DIELECTRIC RELAXATION IN GLYCINE SILVER NITRATE GSN

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Dielectric permittivity and dielectric losses of GSN along the ferroelectric [010] direction have been measured at 1 kHz, 150 MHz, 600 MHz, 1000 MHz and 2200 MHz as a function of temperature. Dielectric relaxation was observed both in the paraelectric and ferroelectric region. The former relaxation was of the Debye type with a single relaxation time even in the immediate vicinity of the Curie point. It was found that the distribution of the relaxation times in the vicinity of the Curie point is observed only in some crystals with a certain amount of dislocations and other imperfections. The dielectric relaxation in the ferroelectric region was complex that is, the characteristics of the relaxation differed with every specimen.

1. Introduction

Glycine Silver Nitrate $NH_2CH_2COOH \cdot Ag\,NO_3$ in the paraelectric phase crystallizes in the monocyclic system with four molecules per unit cell. The basis vectors of the unit cell are [6–8]:

$$a = 5.53\ \text{Å} \quad b = 19.58\ \text{Å} \quad c = 5.51\ \text{Å} \quad \text{and} \quad \beta = 100°$$

At $-55°C$ the substance undergoes a second order phase transition, and the [010] direction is along a ferroelectric axis.

The dielectric relaxation studies of GSN have been undertaken as a continuity of investigation of the series ferroelectrics with the glycine groups [1–3]. It was particularly interesting to note, whether the "critical retardation" process is responsible for the dielectric relaxation in this crystal.

Although the crystal structure is fairly complicated, one expects that a major contribution to ferroelectricity arises from the glycine groups.

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2. Experimental

Glycine silver nitrate GSN was obtained by slow evaporation of the aqueous solution which contained stoichiometric quantities of glycine and silver nitrate. By proper control of temperature and evaporation rate of the solvent one obtaines optically uniform crystals. The crystals were grown in complete darkness.

A crystal was cut to the desired shape and polished to the required dimension of $3 \times 3 \times 1.2$ mm. After polishing the sample, electrodes of conducting silver paint were applied to the polished parallel surfaces, which were perpendicular to the [010] direction.

The measurement methods used in this work were described previously [4, 5].

Dielectric measurements of ε_0 were performed by means of a MERATRONIC Automatic C Bridge type E-315 A at frequency 1 kHz. In the range of 150–2200 MHz two slotted lines were used, Rohde-Schwarz LMMBN 3916/50 and Orion type E2M-1. All dielectric measurements were made only along the [010] direction during the cooling with a cooling rate of about 1°C/h.

A new sample was used for each dielectric measurement, as it was found that reproducible results could not be obtained when the sample was repeatedly cooled and heated through the Curie point.

3. Results and discussion

Table I shows the results of the measurements of ε' and ε'' as a function of frequency and temperature.

The phase transition temperature which was observed in the present work (−55,7°C) differs from the T_c reported in Ref. [10, 11] by about 0.7°C.

Figures 1 and 2 show the values of ε' and ε'' of GSN measured along the [010] direction with frequencies 150, 600, 1000 and 2200 MHz as a function of temperature. It is clear from these results that the dielectric relaxation exists both in the paraelectric and ferroelectric phases.

The Cole-Cole diagrams with the temperature as a parameter in the paraelectric phase are shown in Fig. 3.

Therefore, the dielectric relaxation in paraelectric phase of GSN can be expressed by the Debye equation with a single relaxation time τ

$$\varepsilon(i\omega) = \varepsilon(\infty) + \frac{\varepsilon(0) - \varepsilon(\infty)}{1 + i\omega\tau} . \tag{1}$$

Then, we have the following relation

$$\tau = \frac{\varepsilon''(\omega)}{\omega[\varepsilon'(\omega) - \varepsilon(\infty)]} \tag{2}$$

by which the value τ can be determined experimentally. Fig 4 shows the plot of $\frac{1}{\tau}$ at different temperatures as a function of $T - T_c$ in the paraelectric phase. A linear relation

TABLE 1

	$T-T_c$			0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0
1	Frequency MHz	150	ε'	329	271	226	196	151	120	102	89
			ε''	29	21	13	10	6	4	3	2
		600	ε'	301	260	221	191	148	119	100	89
			ε''	120	71	50	35	22	14	10	7
		1000	ε'	210	196	179	161	137	111	98	88
			ε''	147	104	78	58	35	21	15.6	12
		2200	ε'	117	121	120	115	105	95.5	86	77
			ε''	152	136	114	90	58	44.5	32	12
2	ε_0			339	276	225	194	147	121	102	89

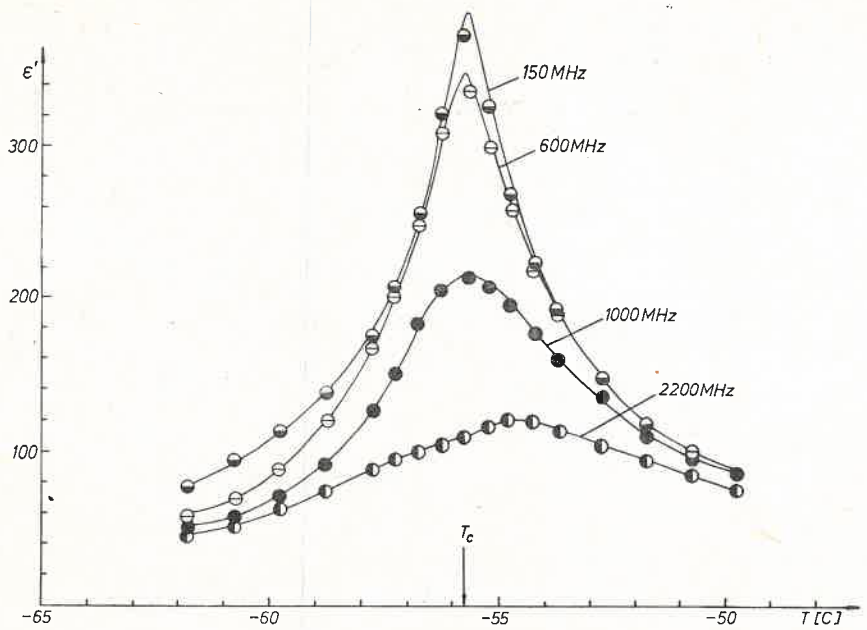

Fig. 1. The real part of the dielectric permittivity of GSN versus temperature at various frequencies

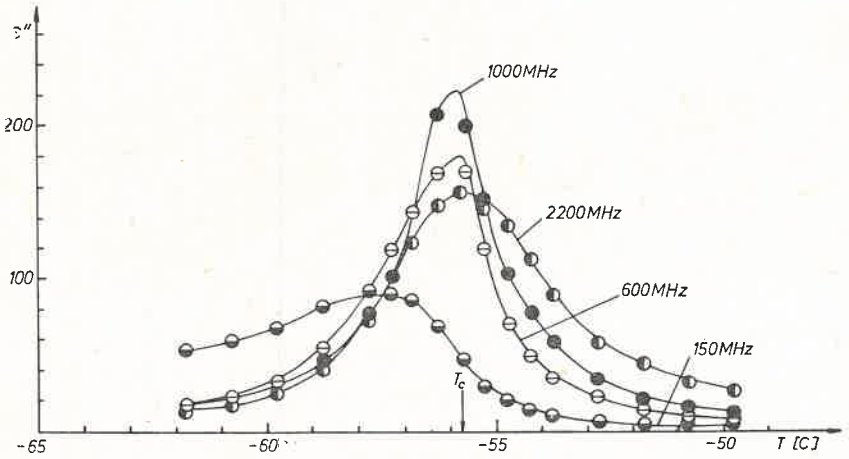

Fig. 2. The imaginary part of the dielectric permittivity of GSN versus temperature at various frequencies

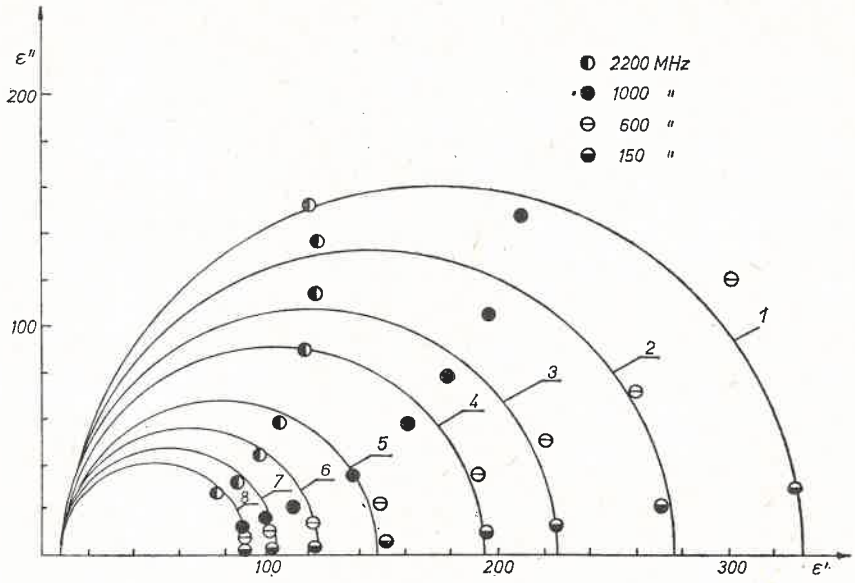

Fig. 3. Cole-Cole diagrams of GSN with temperature $T-T_c$ as a parameter: *1* — 0.5 K, *2* — 1.0 K, *3* — 1.5 K, *4* — 2.0 K, *5* — 3.0 K, *6* — 4.0 K, *7* — 5.0 K, *8* — 6.0 K

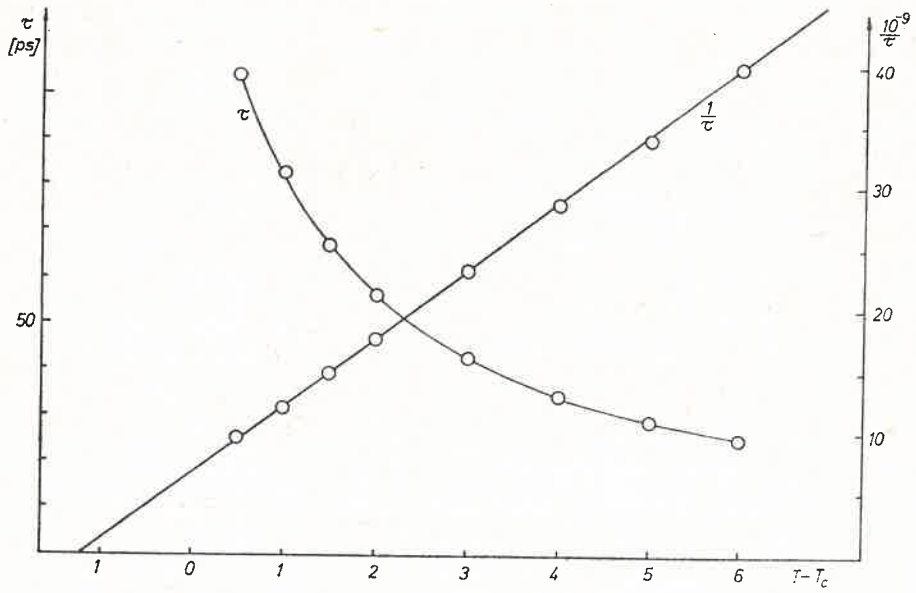

Fig. 4. The relaxation time τ and the reciprocal value $\frac{1}{\tau}$ versus temperature

TABLE II

1	$T-T_c$[K]		0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0
2	T [K]		217.0	218.4	218.9	219.4	220.4	221.4	222.4	223.4
3	τ [pS]		104.4	82.8	67.1	56.7	43.0	35.1	29.5	25.3
4		τ_0 [pS]	2.85	2.80	2.80	2.76	2.81	2.82	2.86	2.85
		$\Delta F^*\left[\frac{\text{cal}}{\text{mol}}\right]$	1108	1104	1107	1105	1119	1128	1141	1148
		ΔF^* [kT]	2.56	2.54	2.55	2.54	2.56	2.57	2.58	2.59

actually holds independently of the measuring frequency within the temperature region $T-T_c \geqslant 0.5°C$.

According to the dynamical theory given by Landau and Khalatnikov [10] on the dielectric relaxation of the order-disorder type ferroelectric, the following relation can be derived:

$$\tau = [\varepsilon(0)-\varepsilon(\infty)]/\Gamma, \tag{3}$$

where Γ is a constant.

Müser et al. [9] proposed for the ferroelectric crystals with the second-order transition the following relation for Γ

$$\Gamma = \frac{\tau_0}{\varepsilon(\infty)}, \tag{4}$$

were τ_0 is the so-called molecular relaxation time associated with the motion of the individual relaxator.

According to relations (3) and (4) the value of τ_0 were calculated and shown in Table II.

By using the above results and the following equation:

$$\tau_0 = \frac{h}{kT} \exp \frac{\Delta F^*}{kT}, \tag{5}$$

the value of the activation free energy for the orientation of the relaxator in the lattice may be obtained. In this case $\Delta F^* = 1.1 \pm 0.5$ kcal/mol. Such a low energy barrier may perhaps indicate that the dielectric relaxation process is associated with the motion of unbonded glycine groups. It seems that the same mechanism of dielectric relaxation is responsible for the dielectric absorption in triglycine sulphate TGS and diglycine nitrate DGN where as well as ΔF^* (1.6 kcal/mol and 1.3 kcal/mol respectively) and τ_0 are very close to the values for GSN.

The dielectric relaxation observed in the ferroelectric phase of GSN is found to be difficult to represent by a simple model. The characteristics of the dielectric relaxation differ with every different sample. This may be due to the complex domain motion in the ferroelectric region.

4. Conclusions

From the present studies for GSN the following may be concluded:

(*i*) The dielectric relaxation observed can be theoretically described to a good approximation by a monodispersive process in the paraelectric phase only;

(*ii*) The crystal shows the critical retardation process of the dielectric relaxation observed in the vicinity of the transition point.

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