DIELECTRIC RELAXATION IN METHYLAMMONIUM GALLIUM SELENATE — MGaSeD

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The dielectric dispersion of the MGaSeD crystal in the [100] direction was investigated over the frequency range from 5 to 2000 MHz in the vicinity of the transition temperature. It was found that, as in other alums investigated so far, the dielectric relaxation is monodispersive and the critical slowing-down critical retardation effect occurs. The relaxation time at the Curie point 207.5 K is 1.95×10^{-9} sec. The energy barrier of the dipole reorientation ΔF^* is 2.92 kcal/mole.

1. Introduction

The dielectric relaxations of several methylammonium alums have already been investigated [1–5]. In earlier papers the influence of the M^{+3} cationic effect in sulphate alums was investigated and recently the dielectric relaxation of a new selenate alum — MCrSeD was measured [5].

The results obtained enabled us to formulate certain generalizations about the variations of the relaxation times and ΔF^* values in the sulphate and selenate alums, respectively.

Within the same groups of alums — i.e. the sulphate alums or selenate alums — the macroscopic relaxation time is found to increase with increasing M^{+3} cation radius. It was particularly interesting to note the stability of the dipole reorientation barrier within two groups of alums: for the sulphate alums $\Delta F^* = 2.55$ kcal/mole whereas for the selenate alums ΔF^* equals about 3 kcal/mole.

Hence, it seemed desirable to investigate the dielectric relaxation in the selenate-gallium alum described quite recently [6].

2. Experimental

Methylammonium gallium selenate — MGaSeD was prepared from a stoichiometric quantity of aqueous methylamine solution, freshly prepared gallium hydroxide and selenic acid.

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As was mentioned [6] the monocrystal was grown by slow evaporation of an aqueous solution at a constant temperature of about 0°C. The $5 \times 5 \times 1$ mm monocrystal plates used for measurements were oriented along the [100] direction and the electrodes in the form of silver paste were applied to the crystal surface. The samples were prepared at temperatures below 15°C because of the tendency for crystal dehydration.

The measurements from 5 to 30 MHz were performed by means of an "Inco" type MQL-5 Q-meter whereas those in the 100–2000 MHz range were performed by means of "Rohde-Schwarz" type LMMBN3916/30 and "Orion" type EZM-1 coaxial slotted lines by the technique described previously [7].

3. Results and discussion

The results of measurements were analyzed for the paraelectric phase.

Dependences of ε' and ε'' on temperature at various frequencies are presented in Figs 1 and 2.

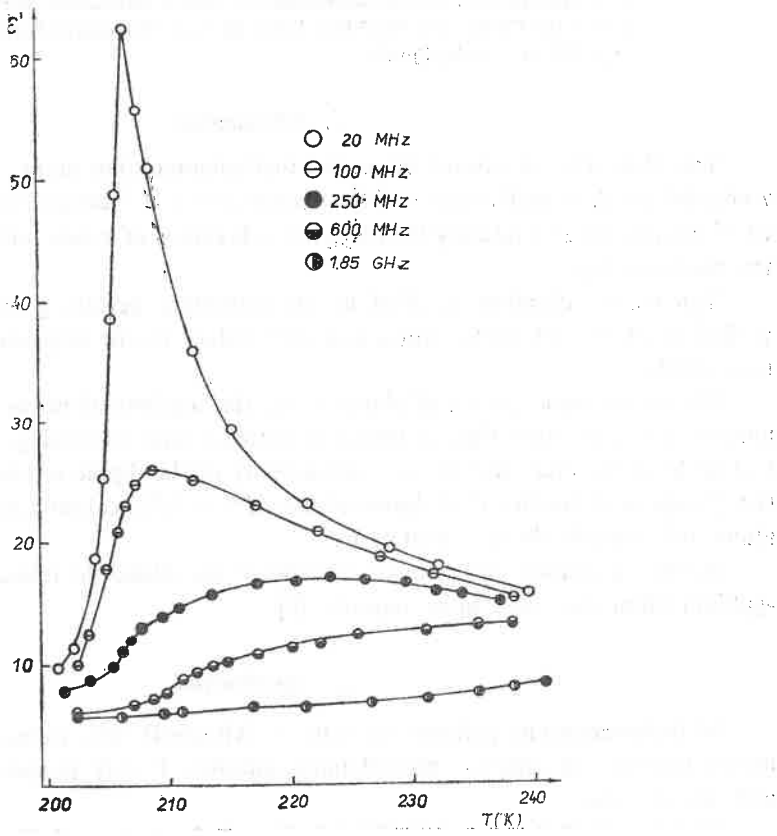

Fig. 1. Dielectric permittivity of MGaSeD plotted against temperature with the frequency as a parameter

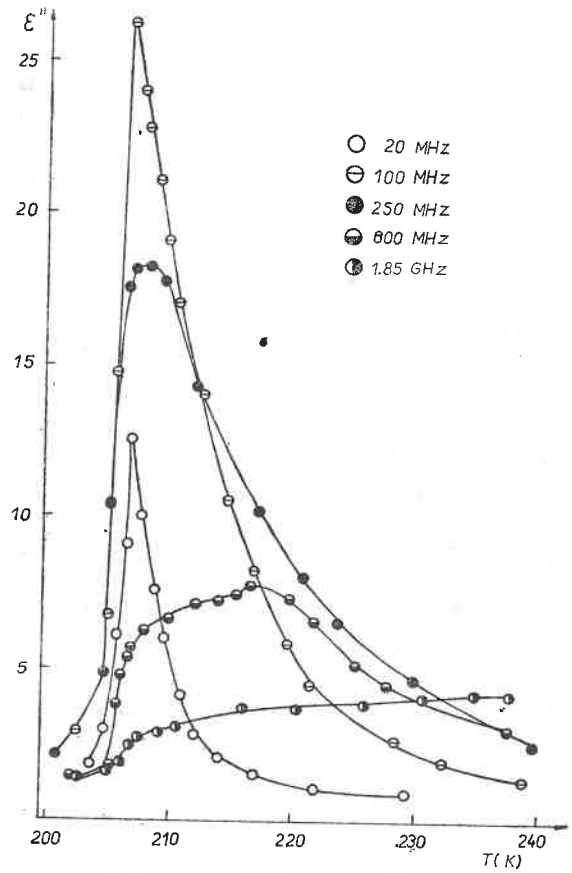

Fig. 2. Dielectric losses of MGaSeD plotted against temperature with the frequency as a parameter

Frequency relations ε' and ε'' satisfy well the Debye equation:

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

The Cole-Cole diagrams for various temperatures are shown in Fig. 3. These results, as in the case of other ferroelectric alums confirm a clearly monodispersive nature of the dielectric relaxation near the phase transition point including the T_c temperature.

The macroscopic relaxation time (Table I) was determined from the relation

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

where $\varepsilon(\infty) = 6.5$. The molecular relaxation time τ_0 was determined from the equation proposed by Müser [8]

$$\tau_0 = \tau\varepsilon(\infty)\frac{1}{\varepsilon(0)-\varepsilon(\infty)}. \tag{3}$$

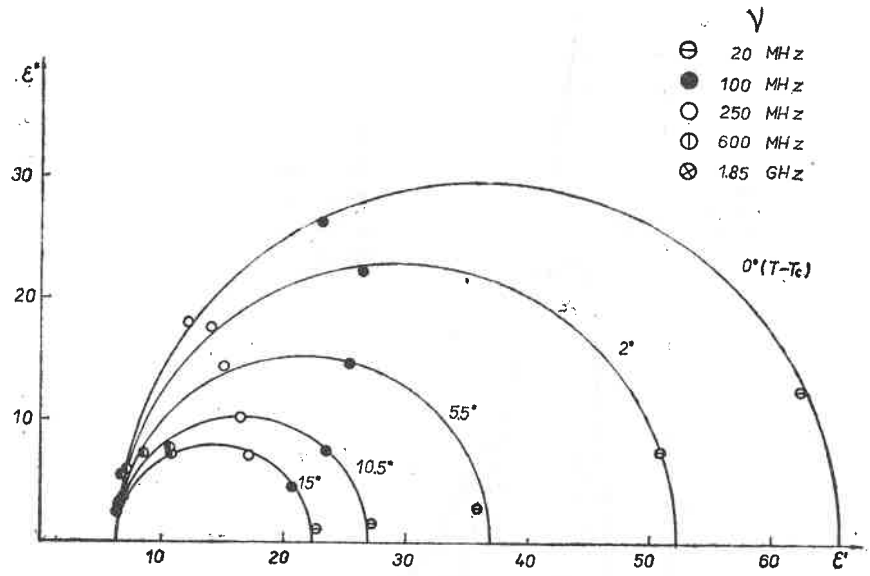

Fig. 3. Cole-Cole diagrams for MGaSeD

TABLE I

Values of macroscopic τ and molecular τ_0 relaxation time for MGaSeD

$T-T_c$/K	0	2	5.5	10.5	15.5
$\tau \times 10^{-9}$ sec	1.98	1.60	0.97	0.59	0.45
$\tau_0 \times 10^{-10}$ sec (Müser equation)	2.19	2.17	2.07	1.92	1.83
$\tau_0 \times 10^{-10}$ sec (Makita's equation)	4.78	4.52	4.33	4.28	4.22

The results obtained are presented in Table I. For comparison, the respective values of τ_0 determined from the relationship provided by Makita and Sumita [1]

$$\tau_0 = \tau \frac{C}{T} \frac{1}{\varepsilon(0)-\varepsilon(\infty)}$$

(where C—Curie constant) have been included.

The values of τ_0 determined from equation (3) were used to determine ΔF^* according to the formula:

$$\tau_0 = \frac{h}{kT} \exp\left(\frac{\Delta F^*}{kT}\right). \tag{4}$$

The mean value of $\Delta F^* = 2.92$ kcal/mole calculated in this way is very close to that found for the two methylammonium selenates investigated earlier [5]. Thus, we are now in posses-

sion of the dielectric relaxation data for all methylammonium alums of the general formula $CH_3NH_3^+M^{+3}(XO_4)_2 12H_2O$, where $M^{+3} = Al^{+3}$, Cr^{+3} or Ga^{+3} and $X = S$ or Se. The data obtained under the same experimental conditions for six possible combinations of the above mentioned cations and anions are summarized in Table II.

TABLE II

Comparison of the τ and ΔF^* for all alums calculated by means of Makita and Müser equations

Alums	T_c	Lattice constant [Å]	τ [sec]	Makita's equation		Müser equation	
				τ_0 [sec]	ΔF^* kcal/mole	τ_0 [sec]	ΔF^* kcal/mole
MASD	177	12.502	3×10^{-9}	1.25×10^{-10}	2.18	3.87×10^{-10}	2.54
MGaSD	170	12.543	5.2×10^{-9}	1.98×10^{-10}	2.19	5.62×10^{-10}	2.57
MCrSD	164	12.538	3.8×10^{-9}	2.2×10^{-10}	2.20	6.42×10^{-10}	2.53
MASeD	216	12.684	1.4×10^{-9}	4.5×10^{-11}	2.03	1.91×10^{-10}	3.0
MGaSeD	207.5	12.664	1.98×10^{-9}	4.78×10^{-11}	2.20	2.19×10^{-10}	2.92
MCrSeD	201.3	12.486	3.26×10^{-9}	7.8×10^{-11}	2.40	4.06×10^{-10}	2.97

It seems now that this barrier is, in fact, higher by about 0.5 kcal/mole for the selenate anions than for the sulphate anions.

This fact may provide strong evidence supporting the reorientation of the methylammonium cations through the barriers corresponding to the larger hindrance due to shorter distances. The average contact distance of $CH_3NH_3^+ \ldots O$ is 3.49 Å [11] in comparison to 3.58 Å in case of $SO_4^=$ groups. In particular if one compares the molecular relaxation times given in Table III one can see that at room temperature relaxation times for alums

TABLE III

Values of intrinsic (molecular) relaxation time for all alums at room temperature

Alums	τ_0
1. MASD	1.1×10^{-11} sec (Makita and Sumita 1971)
2. MGaSD	1.2×10^{-11} sec (Jakubas et al. 1978)
3. MCrSD	1.1×10^{-11} sec (Czapla et al. 1975)
4. MaSeD	2.5×10^{-11} sec (Czapla et al. 1977)
5. MGaSeD	2.2×10^{-11} sec This work
6. MCrSeD	2.3×10^{-11} sec (Czapla et al. 1976)

with $SeO_4^=$ are longer by a factor 2 than those with $SO_4^=$. These facts once more confirm that at room temperature the 180° reorientation of $CH_3NH_3^+$ ions around the threefold axis is responsible for the dielectric relaxation. Obviously, this situation is rather different from that observed in the vicinity of the transition temperature, where the dielectric permittivity increases rather dramatically to a value of about 60–70 which, in fact, gives

a contribution to the dielectric increment being a measure of the resultant dipole moment of the relaxator. It seems that such an increase of an effective dipole moment may be induced by so-called tilting of the $CH_3NH_3^+$ ion around the directions perpendicular to the threefold axis which is shown schematically as a (011) projection in Fig. 4. Such

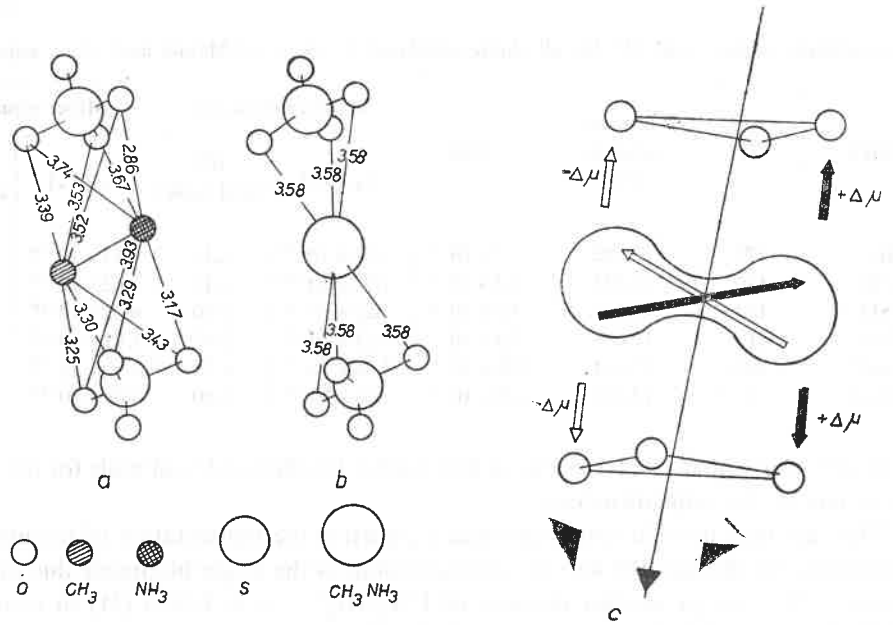

Fig. 4. a) distances between $CH_3NH_3^+$ and $SO_4^=$ in ferroelectric phase (after Fletcher and Steeple 1964); b) average distances between $CH_3NH_3^+$ and $SO_4^=$ in paraelectric phase (after Fletcher and Steeple 1964); c) proposed model of tilting of the $CH_3NH_3^+$ dipole in immediate vicinity of T_c ((011) projection); empty arrows represent one of possible 180° reversal polarizations with respect to 0° (full arrows); $\Delta\mu$ represents an induced dipole moment due to the possibility of N—N ... O H-bond formation

a tilting may obviously lead to a relatively weak N–N ... O bond formation and gives a contribution to the resultant effective dipole moment.

This point of view is consistent with the behaviour of alums in the NMR [10] and EPR [9] experiments.

Large differences in the values of free energies of reorientation correspond to the considerable increase in the phase transition point up to 40 K. This is a rule for all three pairs of alums with the same trivalent cation. The transition to the paraelectric phase associated with the liberation of the freedom of motion for the methylammonium cations requires much higher temperatures. The results obtained for MGaSeD make it also possible to introduce more confidently certain generalizations concerning the trivalent cation. There are no doubts that this effect is much weaker than that of the anion and is reflected by barely perceptible changes of the lattice constant.

However, this is reflected clearly in phase transition temperatures. The quantitative effects in this respect are almost identical for both series of alums with the same anions.

Variations in the values of activation free energy are not observed within the experimental error whereas regular variation may be found with respect to the relaxation times.

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