Mechanical Properties of TGS_xP_{1-x} Single Crystals

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***Abstract:* - $TGS_x P_{1-x}$ binary mixed crystals were grown from an aqueous solution by slow evaporation technique. The grown crystals were characterized structurally and chemically by taking XRD, EDAX, FTIR, density and Vicker's microhardness measurement. The XRD data shown that the mixed crystals belong to monoclinic structure. The composition of the mixed crystals was determined using the measured density. Vicker's hardness number was determined from the microhardness data. Work hardening coefficient and the Bulk modulus of all the grown crystals were determined from the hardness value. The work hardening coefficient values shown that all the mixed crystals belong to hard materials category.**

I. INTRODUCTION

Triglycine sulphate (TGS) family single crystals have drawn considerable interest in recent years due to their potential applications in IR detectors, storage devices and laser devices [1]. TGS and phosphate substituted TGS (TGSP) single crystals show a typical second order phase transition at curie temperatures of 49°C and 51°C respectively [2]. TGS family crystals belong to the monoclinic system with the non-polar space group $P2_1$ in the ferroelectric phase and $P2_{1m}$ in the para electric phase. TGS has a wide polarizing b-plane, which is advantageous in device fabrication.

II. EXPERIMENTAL DETAILS

Armingtor et al [3] discussed two methods of improving the hardness of alkali halides : (i) Solid solution hardening and (ii) impurity hardening. Chin et al [4] studied the effect of divalent impurities (doping) on the hardness of Sodium and Potassium halides. In this view, inorder to strengthen TGS crystals Phosphate is mixed with Sulphate. The expect in addition to the hardness, other properties like electrical conducitivity, ferro and pyroelectricity may improve.

The TGS, TGP and TGSP salts were synthesized from the following reactions.

For TGS

$$3(NH_2CH_2\ COOH) + H_2SO_4 \rightarrow (NH_2CH_2COOH)_3\ (H_2SO_4)$$

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 sugar 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. The density of all the grown crystals were determined by using the floatation technique for quantitative analysis [5], and the composition of all the mixed crystals were determined from the measured density values using the relation.

$$d = xd_1 + (1-x)d_2$$

where d is the density of the mixed crystal, d_1 and d_2 are the densities of TGP and TGS respectively.

Vicker's microhardness measurements were done on all the seven crystals grown using Leitz Wetzler hardness tester fitted with a 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 used for indentation. The 'd' values were measured and the average value of the diagonal lengths of the indentation marks in each trial was calculated. Hardness of the crystal was calculated using the relation [6-7].

$$H_v = 1.8544\ (P/d^2)\ kg/mm^2.$$

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

The Bulk modulus of the crystals can be determined by multiplying the hardness number with 9.8×10^{-3}. The reciprocal of the Bulk modulus gives the compressibility [8].

III. RESULTS AND DISCUSSION

The photograph of all the grown crystals are shown in fig.1. The density and estimated composition of all the grown crystals are provided in Table 1. It is found that all the grown crystals are good quality transparent crystals. The estimated composition of all the mixed crystals are well agreed with the actual composition taken.

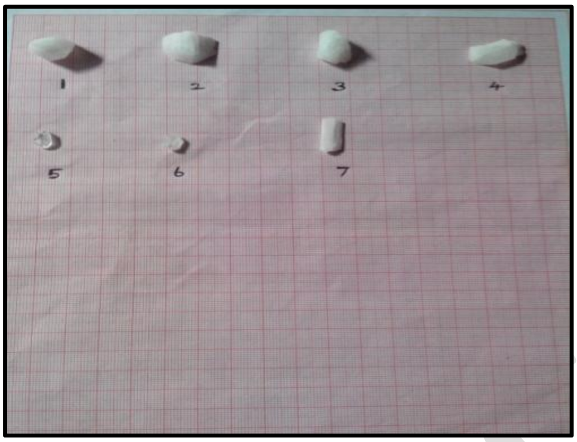

Fig.1. Photograph of all grown crystals

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	$TGS_{0.746}P_{0.25}$

The Vicker’s microhardness value along with Bulk modulus, compressibility and work hardening coefficient are given in Table 2. It is found that the hardness number increases with the load and it is more for mixed crystals than the pure crystals. Also it varies non-linearly with composition. The non linear variation is due to the presence of imperfections. These imperfections can be vacancies, impurity - vacancy pairs, dislocations, low-angle grain boundaries etc. The results on dislocation morphology [9] 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 the origin of low angle grain boundaries in mixed crystals [10]. The vacancies, dislocations and grain boundaries appear to be the dominant imperfections in mixed crystals and these may be responsible for the observed non-linear variation of microhardness in them.

Table 2. Mechanical Properties of TGS_xP_{1-x} single crystals

System	Vicker’s hardness (kg/mm²)			Bulk Modulus (GPa)			Compressibility $\Psi = \frac{1}{k}$			Work hardening coefficient n
	25 (gm)	50 (gm)	100 (gm)	25 (gm)	50 (gm)	100 (gm)	25 (gm)	50 (gm)	100 (gm)	
TGS_{pure}	30.394	47.081	77.226	0.2978	0.4613	0.7568	3.357	2.167	1.321	0.163
TGP_{pure}	30.609	45.403	49.827	0.2999	0.4449	0.4883	3.333	2.247	2.047	0.324
TGSP										
$TGS_{0.2}P_{0.8}$	13.933	16.903	27.186	0.1365	0.1656	0.2664	7.326	6.038	3.753	0.258
$TGS_{0.4}P_{0.6}$	33.880	46.596	63.966	0.3320	0.4566	0.6268	3.012	2.189	1.595	0.270
$TGS_{0.5}P_{0.5}$	49.803	81.111	107.375	0.4880	0.7948	1.0522	2.048	1.258	0.950	0.222
$TGS_{0.6}P_{0.4}$	61.135	77.248	93.529	0.5991	0.7570	0.9165	1.669	1.320	1.091	0.346
$TGS_{0.8}P_{0.2}$	54.521	76.309	102.280	0.5343	0.7478	1.0023	1.871	1.337	0.9976	0.273

Sirdeshmukh [11] and Srinivas [11] pointed out in their review paper that the replacement of an ion by another ion of different size (“size effect”) in mixed crystals in a highly non-linear composition variation in properties like the Debye-Waller factor, the dislocation, density and hardness. This is known as size effect. In the present study replacement is possible between sulphate and phosphate ions. Subba Rao and Haribalbu [12] pointed out that in a mixed crystal, lattice interaction as well as the disorder due to size effect contribute to the hardness. The Bulk modulus of the mixed crystals is more for intermediate composition. The variation of Bulk modulus with sulphate concentration is shown in Fig. 2.

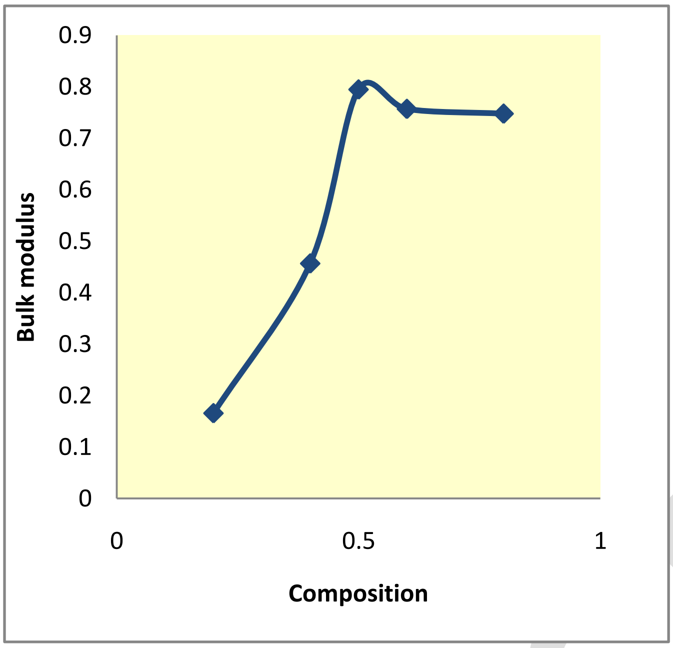

Fig. 2 Variation of bulk modulus with composition

The variation of logPvs logd is shown in Fig. 3. The work hardening coefficient determined from the above curve is provided in Table 2. According to Onitch [13] that if n > 2, the microhardness number increases as the load is increased and he showed that if n > 2, the materials belong to soft category, if n < 2, the materials belong to hard category. In the present work it is found that the 'n' values of all the grown crystals are less than 2. It shows that belong to hard materials category.

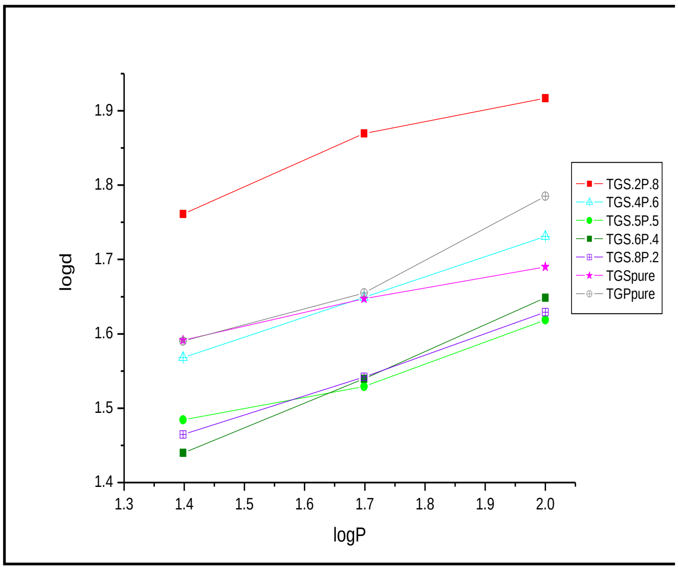

Fig. 3 Variation of logP vs logd

IV. CONCLUSION

Hardness number for the mixed crystals are more than the end member crystals. The work hardening coefficient of all the mixed crystals show that they belong to hard materials category. Bulk modulus determined from the hardness number varies non-linearly with composition.

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