Journal of Thermal Analysis, Vol. 32 (1987) 1531–1537

EFFECT OF AN ADMIXTURE ON THE ELECTRICAL AND THERMAL PROPERTIES OF TRIGLYCINE SULPHATE CRYSTALS

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(Received January 6, 1987)

The influence of chloroacetic acid amide (AC) on the temperature-dependence of the electrical conductivity (σ), thermal expansion (α_{ij}) and specific heat (C_p) of triglycine sulphate crystals was studied in the phase transition range ($T_c = 49°$). The addition of isostructural AC increased the electrical conductivity, decreased the thermal expansion and changed the C_p peak. The mechanism is discussed on a thermodynamic basis.

Triglycine sulphate (TGS) with the chemical formula $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ crystallizes in the monoclinic system with space group $P2_1$ at room temperature. TGS crystals undergo a structural phase transition along the *b* axis, in which the space group is changed to $P2_1/m$.

The introduction of defects through the admixture of ions or molecules during the process of crystallization provides the essential means of modifying the structure.

Admixture defects occur in two varieties. The simplest are paramagnetic ions, occupying intermediate positions. Additives isostructural to the glycine molecule replace the latter within the structure. The effects of organic admixtures on the dielectric properties of TGS group crystals have been studied [1–5].

Stankowska et al. [6] observed double and triple permittivity maxima during their studied on the effect of chloroacetic acid amide on TGS crystals.

The electrical properties are important features of dielectric crystals, which are required not only for practical applications but also for the interpretation of various physical phenomena.

The thermal expansion is also an important thermodynamic property of crystals, since it is a result of the interactions and excitation of their constituent elements.

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The aim of the present work was to study the influence of chloroacetic acid amide (AC) on the electrical conductivity, thermal expansion and specific heat in the phase transition range of TGS crystals.

Experimental

Crystal growth

Single-crystals of TGS were grown from aqueous solutions via dynamic and isothermal evaporation [7]. The concentration of AC in a crystal was determined by a chromatographic method. The samples to be studied were cut along the (001) and (110) growth pyramid planes for electrical measurements. For thermal expansion measurements, five directions were used: that of the ferroelectric axis, and four directions in the plane perpendicular to the cleavage plane: those of the HOPa and C axes, and X and Z axes of Stankowski [8].

Electrical measurements

Specimens in the form of thin slabs ($0.5 \times 0.5 \times 0.1$ cm^3) were coated with a protective edge by silver electrodes. The temperature could be controlled from 20° to 90° with a stability and accuracy better than ±0.2 deg. The temperature measurements were carried out with a copper constantan thermocouple, and the electrical measurements were carried out in the single domain state using the circuit described elsewhere [9].

Thermal measurements

(a) Thermomechanical analysis (TMA) was performed using a Heraeus TMA 500 dilatometer, while the temperature was monitored by means of a NiCrNi thermocouple fitted in a sample holder of standard design. The linear thermal expansion coefficient was calculated on the assumption that the quartz expansion coefficient has an insignificant effect on the values produced.

(b) The specific heat was determined by applying differential scanning calorimetric techniques using the baseline method [10]. Lidded pans made of aluminium were used to eliminate baseline sloping. A platinum 100 thermocouple was used as a temperature sensor. A 10 mg sample was used and the heating rate was 2 deg/min.

Results and discussion

The molecule of AC, NH_2COCH_2Cl, has a structure and dimensions similar to those of the glycine molecule. However, its different configuration stimulated us to study its influence on the thermal expansion coefficient.

Figure 1a shows the relative change in length measured along the ferroelectric *b* axis of TGS and isostructural AC crystals with temperature. It is observed that the mean expansion varies non-linearly and increases when the glycine molecule is replaced by AC. This behaviour may be due to the effect of the mass of AC upon the thermal expansion coefficients of TGS crystals. It is also clear from Fig. 1b that in

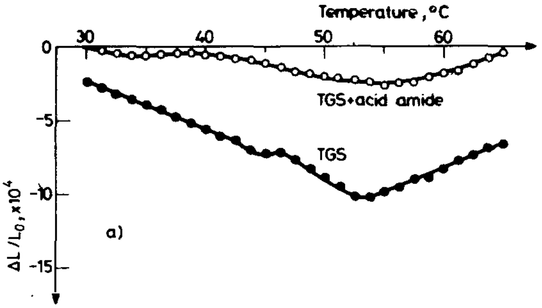


Fig. 1a The relative change of length with temperature along the ferroelectric *b* axis of TGS and isostructural AC crystals

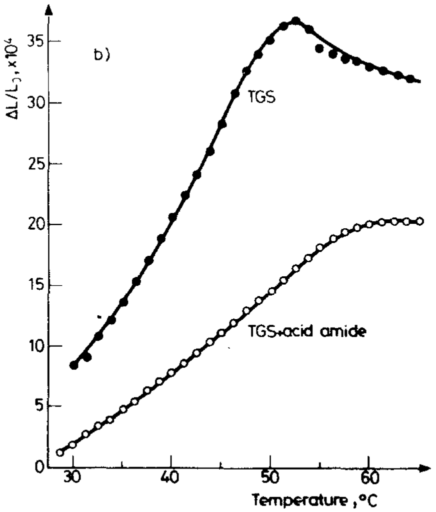


Fig. 1b Variation of $\frac{\Delta L}{L_0}$ with temperature in TGS and TGS + AC crystals in the (010) plane (*c* direction)

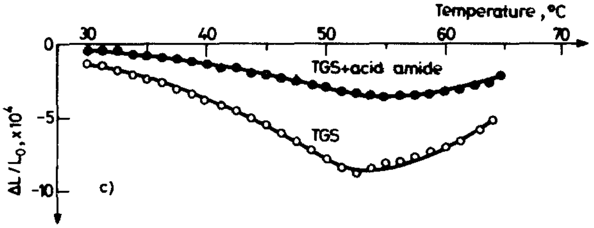
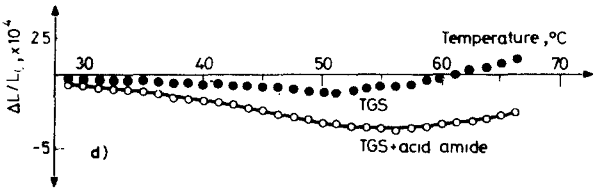


Fig. 1c Variation of $\frac{\Delta L}{L_0}$ with temperature along the *a* axis of TGS + AC and TGS crystals



Figl 1d Variation of $\frac{\Delta L}{L_0}$ with temperature in the α_{11} director of TGS and TGS + AC crystals

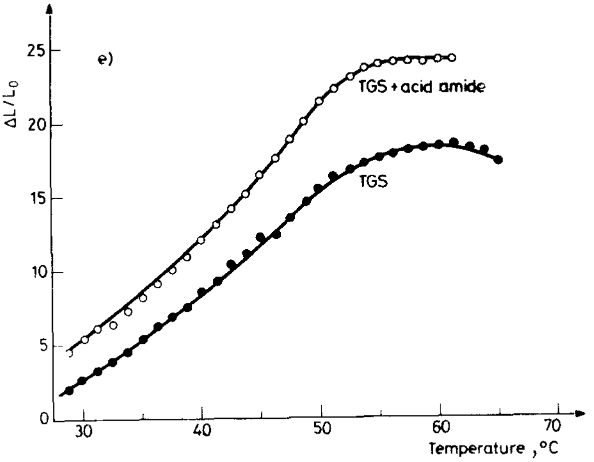


Fig. 1e Variation of $\frac{\Delta L}{L_0}$ with temperature in the α_{33} direction of TGS and TGS + AC crystals

the (010) plane, which involves α_{33}, the thermal expansion is maximum for pure TGS and decreases for TGS + AC, while the singularity in $\frac{\Delta L}{L_0}$ *vs* *T* has disappeared. These results are in good agreement with those obtained elsewhere [6]. It may also be observed from Fig. 1c that the variation of $\frac{\Delta L}{L_0}$ with temperature along the *a* axis increases for TGS + AC more than for pure TGS. The difference in the thermal behaviour of α_{11} (Fig. 1d) and α_{33} (Fig. 1e) in the (010) plane in the TGS crystal and the isostructural AC may be due to the presence of AC in the crystal structure of TGS crystals [11]. From Fig. 2, it is clear that the singularity in the temperature-dependence of the specific C_p changed as a result of the substitution of glycine molecules by AC in the TGS crystals.

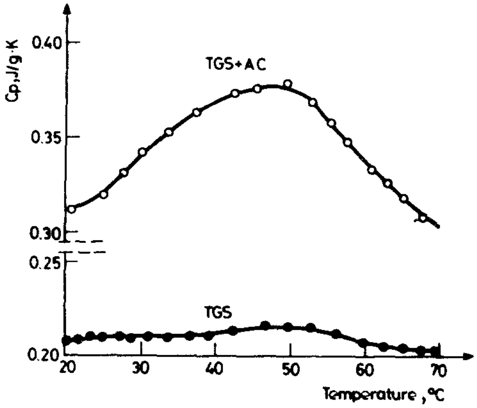


Fig. 2 Variation of specific heat, C_p, with temperature in TGS and TGS + AC crystals

The conductivity data were obtained during heating and cooling of the samples. Figure 3 shows the temperature-dependence of the ionic conductivity, σ, expressed as $\log \sigma T$ vs $\frac{1}{T}$. Over the temperature range of interest, the conductivity exhibited two segments, intercepting at the transition temperature ($T_C = 49°$). In segment I ($T > T_C$) for TGS + AC and pure TGS, the conduction is known to be intrinsic [12]. The values of the activation energies

are $E_1 = 0.55 \pm 0.02$ eV for TGS + AC,

and $E_1 = 0.26 \pm 0.02$ eV for pure TGS.

In segment II ($T < T_C$) for both TGS + AC and pure TGS, the conduction is known to be extrinsic [12] and the values of the activation energies are

$E_2 = 1.7 \pm 0.02$ eV for TGS + AC,

and $E_2 = 0.82 \pm 0.02$ eV for pure TGS.

The change in the activation energies at the transition point from phase I to phase II may be due to the large-scale availability of the carriers released during the

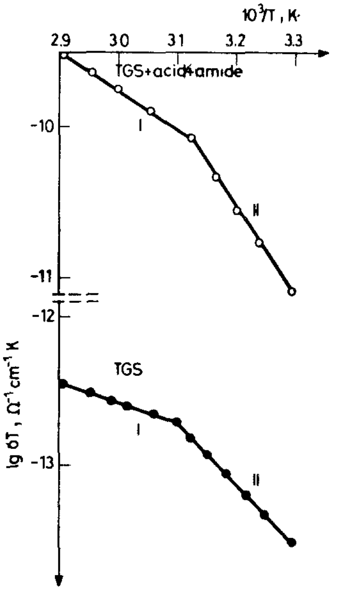


Fig. 3 Variation of ionic conductivity with temperature for TGS and TGS + AC crystals

rearrangement of the crystal lattice or due to its loosening. It is clear that the value of the activation energy for TGS + AC is nearly two times higher than that for pure TGS.

References

1 P. J. Lock, Appl. Phys. Lett., 19 (1971) 390.
2 E. T. Keve, P. W. Whipps, K. L. Bye and A. D. Annis, Ferroelectric, 3 (1971) 39.
3 T. G. Galietyan, IZV. Ap. SSR, 11 (1976) 472.
4 J. Eisner, Phys. Stat. Sol., 43, K_1 (1977).
5 T. Jasinki and J. Stankowska, Material Science, 9 (1983) 61.
6 J. Stankowska and S. Miclcarek, Acta Phys. Polon., A 62, (1982) 181.
7 B. M. Bertlett, J. Sci. Instr., 38 (1961) 54.
8 J. Stankowska, Acta Phys. Polon., 33 (1968) 387.
9 M. E. Kassem, E. F. El-Wahidy, S. H. Kandil and H. Gado, Ferroelectric Letters, 5 (1986) 71.
10 T. Danials, Thermal Analysis, Kogom Page Limited, London, 1973, p. 127.
11 J. Stankowska, IZV. Ak. Nauk. SSSR (S. fiz.), 39 (1975) 708.
12 G. A. Samara, Phys. Rev., B 22 (1980) 6476.

Zusammenfassung — Der Einfluß der Zumischung von Chloressigsäureamid (AC) auf die Temperaturabhängigkeit der elektrischen Leitfähigkeit σ, der Wärmeausdehnung α_{ij} und der spezifischen Wärme C_p von Triglycinsulfat-Kristallen wurde im Phasenübergangsgebiet (T_c = 49 °C) untersucht. Die Beimischung von isostrukturellem AC erhöht die elektrische Leitfähigkeit und vermindert die Wärmeleitfähigkeit, während der C_p-Peak verändert wird. Der Mechanismus kann thermodynamisch diskutiert werden.

Резюме — Изучено влияние примеси амида хлоруксусной кислоты на температурную зависимость электропроводности (σ), термического расширения (α_{ij}) и теплоемкости (C_p) кристаллов триглицин сульфата, в области его фазового перехода при $T_c = 49°$. Прибавление амида хлоруксусной кислоты, как изоструктурной примеси, увеличивает электропроводность, уменьшает термическое расширение при замене молекулы глицина на амид, а также изменяет пик в C_p. Термодинамически обсужден механизм этого явления.