

Studies on Thermal, Microhardness and Di-Electric Properties of Glycine Copper Chloride

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Abstract: Copper Chloride doped Glycine crystals were grown from aqueous solution by natural evaporation method. The grown crystals were subjected to thermal (TG-DTA), Di-electric studies and Microhardness analysis. The grown Copper Chloride doped Glycine crystals were found to be highly transparent and full faced. From TGA/DTA curve, it is found that the crystals were thermally stable and there is an improvement in stability due to dopants added with Glycine. The dielectric properties are correlated with electro-optical properties of the crystals. Copper Chloride doped Glycine has higher dielectric constant and low dielectric loss than pure Glycine. Glycine Copper Chloride crystals have low micro hardness value than that of pure Glycine crystal. The crystals are soft substances. Thus, the grown crystals are useful in fabrication of optoelectronic devices.

Keywords: Glycine Copper Chloride, dopant-copper chloride on Glycine crystal, solution growth, Crystal growth.

1. Introduction

Metal ion dopants have been added to modify the properties of pure Glycine crystal. In the present work, CuCl_2 is used as a dopant to see its effect on the property of pure Glycine crystals. Copper Chloride doped Glycine crystal is considered as one of the potential materials for its wide range of applications, namely, second harmonic generation, reasonably low dielectric constant and due to its thermal stability.

2. Experimental Method

Synthesis and Crystal Growth

Analar Reagent (AR) grade Glycine and Copper Chloride were dissolved in deionized water in the molar ratio of 10 : 1, and the solution was allowed to attain supersaturation state. The synthesized salt was again dissolved in triple distilled water and then re-crystallized by natural evaporation process. This process was repeated three times to improve the purity of the material. Good quality and defect-free seed crystals were used to grow bulk-size crystal. Highly transparent and full-faced crystals were obtained

within 4 weeks. Copper Chloride doped Glycine crystals are found to be pale green and is shown in Fig.1.

3. Results and Discussions

3.1 Thermal Studies

The effect of dopant CuCl_2 with Glycine on thermal behavior was analyzed using NET2SCH Proteus Thermal Analyzer. The TG/DTA analyses of pure Glycine and CuCl_2 doped Glycine were carried out from room temperature to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$. 13.069 mg of Glycine CuCl_2 samples were used for analysis and the resulting thermogram are shown in fig.3.1 (a) and fig. 3.1 (b). The TGA curve shows that the weight loss occurs at two stages in pure Glycine, whereas there are no intermediate stages in CuCl_2 doped Glycine crystals. In the case of CuCl_2 doped Glycine, the samples were thermally stable up to around 260°C respectively. There is an improvement in stability due to dopants added with Glycine. From DTA curve, it is observed that an endothermic peak at around 275°C in pure Glycine but in CuCl_2 doped Glycine sample, the endothermic peak shifted to 265°C , it may be attributed to decomposition of Glycine CuCl_2 crystal.

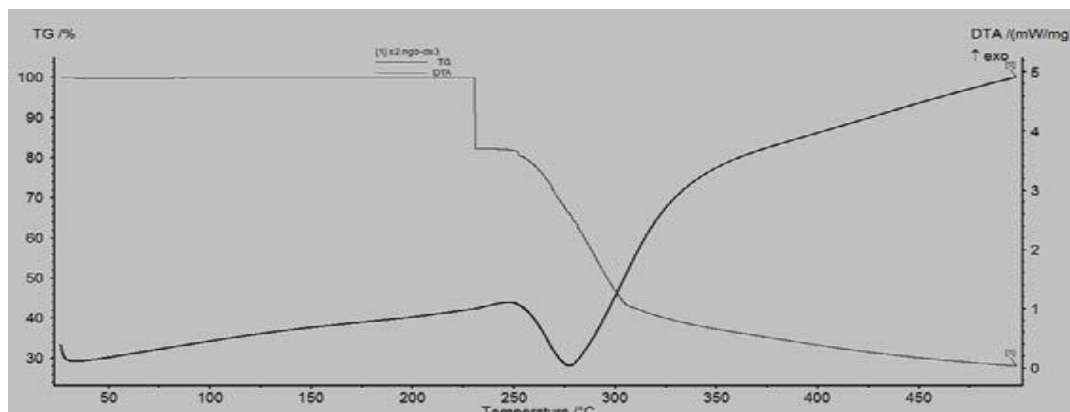


Figure 3.1: (a) PURE GLYCINE

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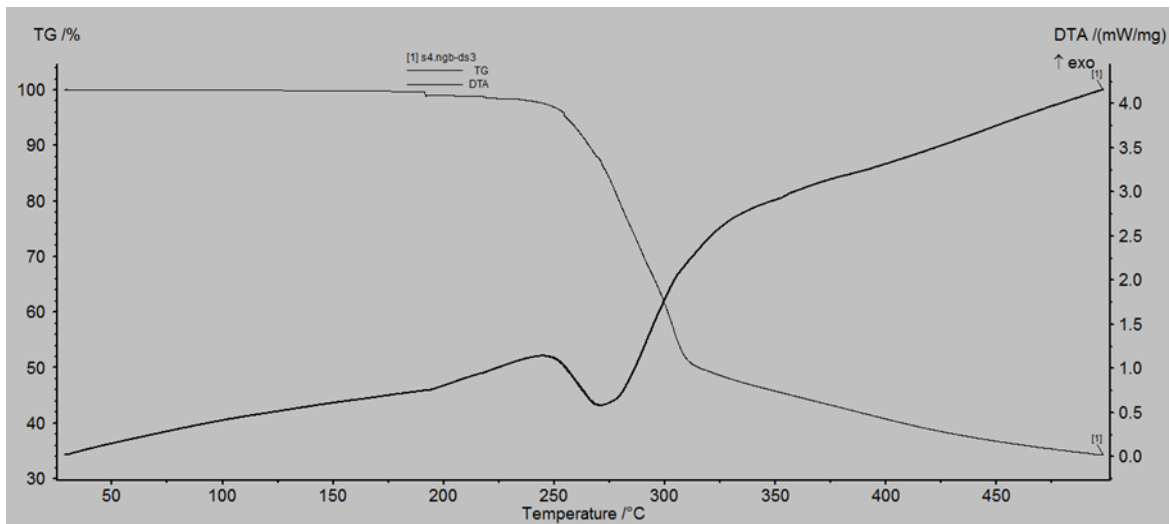


Figure 3.1: (b) GLYCINE COPPER CHLORIDE

3.2 Di-electric Studies

The dielectric properties are correlated with electro-optical properties of the crystals. The dielectric constant ϵ was calculated using the relation $\epsilon = (Cp d) / (A \epsilon_0)$. Fig 3.2 (a) & 3.2 (b) show the plot between the calculated dielectric constant and dielectric loss with respect to logarithm of frequency for pure and Copper Chloride doped Glycine crystals respectively. The graph shown in fig. 3.2 (a) & (b) reveals that the dielectric constant has higher value at lower frequencies and almost constant at higher frequencies beyond 3 KHz. The dielectric constants for pure Glycine and Copper Chloride doped Glycine are 22.54 and 35.40 respectively. The magnitude of dielectric constant depends on degree of polarization and the charge displacement in the crystal. The decrease in dielectric constant at higher frequencies is attributed to the absence of charge polarization near the grain boundary interface. For a material to be potential candidate for NLO applications, dielectric loss (ϵ'') must also be kept as low as possible. From the graph 3.2 (c) & (d), it is clear that above crystals exhibit very low dielectric loss at high frequencies and can be used for NLO applications. Copper Chloride doped Glycine has higher dielectric constant (67.90) and low dielectric loss than pure Glycine crystals which have dielectric constant 22.54.

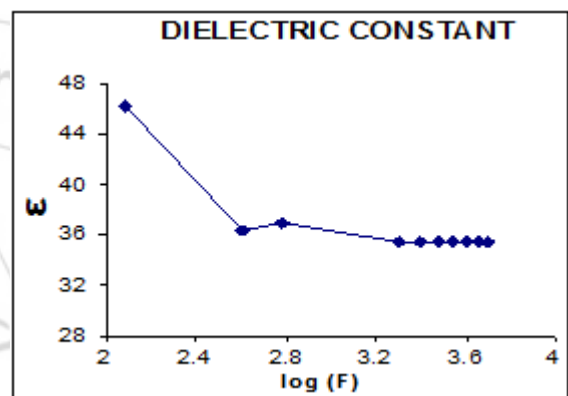


Figure 3.2: (b) CuCl₂ DOPED GLYCINE

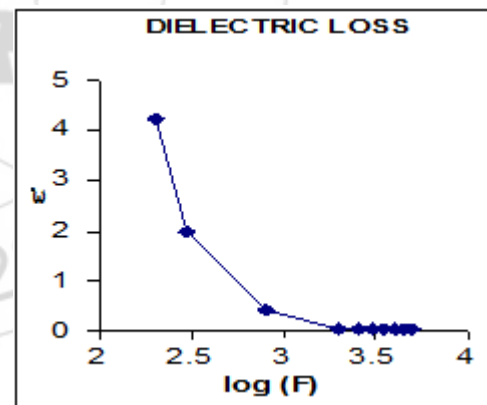


Figure 3.2: (c) PURE GLYCINE

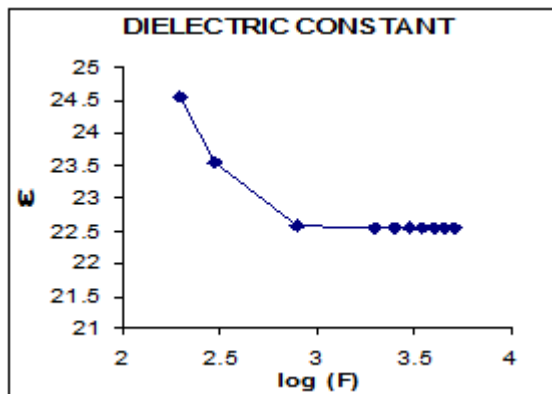


Figure 3.2: (a) PURE GLYCINE

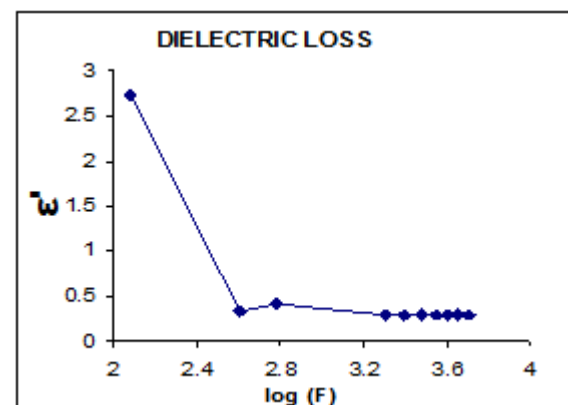


Figure 3.2: (d) CuCl₂ doped GLYCINE

3.3 Microhardness Studies:

Variation of Hardness (Hv) with load P

The gel grown crystals of good quality and in size are selected for the Hardness measurement studies. At large loads, the crystal show brittle behavior. The variation of the hardness with different dopants shows interesting result. The calculated microhardness value (Hv) of pure and Copper Chloride doped Glycine crystals as a function of load is shown in fig. 3.3 (a) & (b). Glycine Copper Chloride crystals have lower Hv value than that of pure crystal. The hardness value of both pure and doped crystals increases with increasing load of up to 100 gm. There were no cracks observed up to a load of 100 gm and hence, it may be suggested that the material may be used for the device fabrication below the applied load of 100 gm. The relation between load and size of the indentation is given by Meyer's law. Fig. 3.3 (c) & (d) shows the plot of logarithmic of load P Vs logarithm of diagonal length of impression. From the slope of log P Vs log d plot, the value of n was estimated, which gives the work hardening index. From careful observations on various materials, Onistch pointed out that an n lie between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials. The value of n observed in the study is more than 2 for pure and doped crystals suggesting that these crystals are soft substances. Hence, pure and Copper Chloride doped Glycine crystals belong to the soft material.

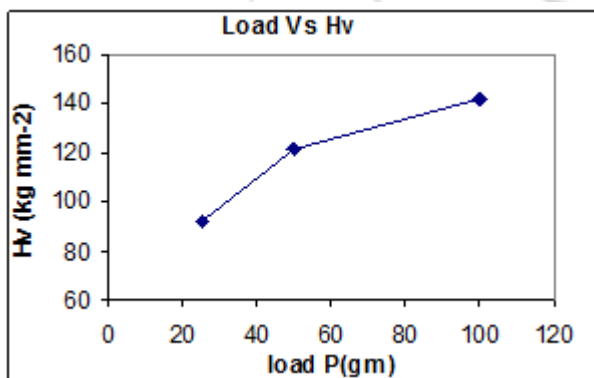


Figure 3.3: (a) PURE GLYCINE

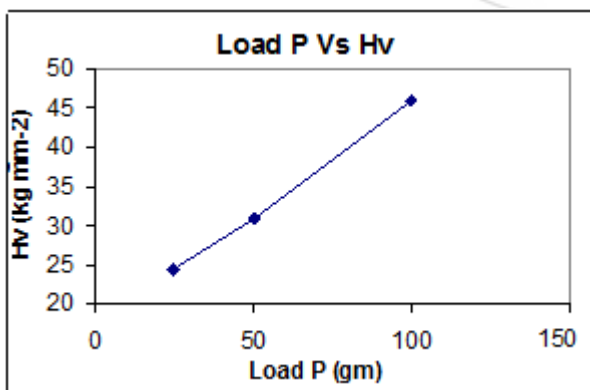


Figure 3.3: (b) CuCl₂ doped GLYCINE

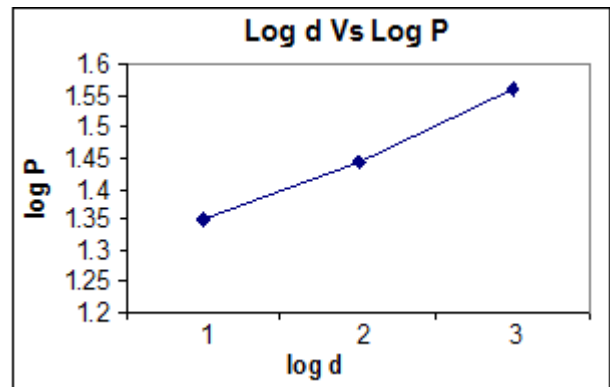


Figure 3.3: (c) PURE GLYCINE

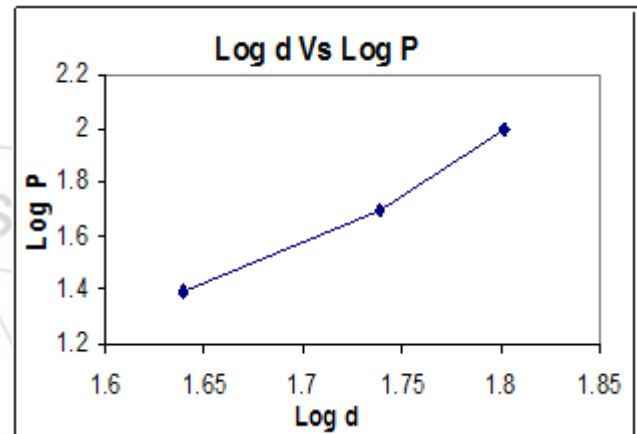


Figure 3.3: (d) CuCl₂ doped GLYCINE

4. Conclusion

Optically transparent single crystals of pure and Copper Chloride doped Glycine crystals have been conveniently grown by slow-evaporation method at room temperature. The crystals are transparent and their shape and size are sensitive to the dopant present in the solution during growth. The Glycine Copper Chloride dopant might be used to yield crystals useful for device fabrication. The TG/DTA reveals that the sample is thermally stable and has relatively higher melting point. There is a high thermal stability observed in Glycine Copper Chloride than in pure Glycine. It is also concluded that the grown crystal decomposes without melting at about 260°C. Carefully selected crystals were subjected to Vickers' microhardness test for various loads (25 to 100 gm) at room temperature. All the crystals show an increasing Vickers Hardness number (Hv) with increasing load P and hence the behavior can be explained by Reverse Indentation size effect. Since, $n > 1.6$ all the materials belong to soft material category. The mechanical properties prove them to an attractive material for optoelectronic applications. The grown crystals show high dielectric properties. Copper Chloride doped Glycine has higher dielectric constant (35.40) and low dielectric loss than pure Glycine crystals which have dielectric constants 22.54

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