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# DIELECTRIC RELAXATION IN METHYLAMMONIUM-ALUMINIUM SELENATE (MASeD)

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Dielectric dispersion in methylammonium aluminium selenate dodecahydrate along the polar direction [100] over the frequency range 80 — 2000 MHz has been measured at temperatures near the transition point. The dispersion can be fairly well described by the Debye monodispersive process. Assuming that the macroscopic relaxation time satisfies the critical retardation model the $\tau_0$ value has been obtained. By using the temperature dependence of $\tau_0$ the value of the Eyring free energy of dipole reorientation has been estimated. The magnitudes of relaxation time $\tau$ and $\tau_0$ and energy barrier have been compared quantitatively with those for other methylammonium alums.

## 1. Introduction

Because of possible changes in their univalent and trivalent cations and also anions with no significant changes in structures, the alums provide possibilities to gain knowledge on the nature of phase transitions and also enable one to examine the effect of such changes on certain physico-chemical properties related to their ferroelectric behaviour. The results of dielectric relaxation studies have been presented previously in papers [1, 2]. The purpose of the present work, apart from studies on the "critical retardation" effect, was to investigate the effect of the replacement of sulphur with selenium in the aluminium-methylammonium alum on such quantities as dielectric constants, relaxation times and energy reorientation barriers.

## 2. Experimental

Aluminium-methylammonium selenate (MASeD) was prepared by adding aqueous methylamine solution and freshly prepared aluminium hydroxide to a selenic acid solution. The MASeD crystals were grown by slow evaporation of the solution at a constant

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temperature. This alum is isomorphic with MASD in its $\beta$-modification. The lattice constant $a = 12.691$ Å (22°C) [4]. The measuring techniques used in the present work were identical to those employed in paper [2].

### 3. *Results and discussion*

Results of $\varepsilon'$ and $\varepsilon''$ measurements as a function of temperature at various frequencies are presented in Figs 1 and 2.
The phase transition temperature obtained is $-56$°C and differs somewhat from the $T_c$ reported previously [4].

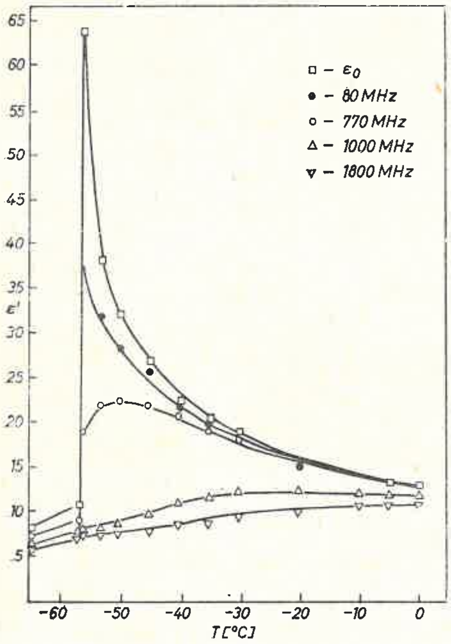

Fig. 1

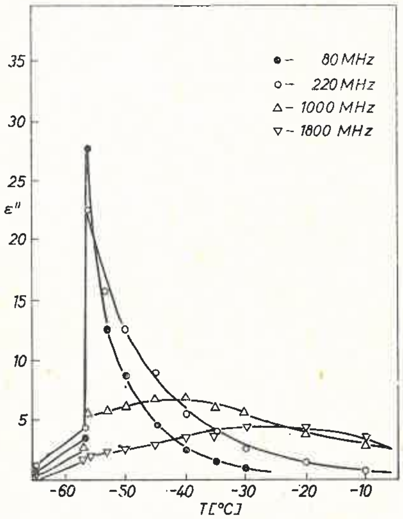

Fig. 2

Fig. 1. Temperature dependence of $\varepsilon'$ at various frequencies for the MASeD crystal
Fig. 2. Temperature dependence of $\varepsilon''$ at various frequencies for the MASeD crystal

The frequency relationship of $\varepsilon'$ and $\varepsilon''$ satisfies fairly well the equation [5]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau}. \tag{1}$$

The Cole-Cole diagrams for MASeD shown in Fig. 3 correspond exactly to the monodispersive character of the relaxation.

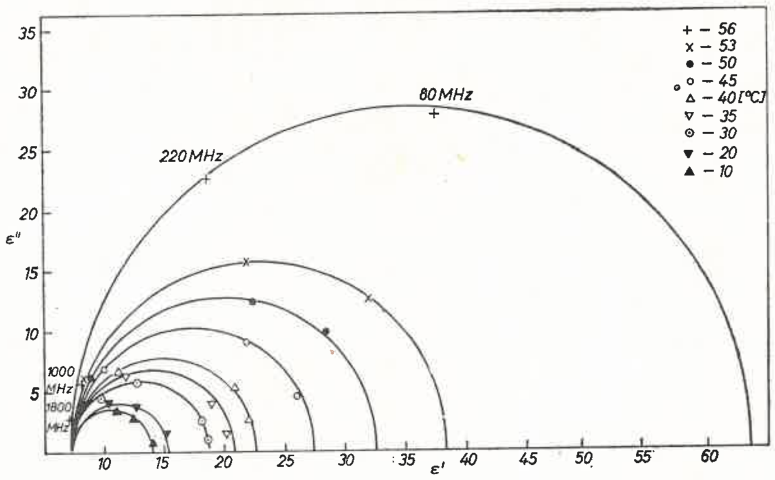

Fig. 3. Cole-Cole diagrams for the MASeD crystal at various temperatures $\varepsilon\infty = 7.5$

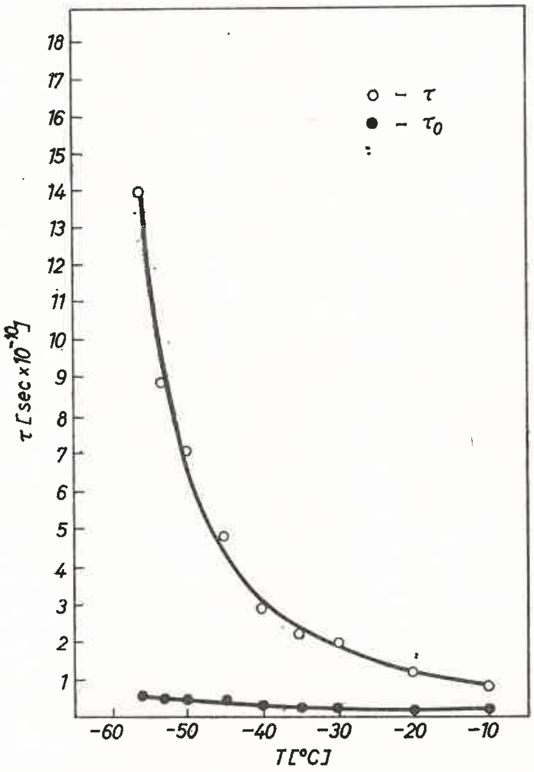

Fig. 4. Temperature dependence of $\tau$ and $\tau_0$ for the MASeD crystal

The dependence of $\tau$ and $\tau_0$ on $T$ found in this work is presented in Fig. 4. $\tau_0$ was estimated from the equation:

$$\tau = \tau_0 T(T-T_0)^{-1}. \tag{2}$$

Using a relationship:

$$\tau(T-T_0) = \alpha(T-T_0)^{-1} \exp(U/kT), \tag{3}$$

where $\alpha = \frac{h}{kT} e^{-\Delta S/k}$, the energy barrier for reorientation of the $CH_3NH_3^+$ dipoles was calculated to be 2.03 kcal/mol.

The results of studies carried out until now on the alums enable one to draw some general conclusions:

1. Dielectric relaxation in the methylammonium alums is related to the reorientation motions of the $CH_3NH_3^+$ ions, the strongest evidence being provided by NMR measurements for MASD [6].
2. The relaxation processes in the alums under investigation may be described with a good approximation by means of the monodispersive Debye's process.
3. As the phase transition point is approached, a sudden increase in the macroscopic dielectric relaxation time (critical retardation) is reached and at suitably high frequencies minima in dielectric permittivity are observed at the Curie point, the maximum values of $\varepsilon'$ and $\varepsilon''$ departing from the Curie point with increasing frequency.

TABLE I

Relaxation times $\tau$ and $\tau_0$ for methylammonium alums as a function of $(T-T_c)$

| $T-Tc$ | | 0 | 4 | 9 | 14 | 19 | 29 | 39 | 49 | |
|---|---|---|---|---|---|---|---|---|---|---|
| MCrSD | $\tau \cdot 10^{10}$ | 38.3 | 26.5 | 15.5 | 7.5 | 4.98 | 2.67 | 1.73 | 1.21 | |
| | $\tau_0 \cdot 10^{11}$ | 22 | 21 | 19.9 | 12.1 | 10.1 | 7.62 | 6.80 | 5.57 | |
| $T-T_c$ | | 0 | 6 | 16 | 26 | 36 | | | | |
| MASD | $\tau \cdot 10^{10}$ | 30 | 13 | 5 | 2.5 | 2.0 | | | | |
| | $\tau_0 \cdot 10^{11}$ | 12.5 | 10 | 7 | 4.5 | 3.5 | | | | |
| $T-T_c$ | | 0 | 3 | 6 | 11 | 16 | 21 | 26 | 36 | 46 |
| MASeD | $\tau \cdot 10^{10}$ | 14 | 8.91 | 7.08 | 4.79 | 2.88 | 2.24 | 1.99 | 1.15 | 0.776 |
| | $\tau_0 \cdot 10^{11}$ | 4.51 | 4.05 | 4.12 | 3.78 | 2.84 | 2.63 | 2.69 | 1.96 | 1.56 |

Now, let us compare quantitatively the magnitudes of relaxation times for the methylammonium under investigation. The values of $\tau$ and $\tau_0$ for particular alums are given in Table I.

The data obtained indicate that the relaxation times for MASeD are considerably shorter than for MCrSD while for MASD they are between the values for MCrSD and MASeD.

It seems that the nature of the energy barriers in alums is mostly affected by the $SO_4^{2-}$ or $SeO_4^{2-}$ ions between which the $CH_3NH_3^+$ cations occupy the position illustrated in Fig. 5 according to [7, 8].

The distance between the oxygen atoms of the $SO_4^{2-}$ groups and the $CH_3NH_3^+$ ions is 3.58 Å for MASD. The $CH_3NH_3^+$ ion occupies simultaneously a position in the centre of an octahedron consisting of six water molecules. The distance between this ion and a particular water molecules is 3.55 Å for MASD. The trivalent metal atoms situated in the centres of octahedra consisting also of six water molecules appear at a distance of 1/2 lattice constant from the $CH_3NH_3^+$ cation (more than 6 Å). If in aluminium-methylammonium sulphate aluminium is replaced with chromium then this substitution will result in an increase in the lattice constant from 12.502 Å (13°C) to 12.559 Å (12°C). This substitution leads to a slight but visible, over the entire temperature range, prolongation of the relaxation times as compared with MASD. A change in the lattice constant results from the appearance of larger octahedra $Cr(H_2O)_6^{3+}$ and may lead simultaneously to certain changes in the distances between the $CH_3NH_3^+$ cations and the water molecules belonging to the surrounding octahedron and from the oxygen atoms of the $SO_4^{2-}$ anions. Prolonged relaxation times might indicate that the freedom of reorientation of the $CH_3NH_3^+$ dipoles is diminished. Maybe in this case the above mentioned distances are reduced. This may lead to an increase or broadening of the energy barrier or to both of these effects simultaneously.

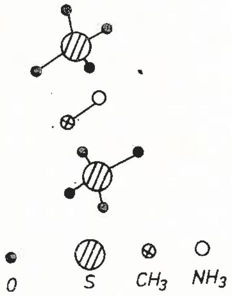

Fig. 5. Location of the $CH_3NH_3$ cation between the two $SO_4^{2-}$ anions in the MASD crystal

Another situation occurs in the case of the selenic alum. This alum exhibits considerably shorter relaxation times than MASD or MCrSD. Introduction of selenium also results in an increase in the lattice constant from 12.502 (13°C) to 12.698 Å (22°C). This change must lead to an increase in the distance between the $Al(H_2O)_6^{3+}$ octahedra and also to an increase in the distance between the $CH_3NH_3^+$ cation and the water molecules belonging to the surrounding octahedron. It is also an increase in the O–O distance in the $SeO_4^{2-}$ anion as compared with the $SO_4^{2-}$ anion which is of significant importance here. This may lead to a decrease or contraction of the energy barrier. In this case, the direction of the

C–N bond with respect to the crystallographic axes is even likely to be changed since this alum exhibits a higher value of spontaneous polarization This fact, however, may result from other causes. It should be mentioned that in the selenic alum $\varepsilon_\infty$ is higher than that for MASD and MCrSD about 6.4 and is 7.5. This is related presumably to the difference in polarizabilities of the $SeO_4^{2-}$ anions.

The energy barrier values obtained are 2.2, 2.18 and 2.03 kcal/mole for MCrSD, MASD and MASeD, respectively. As shown, the barriers for the above mentioned alums are very similar. This is additional evidence that the relaxation is associated with the movements of the same group. Thus, the effect of replacing aluminium by chromium and sulphur by selenium does not affect significantly the magnitude of the barrier. However, the direction of barrier variation together with more significant changes in the relaxation times may demonstrate that the possibilities for structural changes under discussion are correct. It is more probable that structural changes affect more significantly the width than the height of the energy barriers. No structural research studies on MCrSD and MASeD have been reported which might confirm the validity of the above considerations.

Unfortunately, NMR measurements for MASD [6] also do not provide a more detailed explanation of the problem discussed. The height of the energy barrier determined for the reorientation of the $CH_3NH_3^+$ ion is 3.6 kcal/mole for the paraelectric phase and about 4.5 kcal/mole for the ferroelectric phase and thus it is considerably higher than that determined from measurements of the dielectric relaxation.

It is probably important that the values of the relaxation times obtained by both methods alone are similar. A more detailed picture could be obtained after carrying out NMR measurements for other alums.

During the preparation of the present work a paper was published by Aleksandrov et al. [9] where the results of $\varepsilon'$ and $\varepsilon''$ measurements for MASeD were reported. Our results differ considerably from those of Aleksandrov. This applies both to the dispersion region and the permittivity and losses run near the transition point. The above mentioned authors found no "critical retardation" effect which seems to be rather odd.

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