

EFFECT OF ADMIXTURES ON THE CRITICAL BEHAVIOUR OF SPECIFIC HEAT OF TGS

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ABSTRACT

The critical behaviour of specific heat (C_p) of TGS crystals admixed with iodoacetamide (AJ) and chromium (Cr^{3+}) was studied around the phase transition point (T_c). Due to insertion of (AJ) and Cr^{3+} admixtures into the TGS lattice, the ferroelectric phase transition was entirely affected, and an internal electric bias field was formed in the crystals. A logarithmic anomaly in C_p was observed for pure TGS as well as admixed crystals. The range of anomaly was wider in the case of admixed crystals ($T-T_c \leq 5$ K). The effect of defects was more pronounced in the case of crystals doped with Cr^{3+} than that with (AJ). The results were discussed in terms of the rule of defects on the specific heat. The effect of admixtures on the spontaneous polarization (P_s) of the TGS crystals was also considered.

INTRODUCTION

Ferroelectrics generally exhibit the strongest pyroelectric effects and IR sensors using them offer a number of advantages over competing technologies using semiconductors [1]. Single crystals of triglycine sulphate (TGS) and its isomorphous ones are widely used as working substance of pyroelectric transducers [2], since the pyroelectric coefficient of these single crystals is closest to the maximum level limited by the thermodynamic instability of a solid [2].

Attempts to stabilize the properties of these materials by creating an internal field (e.g., by introducing defects into the bulk of the crystal) have been most successful when the impurities were added in the growth stage [3].

The critical phenomena associated with the phase transition have been intensively studied [4]. Recent theories [5-7] predict that all the thermodynamic quantities, such as heat capacity, susceptibility, and spontaneous polarization should behave almost classically except for the appearance of logarithmic correction near the transition temperature (T_c).

In the experimental studies, however there have been substantial disagreement between the results by different

workers. For TGS, the reported region where the logarithmic corrections have been observed varies from less than 1 K [8,9], to about 20 K [10].

In the defected crystal, as approach to the phase transition point, one should observe anomalies, associated with an increase in the dimensions of regions disturbed by defects due to an increase in the correlation radius of the order parameter [11].

An investigation of gamma-irradiated crystals of TGS has revealed that these anomalies actually occur under low doses of radiation [11].

It is undoubtedly of interest to consider from the same viewpoint the critical anomalies in ferroelectric crystals containing interstitial impurities and impurities of substitution.

Admixture defects in TGS occur in two varieties. The simplest are paramagnetic ions (Mg^{2+} , Cu^{2+} , Cr^{3+} , Fe^{3+} , ... etc) occupying positions in between the molecules (interstitial) [12]. Admixtures isostructural to the glycine molecules (L- α alanine, chloro- acetamide; iodoacetamide,...etc.) replace the glycine within the structure (substitutional) [12]. There are literature data

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concerning the physical proprieties of impure TGS crystal [13-15].

The anomalies in the heat capacity of these crystals were studied in particular by Strukov et al. [11,16] and Novik et al. [17].

The present paper contains results concerning the influence of impurities (interstitial and substitutional) on the critical behaviour of specific heat (C_p) of TGS crystals, with special attention to the temperature range adjoining the phase transition point.

EXPERIMENTAL

Triglycine sulphate (TGS) crystals were obtained from stoichiometric aqueous solution of aminoacetic acid ($NH_2 NH_2 CH_2 COOH$) and sulphuric acid ($H_2 SO_4$) and purified by threefold recrystallization from water.

The admixed crystals were aqueous solutions containing 20% in solution iodoacetamide (AJ) and 1% in solution $Cr_2 (SO_4)_3 \cdot 6H_2O$.

The single crystals of TGS and TGS doped with (AJ) as well as (Cr^{3+}) were grown from the aqueous solution at constant temperatures (48.5 and 52°C) by the slow evaporation method [18].

The specific heat was measured in the temperature range from 305 to 335 K using a Perking-Elmer model DSC-4 differential scanning calorimeter.

The melting point of Indium was used to calibrate the DSC-4 in terms of temperature and heat of fusion.

Samples weights were chosen between 33 and 34 mg. All measurements were carried out at constant heating rate of 5 K/min.

The measurements of the hysteresis loop parameters (P_s , E_c and E_b) were carried out with the help of DDP-bridge [19]. The uncertainty in measuring P_s , E_c and E_b was less than $9 \pm 5\%$.

RESULTS AND DISCUSSIONS

The specific heat, C_p , of pure TGS crystals were compared with that of crystals containing (AJ) and Cr^{3+} as impurities.

Figure (1) shows the temperature dependence of excess specific heat (ΔC_p) where:

$$\Delta C_p = C_p - C_{po}$$

and C_{po} is the specific heat in the paraelectric region

$T > T_c$ (the normal part).

The main feature of the specific heat curve is similar to the recent results obtained by other workers [11,17,20].

It is seen from Figure (1) that the anomalous specific heat (ΔC_p) exists above T_c , and the influence of impurities consists, to a first approximation, in blurring of the phase transition.

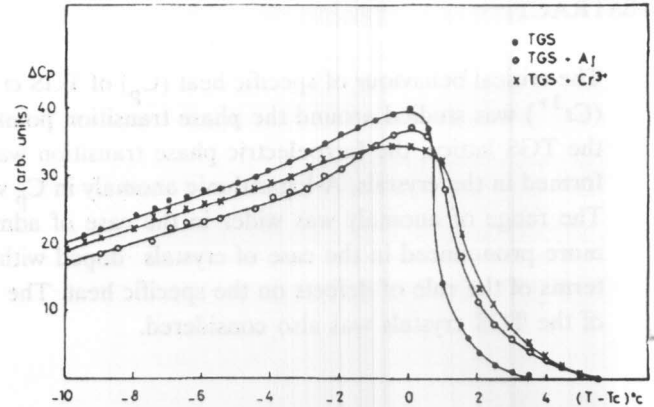


Figure 1. Excess specific heat, ΔC_p , as a function of temperature, for pure and admixed TGS crystals.

This blurring in the phase transition observed for the impure crystals is mainly due to change of the electrostriction constant occurring after introducing the impurities [11].

For the impure TGS crystals, the behaviour of C_p is qualitatively different Figure (1).

The specific heat anomaly in the phase transition region, which is diffuse in the case of TGS+AJ, becomes even more diffuse in the case of crystals doped with Cr^{3+} , i.e., the values of $\Delta C_p (T_c)$ decrease after doping, while the transition temperature is slightly changed.

Why is the phase transition so diffuse? It may be explained by the presence of inhomogeneous zones in the crystals with different T_c .

The anomalous part (ΔC_p) was plotted against, $\ln(T-T_c)$ at $T > T_c$. The data fell on straight lines in a range of $1.2 K \leq T-T_c \leq 3 K$, $2 K \leq T-T_c \leq 5 K$, and $2.5 K \leq T-T_c \leq 5.5 K$ for TGS, TGS+AJ and TGS+ Cr^{3+} crystals respectively as seen in Figure (2).

The upward bending of the graph within $T-T_c \leq 1.2$ to 2.5 K, may be attributed to the smearing of the transition. Thus, we can say that ΔC_p depends logarithmical on $(T-T_c)$ above T_c , in the case of pure as well as impure TGS crystals.

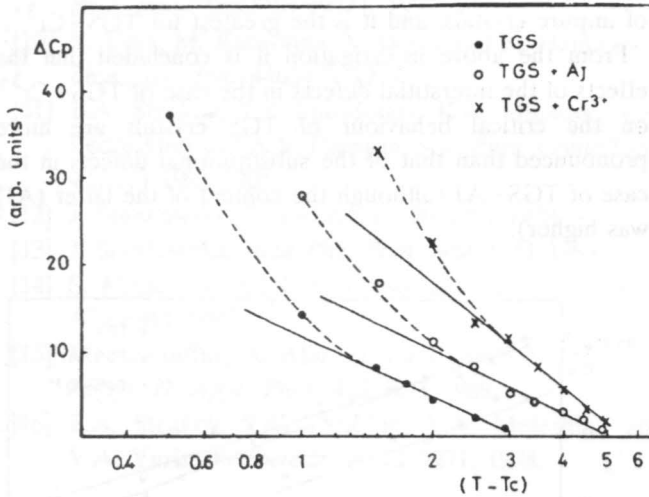


Figure 2. Semi-logarithmic plot of anomalous specific heat above T_c for pure and admixed TGS crystals.

However, the region of the logarithmic anomaly of C_p is wider, in the case of impure TGS crystals, than that in the case of pure ones.

The temperature range of the logarithmic anomaly obtained in the present work for pure TGS crystals is far wider than that reported previously by Taraskin et al. [8], and far narrower than that reported by Ema et al. [10]. But it is in the same order of the range (1 K) reported previously by Tobon et al. [21].

As reported by Strukov et al. [22] the specific heat defects stipulated part can be obtained by the expression:

$$\Delta C_p = \frac{NdP_{20}A_0}{4T_c} \left(1 + \frac{\sqrt{\Pi}}{A_0}\right) \tau^{-1}$$

where $\tau = \frac{T - T_c}{T_c}$, N defect concentration, P_{20} polarization value at the spherical nucleus with a radius d , and A_0 is constant.

The last equation was compared with the experimental results, by plotting, the anomalous part of C_p (ΔC_p) for $T > T_c$ against τ^{-1} for the impure TGS crystals (Figure 3).

It is clear from Figure (3) that the curves have linear parts. According to the data reported by Strukov et al [22], the tilts of the linear parts increase as the concentration of defects increases. So Figure (3) it is conclude that the concentration of defects in the TGS doped with Cr^{3+} is higher than that in the case of crystals doped with (AJ).

This conclusion is true, the case of crystals doped with (AJ). This conclusion is true, since the internal electric bias field, E_b measured in the crystals doped with Cr^{3+} was found to be greater than that in the case of (AJ) doped crystals Table 1.

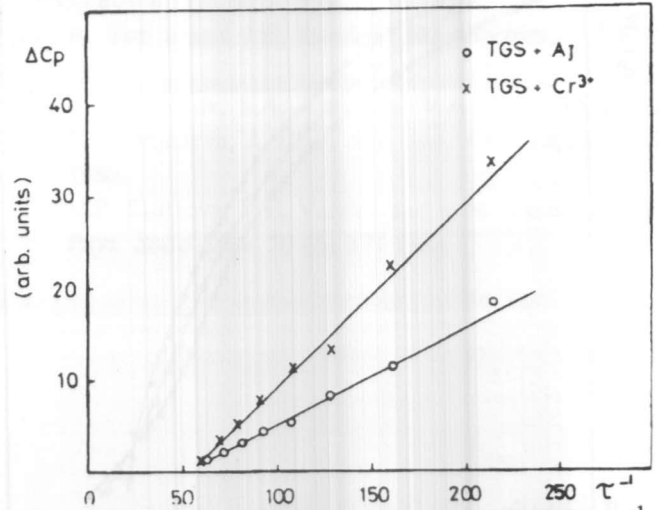


Figure 3. Excess specific heat, ΔC_p , as a function of τ^{-1} , for admixed TGS crystals.

From Table (1) it is seen that the internal bias field E_b and the coercive field E_c are the greatest in the case of TGS crystals doped with Cr^{3+} . This means that the defects are greater in the case of $TGS + Cr^{3+}$, and consequently the stabilization is more pronounced.

Table 1. Internal electric bias, E_b , and coercive field, E_c , for pure admixed TGS crystals, measured at $T = 25^\circ C$.

Crystal	E_b (kV/m) [$T = 25^\circ C$]	E_c (kV/m) [$T = 25^\circ C$]
TGS	8	30
TGS+AJ	15	50
TGS+ Cr^{3+}	60	150

To clarify this point the spontaneous polarization, P_s , was measured as a function of temperature for all studied crystals. Figure (4) presents the obtained results. It is obvious from Figure (4) that, for pure TGS, P_s decreased with temperature and reaches the zero value at the transition point, T_c , while in the case of impure crystals

there is a considerable proportion of P_s remains, even above the transition temperature of pure TGS crystals. Also, P_s decreases after doping.

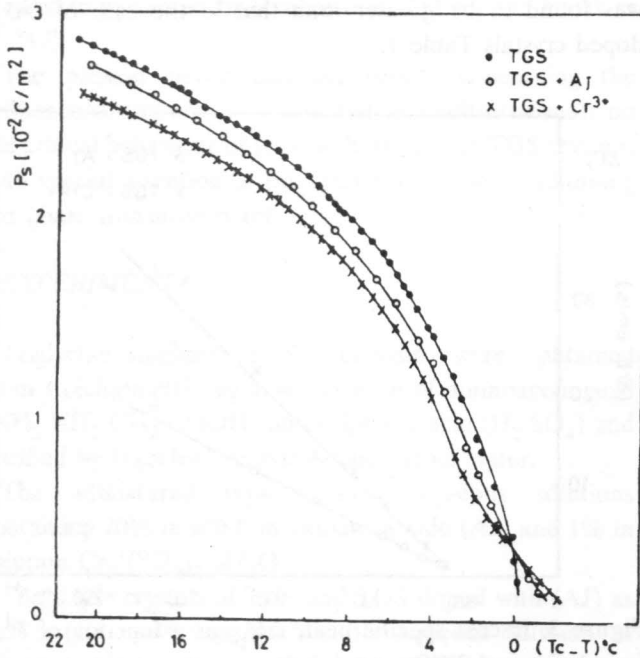


Figure 4. Temperature dependence of spontaneous polarization, P_s , of pure and admixed TGS crystals, (at $E = 180$ V/m).

The remaining P_s , that persists above T_c , is greater in the case of TGS doped with Cr^{3+} . This is attributed to the degree of stabilization occurring owing to the greater bias field (E_b) [23].

The temperature dependence of C_p near a second-order phase transition obeys the exponential law [24].

$$\delta C_p = Z \left(\frac{NU^2}{RT^2} \right) \exp \left(- \frac{U}{RT} \right)$$

where N is the number of atoms displaced from the equilibrium position, U is the activation energy, R is the universal gas constant and Z is the coordination number (the number of neighbors to each atom),.

When $\ln(\Delta C_p T^2)$ was plotted against $1/T$ for the studied crystals, the experimental points showed approximately straight lines, with the exception of temperature in the vicinity of T_c (Figure 5).

From Figure (5) it is noted that the slope in the case of impure crystal is greater than that of the pure one. This

indicates that the activation energy is greater in the case of impure crystals, and it is the greatest for $TGS + Cr^{3+}$.

From the above investigation it is concluded that the effects of the interstitial defects in the case of $TGS + Cr^{3+}$ on the critical behaviour of TGS crystals are more pronounced than that of the substitutional defects in the case of $TGS + AJ$ (although the content of the latter (AJ) was higher).

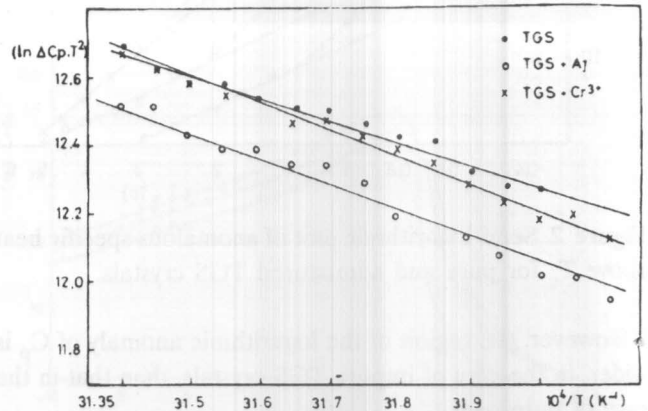


Figure 5. Dependence of $\ln(\Delta C_p T^2)$ on $10^4/T$ for pure and admixed TGS crystals.

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