals are a=5.572(2) Å , b = 7.415(4) Å, c = 23.674(3) Å , α = β = γ = 90° and a= 5.598(4) Å, b=7.465(1) Å, c= 23.592 (2) Å, □□= 90°, □= 90° □=90° respectively. From the data, it is observed that both the grown crystals crystallize in orthorhombic crystal systems. The number of molecules per unit cell (Z) for both crystals of this work is found to be 4. The slight changes in the lattice parameters are due to incorporation of urea in the lattice of LAM crystal.

The mechanical property of crystals can be analyzed by carrying out microhardness studies using a Leitz Vickers microhardness tester. Measuring microhardness gives an idea about the mechanical strength of a material. The hardness of a material is a measure of its resistance to plastic deformation. In an ideal crystal, the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed. This is due to normal indentation size effect (ISE). The hardness number was measured for undoped and urea doped LAM crystals by applying different loads. The Vickers microhardness number was calculated using the relation H_v = 1.8544 P/d kg/mm^2 where P is the applied load and d is the diagonal length of the indentation impression. The variations of Vickers hardness number with the applied load for both the samples are presented in the figure 2.

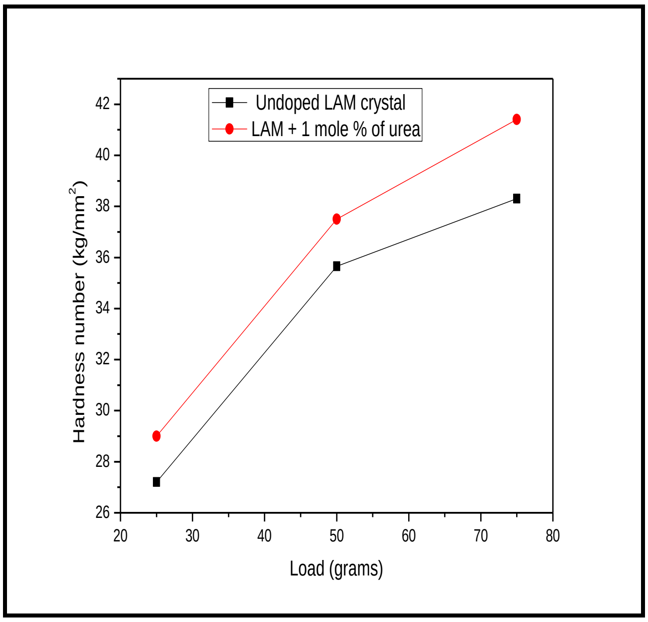


Figure 2. Variation of hardness number with the applied load for undoped and urea doped LAM crystals.

It is observed from the figure that the hardness increases as the load increases. Cracks are formed beyond 100 g and the formation of cracks on the surface of the crystal beyond the load 100 g is due to the release of the internal stresses generated locally by indentation. The increase of microhardness with increasing load is in agreement with the Reverse Indentation Size Effect (RISE) as reported in the literature [6].

Second Harmonic Generation (SHG) test for the grown pure and urea-doped LAM crystals was performed by the powder technique of Kurtz and Perry [7] using a pulsed Nd:YAG laser(Model: YG501C, □=1064 nm). Pulse energy of 4 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz were used. The grown crystals were ground to powder of grain size 300-500 µm and the input laser beam was passed through IR reflector and directed on the powdered sample packed in a capillary tube. Mirocrystalline material of potassium dihydrogen phosphate (KDP) was used as reference in this experiment. Second Harmonic Generation (SHG) from the samples was detected using an optical cable attached to a fluorescence spectroscope(Model: DID A-512 G/R). The SHG efficiency for undoped LAM crystal is found to be 1.15 times and for urea doped LAM crystal is observed to be 1.34 times that of KDP sample and hence the samples are the second harmonic generators.

The dielectric constant determines the share of the electric stress which is absorbed by the material without any dielectric breakdown. When an electric field acts on any matter the latter dissipates a certain quantity of electrical energy that transforms into heat energy. This phenomenon is commonly known as loss of power, meaning an average electric power dissipated in matter during a certain interval of time. The amount of power losses in a dielectric under the action of the voltage applied to it is commonly known as dielectric losses. The lower the dielectric loss the more effective is a dielectric material. Dielectric constant and dielectric loss values of crystalline samples were measured using a two-probe arrangement and an LCR meter. The measured values of dielectric constant and dielectric loss at different temperatures at frequency of 10^3 Hz for the samples viz. undoped and urea doped LAM crystals are presented in the figures 3 and 4.

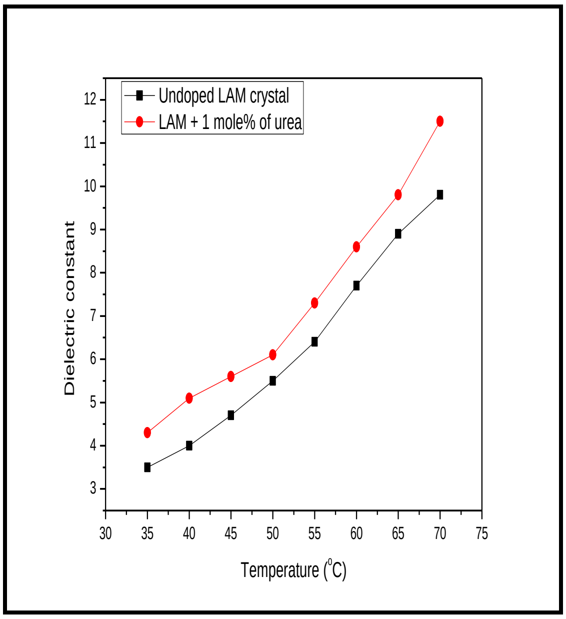


Figure 3. Variation of dielectric constant with the temperature at frequency of 1000 Hz for undoped and urea doped LAM crystals.

From the results, it is observed that dielectric parameters such as dielectric constant and loss factor increase with increase in temperature for both the samples. The same behaviour is exhibited by dielectric loss (tan □). In accordance with Miller's rule, the low value of dielectric constant is a suitable parameter for the enhancement of SHG coefficient and low values of dielectric loss reveals the high optical quality of the crystals with lesser defects, which is the desirable property for NLO applications [8]. Variation of the dielectric parameters of the sample with temperature is generally attributed to the crystal expansion, the electronic, space charge and ionic polarizations and also due to the thermally generated charge carriers. When urea is added into the LAM crystal as the dopant, it is noticed that the dielectric parameters are found to be increasing which may be due to presence of defects in the host crystal.

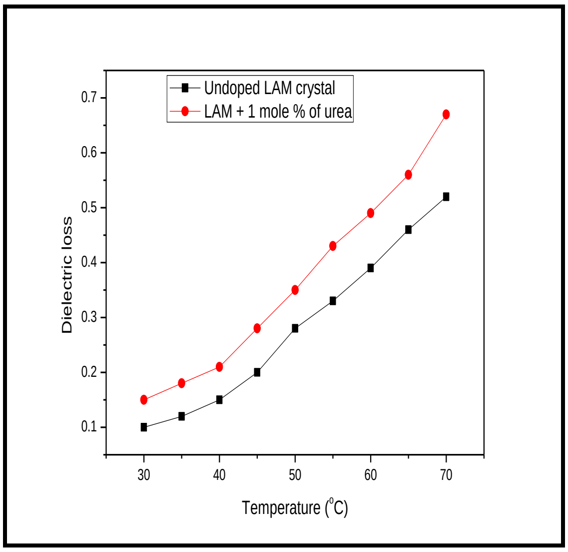


Figure 4. Variation of dielectric loss with the temperature at frequency of 1000 Hz for undoped and urea doped LAM crystals

4. CONCLUSION

Two samples viz. undoped and urea doped L-alanine maleate crystals were grown by solution method. Solubility in water is found to be increasing with temperature for the both samples. XRD study reveals that the grown crystals crystallize orthorhombic structure. The mechanical strength of the samples was analyzed by hardness studies and SHG was tested by Kurtz powder method. The dielectric constant, loss factor and SHG values reveal that the grown crystals are suitable materials for optical communication, electro-optic modulation and optical computing.

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