

## CRYSTAL GROWTH AND ELECTRICAL PROPERTIES OF DTGFB/TGSe SOLID SOLUTIONS

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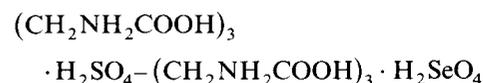
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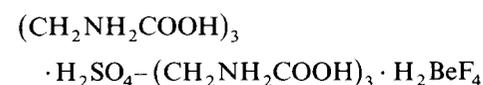
Single crystals of mixed composition from the deuterated triglycine fluoroberyllate – triglycine selenate (DTGFB–TGSe) system were prepared by crystallization from aqueous solutions. The limit of TGSe solubility in DTGFB was determined to lie between 26.4 and 42.3 at% Se in the crystal. Measurements of the spontaneous polarization, pyroelectric and dielectric properties of these materials showed that addition of TGSe lowers the ferroelectric transition as expected.

### 1. Introduction

The use of single crystals from the  $(\text{CH}_2\text{NH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$  (TGS) family of materials for pyroelectric infrared detector applications is well known. Numerous attempts to improve detector properties by impurity incorporation in these materials have been reported [1–6]. In addition, mixed crystals of (TGS–TGSe)



and of (TGS–TGFB):



have been prepared and their electrical properties reported [7,8]. Recently, the growth and properties of (DTGFB):

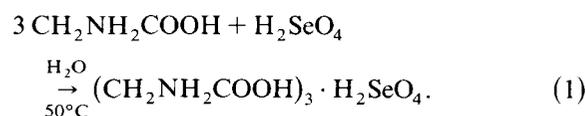


have been described [9] and this material has shown pyroelectric properties superior to those of other members of the TGS family [10]. This present study reports the results of crystal growth and the electrical properties of crystals grown from the DTGFB–TGSe system.

### 2. Experimental

#### 2.1. Synthesis and crystal growth

The synthesis of DTGFB (with  $D = 74\%$ ) has been previously described [9]. TGSe was prepared by reacting glycine and selenic acid in the proper molar ratio according to the reaction:



After cooling to  $20^\circ\text{C}$ , crystalline TGSe was separated from the mother liquor by filtration and allowed to air dry. Considerable care must be taken in the preparation of TGSe due to the strong tendency of  $\text{Se}^{6+}$  to reduce to  $\text{Se}^{4+}$  and under certain conditions to metallic  $\text{Se}^0$  [11]. For example, heating of the solution above  $70^\circ\text{C}$  should be avoided due to the oxidation of glycine which in turn causes accelerated reduction of selenium. The composition and structure of TGSe was verified by X-ray and wet chemical analysis. This TGSe was then added to a previously prepared solution of DTGFB, saturated at  $40^\circ\text{C}$ . The quantity of TGSe required to prepare mixed compositions of nominally 10, 20, 30 and 40 mole% TGSe in DTGFB was determined by use of the solubility curve of DTGFB [9]. The four separate growth

solutions prepared, were equilibrated at 40°C for 3 days, filtered through a 0.4  $\mu\text{m}$  (polyvinylchloride) Millipore filter system and each solution pre-treated at 60°C for 18 h prior to loading. During the saturation step, 30%  $\text{H}_2\text{O}_2$  (based on TGSe) was added to inhibit Se reduction. The final saturated growth solutions (each, 2 liters) were at pH 2.5.

Seed plates of DTGFB, 10 mm in diameter by 4 mm thick, were oriented with the polar [010] axis perpendicular to the plate. The crystallizer was of a special design which consisted of four separate growth chambers with a common seed rotation system and external bath. This configuration permitted equivalent solution flow velocities and temperature control to be used, thus eliminating these growth conditions as a variable during crystal growth. The solution flow velocity and average temperature lowering rate used for growth were 10  $\text{cm s}^{-1}$  and 0.04–0.06°C  $\text{day}^{-1}$ . The average crystal growth rate along the [010] was  $1.0 \pm 0.2$   $\text{mm day}^{-1}$ . The total growth time was 89 days.

### 3. Measurements

Electrical measurements were performed on thin slices ( $4 \times 4 \times 0.1$  mm) cut perpendicular to the polar [010] axis. The polished faces of the slices were coated with evaporated antimony to form conductive electrodes. Attached to these electrodes were 50  $\mu\text{m}$  diameter gold leads by which the sample was suspended in a temperature controlled oven. The sample temperature was measured with a platinum resistance thermometer placed as close as possible to the sample. Before each measurement, samples were poled with a steady field of 5 kV/cm, applied during slow cooling through the transition point down to 0°C. Data were taken during a subsequent heating cycle at  $\sim 2^\circ\text{C}/\text{min}$  in the absence of the biasing field.

Pyroelectric measurements were made using a computer controlled system similar to that previously described [12,13]. The pyroelectric current was measured with a Hewlett Packard 4140 A pA meter. The pyroelectric coefficient was determined by dividing the measured current by the product of the electrode area and the rate of change of temperature. The spontaneous polarization was

obtained by integrating the pyroelectric current.

Measurement of the dielectric constant was made in a field of 5 V/cm at 10 kHz using a Hewlett Packard 4274 A LCR meter.

### 4. Results and discussion

Large single crystals suitable for measurements could only be grown from the 7.3 and 15.4 at% Se solutions (table 1). This could be explained by the small but significant lattice mismatch between TGSe and DTGFB. The limiting concentration of Se lies between 26.4 and 42.3 at% in the crystals and these data agree with a similar observation by Brezina et al. for the TGS–TGFB system [8]. If the electrical properties of the mixed crystals grown had been significantly superior to those of pure DTGFB, crystal growth using seeds prepared by recrystallization (at each TGSe concentration) would have been used for further growth experiments.

The average growth rate in the polar direction [010] was measured and found to lie, for all TGSe concentrations, in the range 0.3 to 0.7  $\text{mm day}^{-1}$ . The morphology of the crystals grown at 7.3 and 15.4 at% Se were typical of pure DTGFB. However, at 20.9 and 31.2 at% Se, severe habit modification and dendritic growth resulted. These crystals grew at the highest rate (0.7  $\text{mm day}^{-1}$ ) observed.

The composition of the growth solutions and crystals in terms of Se and Be concentrations are

Table 1  
Chemical analysis of Be and Se in solutions and crystals

Experiment	Element	Concentration (at%)	
		Solution	Crystal
1	Be	92.7	78.9
	Se	7.3	21.1
2	Be	84.6	73.6
	Se	15.4	26.4
3	Be	79.1	57.7
	Se	20.9	42.3
4	Be	69.4	50.1
	Se	31.2	49.8

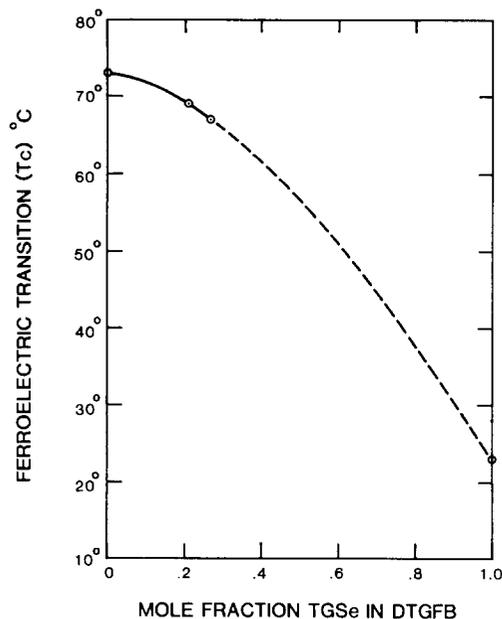


Fig. 1. Effect of TGSe concentration on the ferroelectric transition temperature in DTGFB.

given in table 1\*. The effective distribution coefficient of Se in DTGFB is greater than unity for a solution volume of 2000 cm<sup>3</sup> and a saturation point of 40°C. Changes in concentration during crystallization are not expected to effect the distribution coefficient because the volume of crystal grown was small compared to the growth solution volume. The abnormally high Se concentrations in crystals grown at 20.9 and 31.2 mole% Se (in solution) may be due to the high solvent inclusion density in these crystals.

The ferroelectric phase transition ( $T_c$ ) was observed to decrease as the Se concentration increased in the DTGFB crystals (fig. 1). The magnitude of the decrease in  $T_c$  is comparable to that previously reported in the TGS-TGSe and TGFB-TGSe systems [7,8].

The temperature dependence of the dielectric constant and spontaneous polarization are illustrated in figs. 2 and 3. There is a significant increase in the peak dielectric constant as the

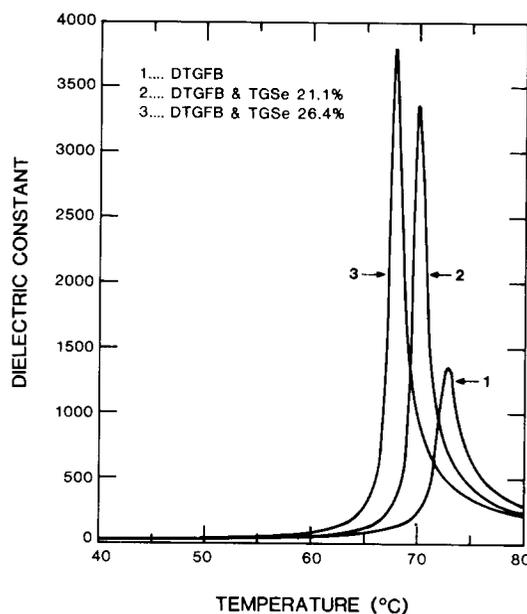


Fig. 2. Temperature dependence of the dielectric constant in mixed crystals of DTGFB-TGSe.

concentration of Se increases in the DTGFB crystal and the shift of the ferroelectric transition to lower temperatures clearly demonstrated. The value of

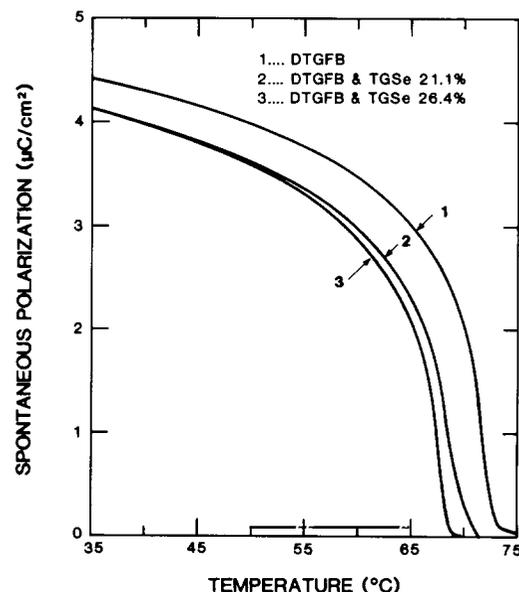


Fig. 3. Temperature dependence of the spontaneous polarization in mixed crystals of DTGFB-TGSe.

\* Concentrations determined by Spectrochem Laboratories of Franklin Lakes, New Jersey. Se and Be were analyzed by atomic absorption.

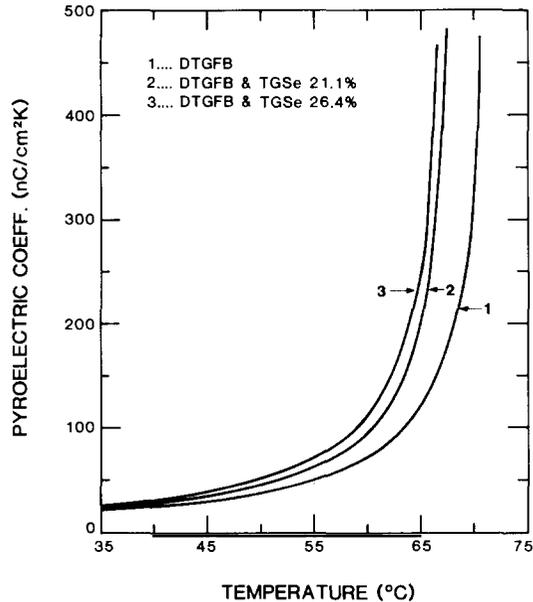


Fig. 4. Temperature dependence of the pyroelectric coefficient in mixed crystals of DTGFB–TGSe.

the spontaneous polarization also decreases as the Se concentration is increased. However, the shape of the  $P_s$  versus temperature curves (fig. 3) indicate an increase of slope which should result in a larger pyroelectric coefficient. This observation was confirmed by the pyroelectric measurements given in

fig. 4. The results of these electrical measurements on the mixed crystals of DTGFB–TGSe show no significant improvement in potential device performance as compared to pure DTGFB.

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