Mechanical and Thermal Parameters of $TGS_x P_{1-x}$ Single Crystals

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Abstract: *Triglycine Sulphate family crystals are best ferro electric materials. They find wide application as pyroelectric detector. Mixed single crystals of TGS_xP_{1-x}crystals were grown by solvent evaporation technique in the present study. The grown crystals were characterized by density, EDS, XRD, Vicker's hardness measurement and TG/DTA measurement. Melting point and Debye temperature were determined and also the activation energy was calculated from the mass change during heating. Mechanical Parameters like Vicker's hardness number, Meyer's Work hardening coefficient and Stiffness constant were also determined from the Vicker's hardness data. The mixed crystals are found to be harder than the end member crystals.*

I.   Introduction

Triglycine sulphate family crystals are well known ferroelectric materials useful for room temperature, IR detector applications [1]. They have also found applications in pyroelectric thermal image woing to its wide spectral range of 8-14Å. TGS and TGP crystatalized in monoclinic structure with non centro symmetric space group P_{21} before curie temperature (46°C for TGS and 44°C for TGP) and changes to centrosymmetric p_{21m} group in the Para electric phase above curie temperature. They show second order ferroelectric phase transition at the Curie point and it is an order- dis order ferroelectric. In the present Investigation mixed crystals of TGS_xP_{1-x}were grown by slow evaporation technique. All the grown crystals were characterized by measuring the density, X-ray diffraction data, Vicker's Hardness measurements and TG/DTA measurements. Melting point, Debye temperature and activation energy were determined from the thermal data and the mechanical Parameters like Vicker's hardness number, Meyers work hardening coefficient, Stiffness constant were also determined.

II.   Experimental Details

Growth of Sample crystals:
The TGS, TGP and TGSP salts were synthesized from the following reactions.
For TGS
$3(NH_2CH_2COOH) + H_2SO_4 \rightarrow (NH_2CH_2COOH)_3 (H_2SO_4)$ For TGP
$3(NH_2CH_2COOH) + H_3PO_4 \rightarrow (NH_2CH_2COOH)_3 (H_3PO_4)$ For TGSP
$3(NH_2CH_2COOH)+(H_2SO_4)_x+(H_3PO_4)_{1-x} \rightarrow (NH_2CH_2COOH)_3(H_2SO_4)_x(H_3PO_4)_{1-x}$
for various values of *x* viz, 0.2, 0.4, 0.5, 0.6 and 0.8.
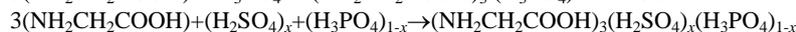
Analar grade glycine, sulphuric acid and phosphoric acids were used for the synthesis of respective salts. After successive recrystallisation process, the purified salts were used for the preparation of super saturated solution. The super saturated solutions of pure TGS, Pure TGP and binary mixed TGSP for various values of *x* were prepared at 45°C using an optically heated constant temperature bath. Growth was initiated by slow evaporation technique. The crystals were harvested after a typical growth period of two to three weeks.

Density and Composition
The density of the grown crystals were determined by using floatation technique. Bromoform of density 2.890 gm/cc and Ethanol of density 0.789 gm/cc are respectively denser and rarer liquids used to determine the density of grown crystals. It has been found that the density values form a linear relationship with the composition for binary mixed crystals [2].
The composition of the mixed crystals were estimated from the density data using the relation
$$d = xd_1 + (1-x) d_2$$
Where d_1 and d_2 are the densities of TGS and TGP crystals.

X-ray diffraction data collection and analysis
X-ray diffraction data were collected from powder samples using an automated X-ray powder diffractometer with scintillation counter and monochromator $CuK_\alpha(\lambda = 1.5406$ A°) radiation. The reflections were indexed following the procedures of Lipson and Steeple [3].

Vicker's microhardness measurement
Vicker's microhardness measurements were done on all the seven crystals grown using Leitz Wetzler hardness tester fitted with diamond Pyramidal indentor and attached with Leitz incident light microscope. Indentation test was done in air at room temperature. Different loads (25g, 50g and 100g) were measured and the average values of the diagonal lengths of the indentation marks in each trial was calculated. Hardness of the crystal was calculated using the relation [4-5].
$$H_v = 1.8544 (P/d^2) Kg/mm^2$$

Where 'P' the applied load in 'Kg' and 'd' the average diagonal lengths of the Vicker's impression in 'mm' after unloading. The Meyer's work hardening coefficient 'n' can be determined by plotting log P vs log d. The 1/slope of the best linear fit graph gives 'n' value.

The elastic Stiffness constant (C$_{11}$) values for various composition as well as different load have been estimated using Wooster's empirical formula

$$C_{11} = H_v^{7/4}$$

Thermal Studies

The melting point of all the grown crystals were determined from the TG/DTA curve using STA 449 F3 Jupiter instrument. The debye temperature of all the grown crystals can be determined from using the formula [6].

$$\theta_D = C \left[\frac{Tm}{Mv^{2/3}} \right]^{1/2}$$

Where 'C' is a constant depending on the X-ray intensity data structure, hence it was estimated as 1000 from the reported Debye temperature values of Pure TGS. Tm is the melting point, M is the molecular weight of the crystal and v is the volume of the unit cell.

Activation energy

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

$$y = \frac{w_t - w}{w_0 - w}$$

$$\ln\left(\frac{1}{y}\right) = \ln\left(\frac{1}{y_0}\right) \exp\left(\frac{-E_v}{KT}\right)$$

Where E$_v$ is the activation energy and K is the Boltzmann's constant.

III. Result and Discussion

The photograph of all the grown crystals are shown in fig 1. It is found that the grown crystals are transparent, thermally stable and good quality crystals. The maximum size of the crystal obtained in the present investigation is 18 × 20 × 5 mm.

Fig.1. Photograph of all grown crystals

The density and the estimated composition of all the mixed crystals grown in the present study is given in Table1. The density of mixed crystals decreases with increase in the TGS concentration and it is very low for equimolar composition. The estimated composition of all the mixed crystals agreed with the actual composition taken.

Table 1. Values of Density and Estimated Composition of all the Grown Crystals

\System	Density (gm / cc)	Estimated Composition
TGS $_{pure}$	1.705	-
TGP$_{pure}$	1.478	-
TGSP	-	-
TGS$_{0.2}$ P$_{0.8}$	1.66	TGS$_{0.177}$ P$_{0.82}$
TGS$_{0.4}$ P$_{0.6}$	1.613	TGS$_{0.41}$ P$_{0.59}$
TGS$_{0.5}$ P$_{0.5}$	1.35	TGS$_{0.46}$ P$_{0.538}$

$TGS_{0.6}P_{0.4}$	1.57	$TGS_{0.6}P_{0.4}$	
$TGS_{0.8}P_{0.2}$	1.53	$TGS_{0.746}P_{0.25}$	

X-ray Diffraction or Lattice Parameter

The P XRD pattern of $TGS_{0.5}P_{0.5}$ is shown in fig2. The lattice parameter calculated from the PXRD data are provided in Table2. The lattice parameter determined in the present investigation shows that all the grown crystals belong to monoclinic system. The calculated lattice parameter of $TGS_{0.5}P_{0.5}$ [7] agreed with the reported values. The lattice parameters of mixed crystals were estimated using Vegards law and Retgers rule.

The Vegards law [8] is

a $=$ $xa_1 + (1 - x) a_2$
b $=$ $xb_1 + (1 - x) b_2$
c $=$ $xc_1 + (1 - x) c_2$

Retgers rule [9] is

a^3 $=$ $xa_1^3 + (1 - x) a_2^3$
b^3 $=$ $xb_1^3 + (1 - x) b_2^3$
c^3 $=$ $xc_1^3 + (1 - x) c_2^3$

The estimated values are given in Table 2.
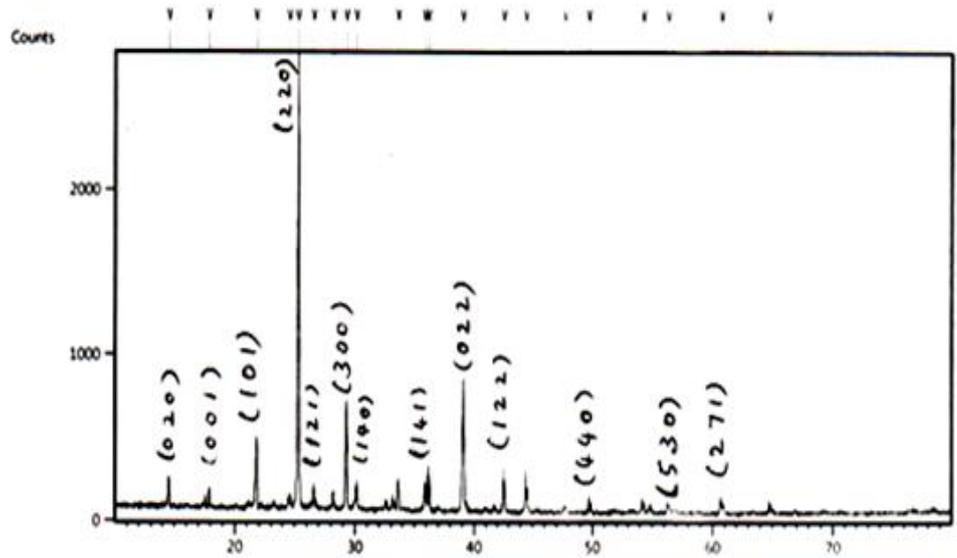
Position [2° Theta]

Fig. 2. The XRD pattern of $TGS_{0.5} P_{0.5}$

Table 2. Values of Calculated and Estimated Lattice Parameters

System	Lattice Parameters									β
	Calculated			Estimated						
				Vegards law			Retgers rule			
	a	b	c	a	b	c	a	b	c	
TGS_{pure}	9.3789 (9.38)	12.7177 (12.634)	5.4855 (5.734)							110° (109° 55')
TGP_{pure}	9.758	12.656	5.331							110°
TGSP										
$TGS_{0.2}P_{0.8}$	9.732	12.457	5.320	9.682	12.668	5.362	9.683	12.668	5.363	110°
$TGS_{0.4}P_{0.6}$	9.752	12.243	5.329	9.606	12.680	5.393	9.610	12.680	5.394	110°
$TGS_{0.5}P_{0.5}$	9.734 (9.150)	12.573 (12.690)	5.272 (5.734)	9.568	12.686	5.408	9.572	12.687	5.409	110°
$TGS_{0.6}P_{0.4}$	9.555	12.712	5.405	9.530	12.693	5.423	9.534	12.693	5.424	110°
$TGS_{0.8}P_{0.2}$	9.733	12.662	5.385	9.454	12.705	5.454	9.457	12.705	5.455	110°

Mechanical Parameters

The Vickers Microhardeness number along with Work hardening coefficient and Stiffness constant are provided in Table 3. It is found from the table that the mixed crystals are harder than the end member crystals (say TGS and TGP). The hardness number of all the grown crystals increases with the load, and it varies non-linearly with the composition of TGS and TGP and it is low for $TGS_{0.2}P_{0.8}$ system and is maximum for equimolar system for higher loads.

Table 3. Mechanical Properties of TGS$_x$P$_{1-x}$ single crystals

System	Vicker's hardness			Stiffness constant			Work hardening coefficient n
	25 (gm)	50 (gm)	100 (gm)	25 (gm)	50 (gm)	100 (gm)	
TGS$_{Pure}$	30.394	47.081	77.226	393.4	846.2	2011.80	6.134
TGP$_{Pure}$	30.609	45.403	49.827	398.3	794.14	934.46	3.086
TGS$_{0.2}$P$_{0.8}$	13.933	16.903	27.186	100.47	140.90	323.67	3.875
TGS$_{0.4}$P$_{0.6}$	33.880	46.596	63.966	475.7	831.01	1446.80	3.703
TGS$_{0.5}$P$_{0.5}$	49.803	81.111	107.375	933.6	2192.2	3581.6	4.504
TGS$_{0.6}$P$_{0.4}$	61.135	77.248	93.529	1336.6	2012.8	2812.9	2.890
TGS$_{0.8}$P$_{0.2}$	54.521	76.309	102.280	1093.9	1970.18	3289.5	3.663

The non linear variation is due to the presence of imperfections. Those imperfection can be vacancies, impurity vacancy pairs, dislocation, low angle grain boundaries etc. The results on dislocation morphology [10] shows that the low angle grain boundaries and dislocations are more in mixed crystals compared to pure crystals. Also Tiller's eutectic crystallization mechanism may be responsible for origin of low angle grain boundaries in mixed crystals [11]. The vacancies, dislocations and grain boundaries appear to be the dominant imperfection in mixed crystals and these may be responsible for the observed non-linear variation of microhardness in them.The variation of log P Vs log d is shown in fig 3. The work hardening coefficient determined from the above curve is provided in Table 3. According to Onitch [12] that if n > 2 the microhardness number increases as the load is increased. He showed that if n >2 the materials belong to soft category. If n < 2 the material belongs to hard category. In the present work it is found that the 'n' values of all the grown crystals are greater than two. It shows that they belong to soft material category.
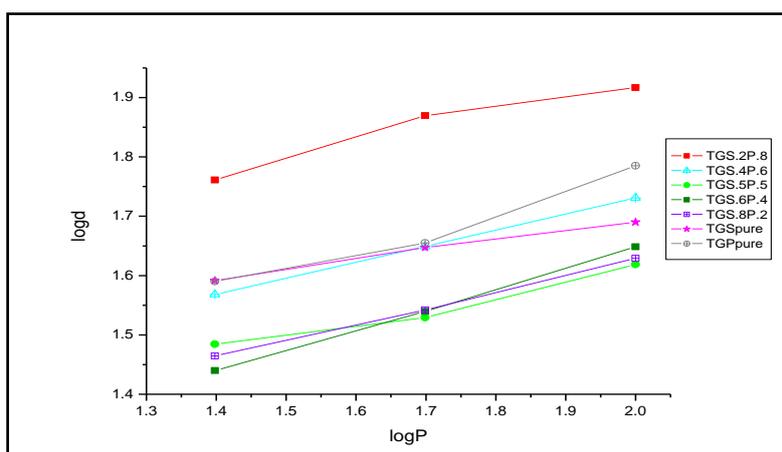
Fig. 3 The Variation of logP vs logd

Thermal Parameters

The TG/DTA curve of equimolar system is shown in fig 4. for illustration. All the crystals grown in the present study are found to be thermally stable upto 220°C. Above 220°C they show mass changes. The melting point and the Debye temperature calculated from the melting point for all the crystals are provided in Table 4. The melting point and Debye temperature calculated for Pure TGS are well agreed with the reported value which is given is bracket (147°C). The Debye temperature of the mixed crystals are found to be less than the end member crystals and they decreased with increased in TGS concentration except for equimolar system. For equimolar system it is higher than that of pure TGS and TGP crystals.
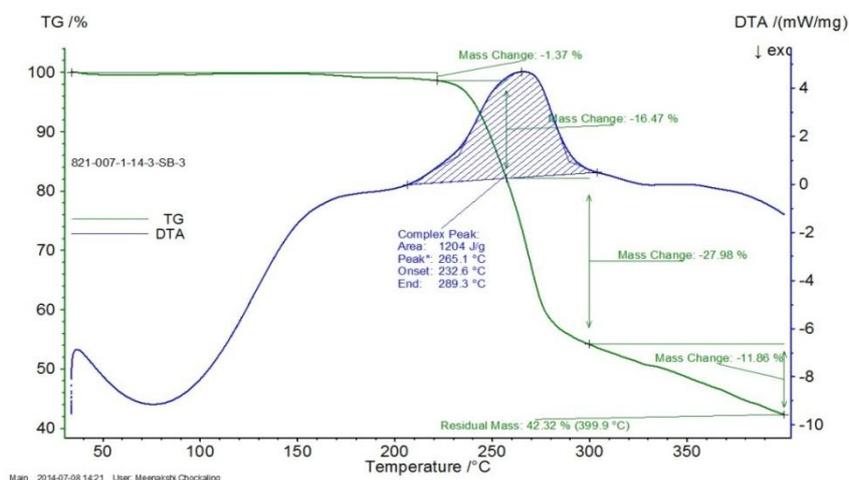
Fig. 4. The TG/DTA curve of TGS$_{0.5}$ P$_{0.5}$ single crystals

Table 4. The melting point and the Debye temperature for all the crystals

System	Molecular weight	Volume	Melting point (°K)	Debye Temperature (°K)
TGS$_{Pure}$	323.2	614.779	260.0	151.05 [147]
TGP$_{Pure}$	323.2	618.598	260.1	150.76
TGS$_{0.2}$P$_{0.8}$	323.2	605.99	256.7	151.3
TGS$_{0.4}$P$_{0.6}$	323.2	597.819	231.7	148.37
TGS$_{0.5}$P$_{0.5}$	323.2	606.245	265.1	152.48
TGS$_{0.6}$P$_{0.4}$	323.2	616.855	229.0	146.03
TGS$_{0.8}$P$_{0.2}$	323.2	623.559	230.4	146.11

The variation of $\dfrac{1000}{T}$ versesln $\ln\left(\dfrac{1}{y}\right)$ for equimolar concentration is shown in fig 5. for illustration. The activation

energy determined from the mass change is provided in Table 5. The activation energy of mixed crystals except for TGS$_{0.8}$ P$_{0.2}$system are found to be less than end member crystals. It is high for TGS$_{0.8}$ P$_{0.2}$ system and even it is higher than end member crystals.
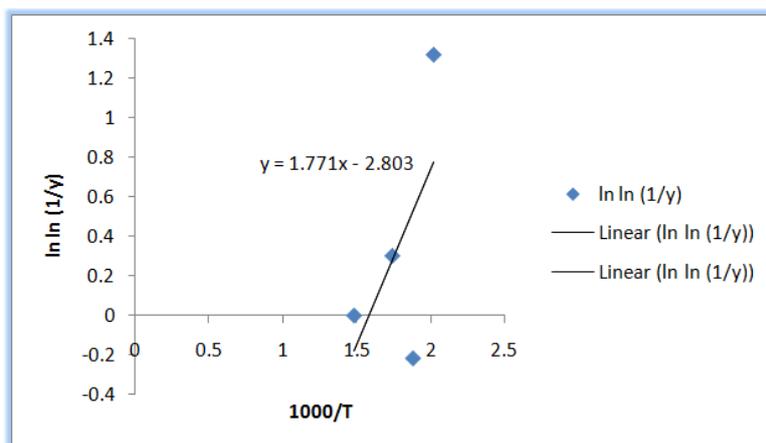
Fig. 5. The variation of 1000/T verses ln ln (1/y)

Table 5. The activation energy from the mass change

System	Activation energy
TGS$_{Pure}$	0.1616
TGP$_{Pure}$	0.1640
TGS$_{0.2}$P$_{0.8}$	0.0678
TGS$_{0.4}$P$_{0.6}$	0.1096
TGS$_{0.5}$P$_{0.5}$	0.1525
TGS$_{0.6}$P$_{0.4}$	0.0859
TGS$_{0.8}$P$_{0.2}$	0.1692

IV.   Conclusion

The mixed crystals are found to be stable and harder than the end number crystals. All the grown crystals in the present investigation belongs to monoclinic system. The hardness value shows that all the grown crystals in the present investigation belongs to soft category system. The hardness value and Debye temperature of equimolar system is found to be greater than the other mixed and end member crystals. The activation energy of mixed crystals are less than that of end member crystals except the system TGS$_{0.8}$ P$_{0.2}$.

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