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THERMAL EXPANSION OF LATGS CRYSTALS *

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ABSTRACT

The thermal expansion of triglycine sulphate crystals doped with L- Ox alanine (LATGS) has been studied around the phase transition temperature (30 - 60°C) using thermomechanical analysis TMA. With increasing the content of admixture, the transition temperature (T_c) was shifted towards higher values, while the relative changes in the dimension of the crystals ($\frac{\Delta L}{L_o}$) of the studied directions varied both in the para-and ferroelectric phases.

The transition width in the case of doped crystals was found to be broad, and this broadening increases with increasing the content of L- Ox alanine.

INTRODUCTION

The use of ferroelectric triglycine sulphate (TGS) crystals as detectors and in thermal imaging has created a need for crystals which have a single domain and do not depole (Bye and Keve, 1972). One method of achieving these requirements were described by Keve, Bye, Whipps and Annis, (1971) and involved the structural inhibition of ferroelectric switching in TGS by certain types of organic additives, e.g. L- ∝ alanine.

The influences of organic admixtures on the electrical properties of TGS crystals have been analysed frequently (Jasinski and Stankowska, 1983, 1987; Stankowska and Jasinski, 1987; Okaz, El-Osairy; Kassem and Hamed, 1988). Asymmetric molecules were found to generate a bias field in the crystal which lowers the permittivity, shifts the Curie point towards higher temperatures (Stankowska and Jasinski, 1987), and decreases the electrical conductivity (Okas el al. 1988).

Keve et al.(1971) have given a model describing the L - ∝ alanine molecule as been built up into the TGS crystal by replacing glycine I, and consequently the crystal was permanently polarized along one direction.

Studies concerning the thermal expansion of crystals of TGS group have been performed repeatedly by various methods (Stankowski and Malinowski, 1980).

The thermal expansion of TGS pure crystal was studied using interference dilatometer, in five directions (Stankowski and Malinowski; 1980). It was found that the plane (010) contains the direction of the α_{33} - axis in which the expansion is maximal.

The specific heat of TGS crystals doped with L- ∝ alanine has been measured at several applied electric fields by del Cerro and Ramos (1985).

Those authors, have found an equivalence between both internal bias field "E_b" and external fields.

More recently, Jimenez et al. (1988), measured the thermal expansion of TGS crystals containing a small amount of L- ∝ alanine admixture in one direction only (b-axis).

The present paper contains results concerning the influence of different amounts of L- ∝ alanine admixture, on the thermal expansion of TGS crystals. The anisotropy of thermal expansion along three crystallographic axes is also considered.

EXPERIMENTAL

Triglycine sulphate was recrystallized thrice and on appropriately chosen mass fractions of the admixture were introduced into the solution.

The crystals were grown at constant temperatures (48.5, 53°C) . Samples with different concentrations of admixture (0,5 and 20% L- ∝ alanine) in solution of TGS were cut perpendicularly to the ferroelectric axis "b" . The samples were prepared in the form of rectangular rods with dimensions of (5X5X3) mm^2.

According to Koralewski et al. (1987), the L- ∝ alanine contents (in weight %) in the studied crystals were found to be 0, 0.07 and 0.27 respectively.

The thermomechanical analysis (TMA) was performed using a Heraeus TMA 500 dilatometer as described previously (Kassem, Kandil, El-Wahidy and El-Gamal, 1984).

The thermal expansion coefficient was calculated on the assumption that the quartz expansion coefficient has an insignificant effect on the produced values. During experiments the heating rate was kept 2°C/min. For each crystal, measurements were made in three directions i.e. in that of the ferroelectric axis "b" and in two directions in the plane perpendicular to it, namely a^* and c Bline system (Stankowski and Malinowski , 1980).

RESULTS AND DISCUSSION

The introduction, of organic admixture e.g. amino proponic acid or L- ∝ alanine $CH_3\ CH(NH_2)\ COOH$ molecule, into the crystal lattice of TGS during its growth creates high internal electric fields (E_b) which stabilize the spontaneous polarization. For the studied crystals the values of E_b are given elsewhere (Okaz et al. 1988).

The temperature dependence of the relative change of length measured along the chosen crystallographic axes of TGS containing different amounts of L- ∝ alanine showed a considerable change in its behaviour as given in figure 1 (a,b, and c). Due to the insertion of L- ∝ alanine, the singularity which was observed in $\frac{\Delta L}{L_o}$ vs.T for pure TGS at the transition temperature became broad. This broadening in the phase transition can be attributed to the presence of internal bias field which stabilizes the spontaneous polarization, Keve et al. (1971). The degree of stabilization of this spontaneous polarization increases with the increase of the bias field, which is a function of the L- ∝ alanine content (Okaz et al.

1988). This agrees with previous results obtained by other workers using dielectric measurements (Bye and Keve, 1972; Keve et al. 1971; Jasinski and Stankowska, 1987; Stankowska and Jasinski, 1987).

It is noted from fig (1)- (for all studied crystals in b and a^* axes) that there is a contraction in $\frac{\Delta L}{L_o}$, as the temperature is increased in the ferroelectric region, while there is an expansion in c axis. In the paraelectric region, $\frac{\Delta L}{L_o}$ increases with temperature in b and a^* axes, which is in good agreement with the reported data (Stankowski and Malinowski, 1980), while it seems to be constant in the c axis.

The transition temperature (T_c) can be determined from the intersection of the two extrapolations of the straight portions coming from the para- and ferroelectric regions; fig.(1). According to the obtained values, it was found that T_c shifts towards higher values (49.5, 50.25, 50.75°C) as the content of L- ∝ alanine increases (0;5;20%) respectively.

Also it is seen from figure 1. that in the paraelectric region the relative changes in the dimensions ($\frac{\Delta L}{L_o}$), measured along a^*, b and c axes, decrease due to the insertion of L- ∝ alanine molecule. This can be attributed to the increase of mass as a result of replacement of glycine I molecule by an L- ∝ alanine molecule (Keve et al. 1971).

In the ferroelectric region the situation is more complicated due to the presence of the internal bias field (E_b) created inside the admixtured crystals; and also the spontaneous polarization contribution which is effective in the ferroelectric region.

To clarify the degree of stabilization of the spontaneous polarization in TGS as the result of introduction of L- ∝ alanine into the lattice, the spontaneous tensile strain γ^S_{ii} as a function of temperature was estimated (Osaka , 1978). The estimated values of γ^S_{ii} (with

i = 1,2 or 3) as a function of temperature were presented in figure 2 (1,b, and c). These values decrease with temperature continuously and reach zero at the transition temperature for the pure TGS crystals. In the case of crystals containing L- ∝ alanine, the values of spontaneous tensile strain decrease with temperature, but a considerable proportion of the spontaneous tensile strain persist even above the transition temperature of pure TGS. When the amount of L- ∝ alanine content increased the remaining η^{S}_{ii} which persisted above T_c became greater. This is due to the increased degree of stabilization which originated from the presence of a self bias field within the crystal caused by the polar strain field (Keve et al., 1971).

Fig.3 presents the obtained relative changes in the volume ($\frac{\Delta V}{V_o}$) versus temperature. This figure shows that($\frac{\Delta V}{V_o}$) increases linearly with temperature up to certain value followed by a slight decrease in the rate volume expansion both in pure and admixtured crystals. However in the case of admixtured crystals,there is a broadening in the transition region, due to internal bias field (E_b).

CONCLUSION

The electrical measurements reported in literatures indicating that LATGS crystals possess internal bias field strongly affecting the ferroelectric phase transition (round effect of the phase transition), Bye and Keve, 1972; Keve et al. 1971; Jasinki and Stankowska, 1963; Stankowska and Jasinki, 1987; Okaz et al. 1988.

Similar rounding effect was observed by us in thermal expansion anomaly at the ferroelectric-paraelectric phase transition of LATGS.

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FIGURE CAPTIONS

1.a. *The temperature dependence of the relative change of the length* $(\frac{\Delta L}{L_o})$, *measured along "b"-axis for TGS crystals having different contents of L- ∝ alanine.*

1.b. *The temperature dependence of the relative change of the length* $(\frac{\Delta L}{L_o})$, *measured along a-axis for TGS crystals having different contents of L- ∝ alanine.*

1.c. *The temperature dependence of the relative change of the length* $(\frac{\Delta L}{L_o})$, *measured along c-axis for TGS crystals having different contents of L- ∝ alanine.*

2.a. *The spontaneous tensile strain* $\xi\eta_{11}$ *as a function of temperature for TGS crystals having different contents of L- ∝ alanine, along "b" -axis.*

2.b. *The spontaneous tensile strain* $\xi\eta_{11}$ *as a function of temperature for TGS crystals having different contents of L- ∝ alanine, along "a"-axis.*

2.c. *The spontaneous tensile strain* $\xi\eta_{11}$ *as a function of temperature for TGS crystals having different contents of L- ∝ alanine, along "c"-axis.*

3. *The relative change of the volume* $(\frac{\Delta V}{V_o})$, *versus temperature for TGS crystals having different contents of L- ∝ alanine.*

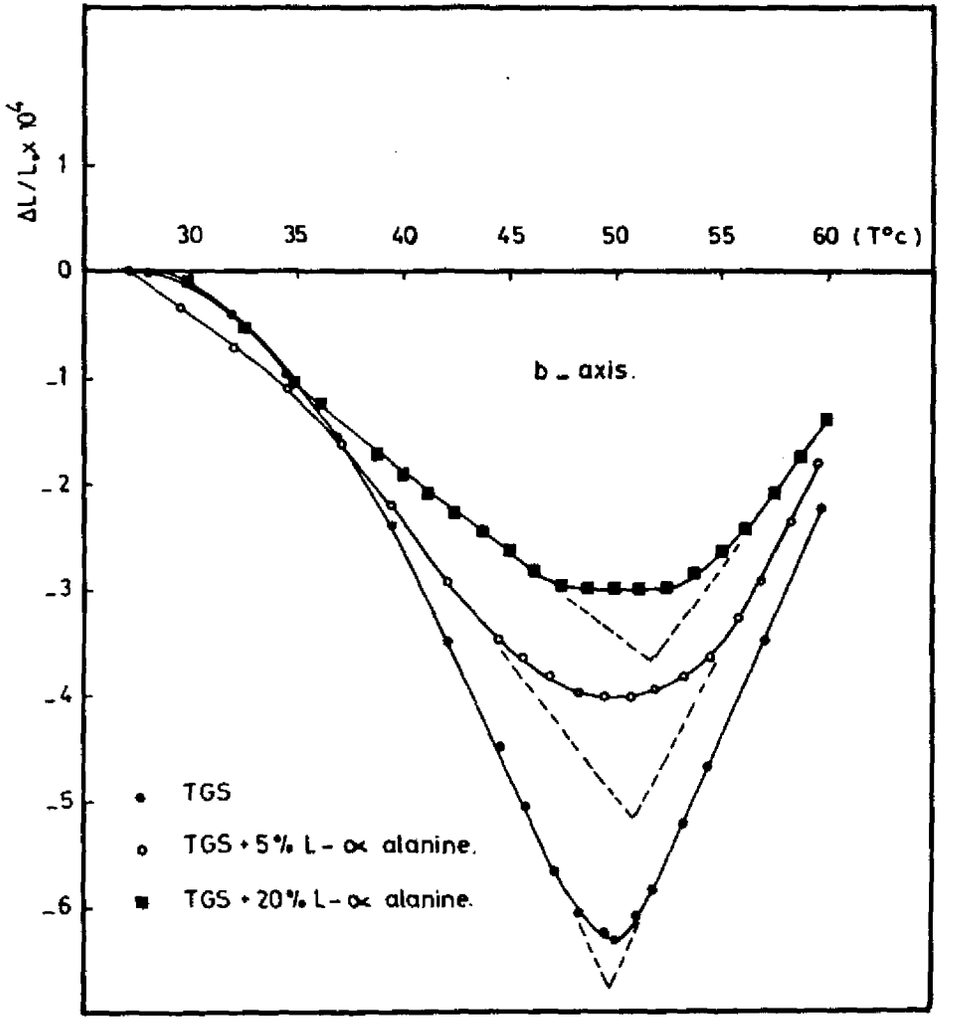

Fig-(1-a)

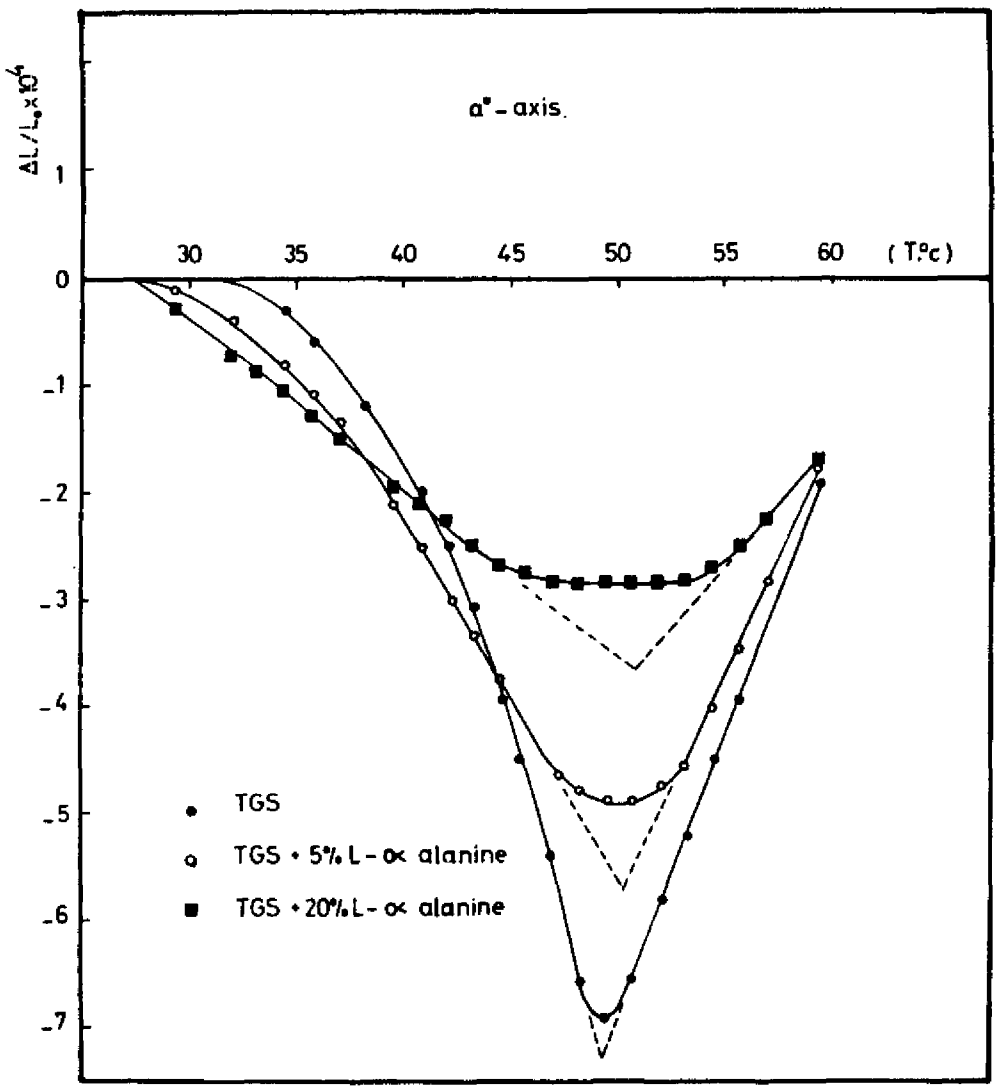
a* - axis.
ΔL/L₀ x 10⁴
1
0
-1
-2
-3
-4
-5
-6
-7
30
35
40
45
50
55
60
(T°c)
TGS
TGS + 5% L - α alanine
TGS + 20% L - α alanine

Fig. (1 - b)

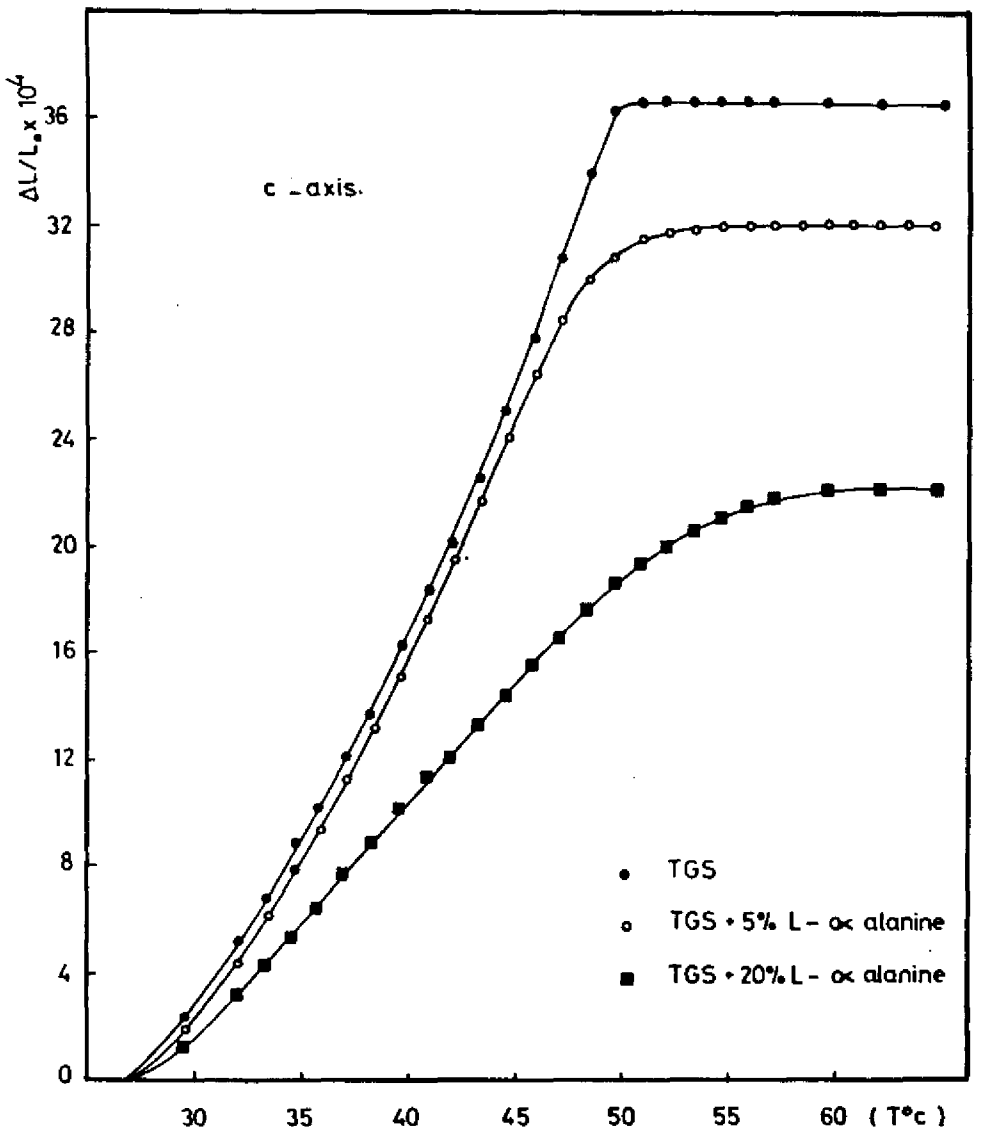
c - axis.
ΔL/L₀ x 10⁴
36
32
28
24
20
16
12
8
4
0
30
35
40
45
50
55
60
(T°c)
TGS
TGS + 5% L - α alanine
TGS + 20% L - α alanine

Fig. (1 - c)

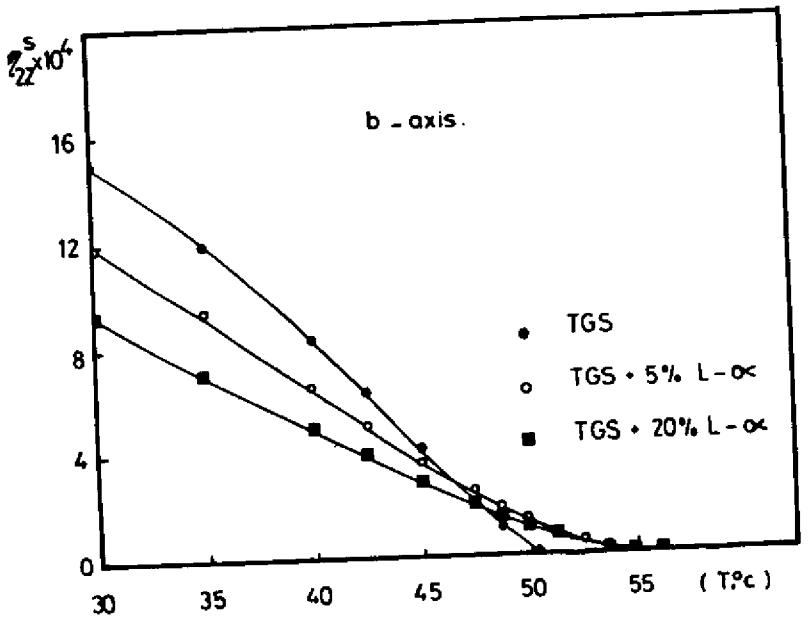
$\eta_{22}^{s} \times 10^{4}$
b - axis.
16
12
8
4
0
30
35
40
45
50
55
(T°c)
TGS
TGS + 5% L-α
TGS + 20% L-α

Fig.(2-a)

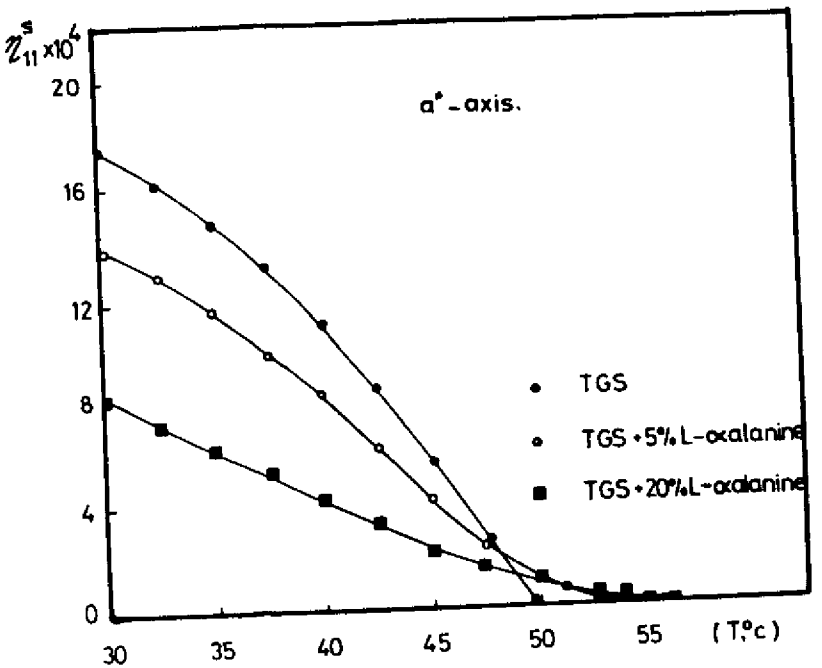
$\eta_{11}^{s} \times 10^{4}$
a* - axis.
20
16
12
8
4
0
30
35
40
45
50
55
(T°c)
TGS
TGS +5% L-αalanine
TGS +20% L-αalanine

Fig.(2-b)

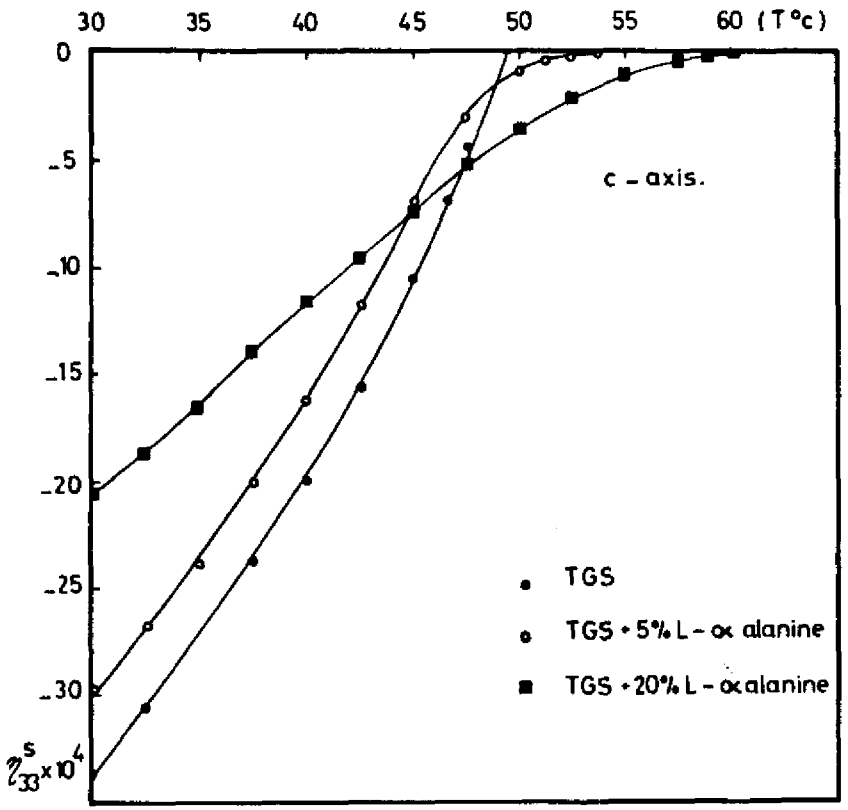
30
35
40
45
50
55
60 (T°c)
0
-5
-10
-15
-20
-25
-30
c - axis.
TGS
TGS + 5% L - α alanine
TGS + 20% L - α alanine
$\chi_{33}^{S} \times 10^{4}$

Fig.(2-c)

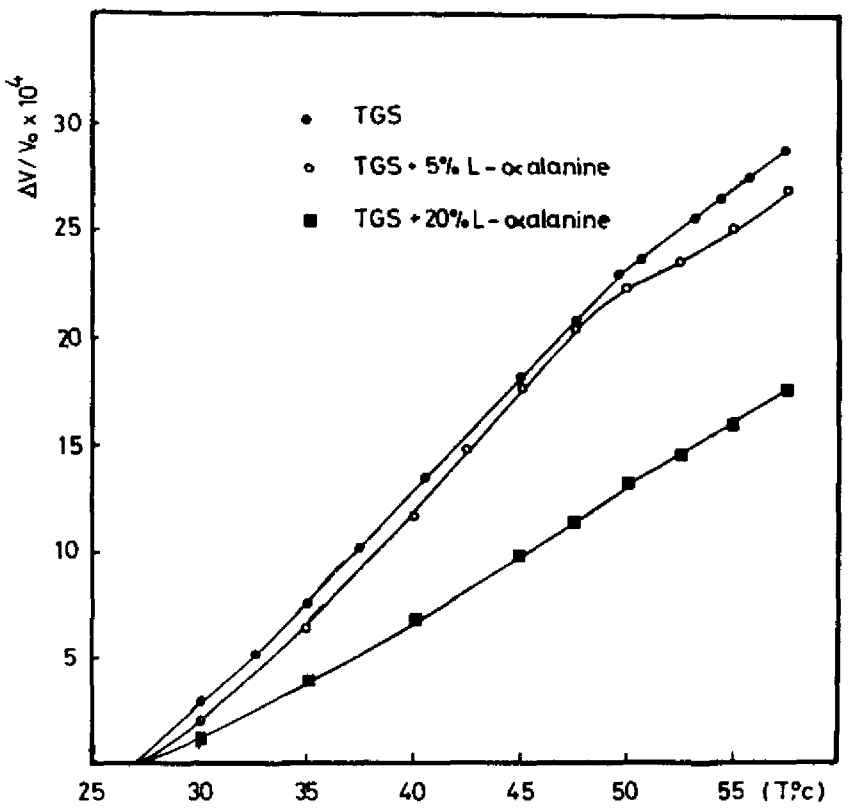
$\Delta V / V_o \times 10^{4}$
30
25
20
15
10
5
TGS
TGS + 5% L - α alanine
TGS + 20% L - α alanine
25
30
35
40
45
50
55 (T°c)

Fig.(3)