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Thermal studies on calcium and lanthanum doped TGS crystals

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ABSTRACT

Triglycine Sulphate (TGS) is one of the best ferroelectric material. It finds wide application as pyroelectric detector, single crystal of Triglycine Sulphate was grown from the aqueous solutions by slow evaporation technique. The Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) were made ,debye temperature of the grown crystals were determined from the melting point and the activation energy was calculated from the mass change , the value of activation energy thus calculated from the mass change well agreed with the reported value.

Key words: TGS, Mass change, Activation energy, Debye temperature, TGA, DTA

INTRODUCTION

Triglycine sulphate (TGS) crystal is a useful ferroelectric material founded in 1956 [1] and has low dielectric constant and large pyroelectric coefficient. It finds applications in the fabrication of pyroelectric vidicon tubes, capacitors, tranducers, sensors and also it is used in the infrared detection techniques as commercial product [2-3]. TGS crystal shows a ferroelectric phase transition at the curie point ($T_c = 49^{\circ}$ C). Below the T_c , TGS possesses the polar point symmetry of group 2 of monoclinic system, spontaneous polarization arises along the b-axis and above T_c , it possesses the non-polar point group 2/m of the monoclinic system [4-5].

Growth of sample

TGS salts were synthesized from the following reaction [6]

 $3(NH_2CH_2COOH) + H_2SO_4 \rightarrow (NH_2CH_2COOH)_3(H_2SO_4)$

AnalaR Grade Glycine and Sulphuric acid were used for the synthesize of TGS salt, after successive recrystallization processes the purified salt were used for the preparation of the solution. Calcium carbonate and Lanthanum sulphate was added in the ratio viz. 1:0.000, 1:0.002, 1:0.004, 1:0.006, 1:0.008 and 1:0.010 to the TGS solution and saturated at 45° C.

Growth was initiated by a temperature reduction of the solution and slow cooling was employed. The good quality crystals were harvested after a typical growth period of 10 days. The photograph of the grown crystals were given in figure 1 and figure 2. Which Shows that the grown crystals were hard, strong and transparent.

The concentration of calcium in the calcium doped TGS were determined from the Atomic absorption spectra taken, and the concentration of lanthanum in the lanthanum doped TGS crystals were determined from EDAX

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spectrum taken. Which confirm the presence of calcium and lanthanum in calcium doped TGS and lanthanum doped TGS respectively. The EDAX spectrum for TGS:0.010La is given in figure 3. for illustration, and the concentration of calcium and lanthanum present in the doped TGS crystals were provided in the table 1. and 2.



1-Pure TGS, 2-*TGS*:0.002*Ca*, 3-*TGS*:0.004*Ca*, 4-*TGS*:0.006*Ca*, 5-*TGS*:0.008*Ca*, 6-*TGS*:0.010*Ca* **Figure:1. Photograph of grown Pure and calcium doped TGS**



L1- TGS: 0.002La, L2- TGS: 0.004La, L3- TGS:0.006La, L4- TGS :0.008La, L5-TGS :0.010La Figure:2. Photograph of grown lanthanum doped TGS

System	Calcium concentration (ppm)	
Pure TGS	-	
TGS:0.002Ca	9.913	
TGS:0.004Ca	10.645	
TGS:0.006Ca	17.39	
TGS:0.008Ca	26.145	
TGS:0.010Ca	85.516	

Table 1: Concentration of Calcium in Pure and Calcium doped TGS

Table 2: Concentration of Lanthanum in Pure and Lanthanum doped TGS

System	Lanthanum concentratio (ppm)	
Pure TGS	-	
TGS:0.002La	0.00175	
TGS:0.004La	0.00246	
TGS:0.006La	0.00263	
TGS:0.008La	0.0035	
TGS:0.010La	0.00596	



Thermal study

The TG/DTA spectrum of all the eleven samples were recorded using. STA 449 F3 Jupiter^R - simultaneous TGA-DSC (Temperature range is 50 to 500°C in present study) at Netzsch Technologies India pvt Ltd, Chennai

Melting point and Debye Temperature:-

The melting point of all the grown crystals were determined from the thermal analysis curve. The Debye Temperature of all the grown crystals can be determined from using the formula [7]

 $\theta_{D} \ = C \, \left[T_{m} \, / \, M V^{2/3} \, \right]^{1/2}$

Where, C is a constant depending on the X-ray intensity data structure, Here it was estimated as 1000 from the reported debye temperature values of pure TGS. T_m is the melting point, M is the molecular weight of the crystal and V is the volume of the unit cell.



Figure 5: TG/DTA curve for 1:0.010La doped TGS crystal

Activation Energy

Activation energy from the differential thermal analysis (DTA) data with Broido method can be calculated by plotting two exponential of reciprocal of numbers of non-decomposed molecules at initial stage against inverse of temperature, using the relation,

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$ln(1/y) = ln(1/y_0) exp(-E_v/KT)$

Where E_v is the activation energy and K is the Boltzmann's constant



Figure 6: The graph between 1000/T Vs lnln(1/y) for Pure TGS



Figure 7: The graph between 1000/T vs lnln(1/y) for TGS:0.010Ca

RESULTS AND DISCUSSION

The TG/DTA curve of Calcium and lanthanum doped TGS crystal has shown in the figure 4 and 5. for illustration. The curves drawn between 1000/T and lnln (1/y) for pure and 0.010 calcium doped TGS has shown in the figure 6 and 7. for illustration. The melting point, debye temperature and the activation energies of all the CaTGS and LaTGS crystals were provided in the table 3.

The melting point of pure TGS crystal well agreed with those reported by [8]. It is found from the table that the dopant addition has non-linear influence in the melting point of the crystal. The debye temperature thus calculated from the melting point also agreed with the literature value [9], like melting point the dopant addition has non-linear influence on the debye temperature of the doped TGS crystals.

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The activation energy calculated for pure TGS crystal agreed with the reported value given in the bracket [10].

System	Melting point(°C)	Debye temperature (Kelvin) [190K]	Activation energy (eV) [1.6eV]
Pure TGS	232.5	147.39	1.14
TGS:0.002Ca	231.6	148.81	1.06
TGS:0.004Ca	237.6	147.36	0.706
TGS:0.006Ca	229.2	147.41	0.812
TGS:0.008Ca	231.9	148.19	1.07
TGS:0.010Ca	231	146.72	0.683
TGS:0.002La	231.5	145.8	1.41
TGS:0.004La	232.1	146.39	0.3
TGS:0.006La	226.9	144.56	0.531
TGS:0.008La	227.1	148.42	1.141
TGS:0.010La	226.1	149.03	0.467

Table 3: Melting point temperature and debye temperature for calcium and lanthanum doped TGS

REFERENCES

[1]B.T.Mathias, CE.Millerand, J.P.Remeika, Phys. Rev. 1956, 104, 849

[2] D.Sun, X.Yu, Q.Gu, Cryst., Res. Technol 1999, 34,1255.

[3] T.Krajewski, T. Breczewki, Ferroelectrics 1980, 25,547

[4] E.A. Wood, AN.Holden, Acta crystallogr 1957, 10,145

[5] H.Newman, H.Budzier, Ferroelectrics 1992, 133,41

[6] P.Manoharan, and N.Neelakanda Pillai, *Scholar Research Library*, *Archives of Applied Science Research*, **2013**, 5 (1):93-97

[7] C.V. Somasundari and N.Neelakanda pillai, IOSR journal of Applied Physics, 2013, 3,5.

[8] Farhana Khanum and Jiban Podder, *Hindawi publishing corporation, International Journal of optics*, 2012, 2012.

[9] S.Lijewski, J.Goslar and S.K.Hoffmann, Journal of Physics ; condensed matter, 2006, 18, 26.

[10] G.Arunmozhi, S.Lanceros-M'endez, E.de Matos Gomes, Materials Letters 2002,54, 329-336.