

DIELECTRIC DISPERSION STUDIES IN (CH₃)₂NH₂Ga(SO₄)₂ · 6H₂O (DMAGaS) CRYSTAL

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(Received August 27, 1997; in final form December 10, 1997)

The paper presents the new data of dielectric dispersion in DMAGaS crystal. The very pronounced dispersion above $T_{c1} = 136$ K is observed in the frequency range 100 Hz–30 MHz with a single relaxation process. The relaxation time τ of an electric dipole reaches 2.17×10^{-7} s at the T_{c1} . The activation free energy ΔF of the dipoles is estimated to be equal to 0.087 eV. The order-disorder type of phase transition is confirmed.

PACS numbers: 77.80.Bh

1. Introduction

DMAGaS crystal belongs to the subfamily of organic-inorganic crystals containing dimethylammonium cations. So far, this subfamily consists of two crystals, namely: DMAAS — (CH₃)₂NH₂Al(SO₄)₆ · 6H₂O and DMAGaS — (CH₃)₂NH₂Ga(SO₄)₆ · 6H₂O [1–3]. DMAAS undergoes continuous para-ferroelectric phase transition of $T_c = 153$ K and DMAGaS undergoes two successive phase transitions at $T_{c1} = 136$ K and at $T_{c2} = 118$ K [4, 5].

The phase transition at T_{c1} is a first-order one and close to tricritical point [3, 6]. The crystal belongs to monoclinic system with point group symmetry $2/m$ above T_{c1} and m below T_{c1} [6]. The phase transition at T_{c2} is strongly of the first-order. At T_{c1} para-ferroelectric phase transition of the order-disorder type is connected with an ordering of the dimethylammonium cations [3–7]. At T_{c2} a rearrangement of dimethylammonium cations takes place and ferroelectric properties disappear [7].

Dielectric dispersion in DMAGaS crystal has been already studied [3]. However, the strange behaviour of dispersion as a very large contribution to the permittivity at low frequency range was found. This strange contribution may be related to the quality of the crystal or an influence of humidity. The aim of our work is to grow good quality DMAGaS crystal and reexamine its dielectric dispersion.

2. Experimental

Single crystals of DMAGaS were grown from water solution containing gallium sulfate and excess of dimethylammonium sulfate by slow evaporation method at constant temperature of 302 K. The x -cut samples (where x denoted the spontaneous polarization direction) were prepared, carefully dried (to avoid the humidity influence on the surface of the sample) and covered with silver paste.

Dielectric permittivity was measured by using LCR-meters HP 4284A at the frequency range 100 Hz–1 MHz and HP 4285A in the range 75 kHz–30 MHz.

3. Results and conclusion

As can be seen in Fig. 1 very pronounced dispersion is observed in the frequency range 100 Hz–30 MHz up to about 35 K above T_{c1} (Fig. 1a,b). The maxi-

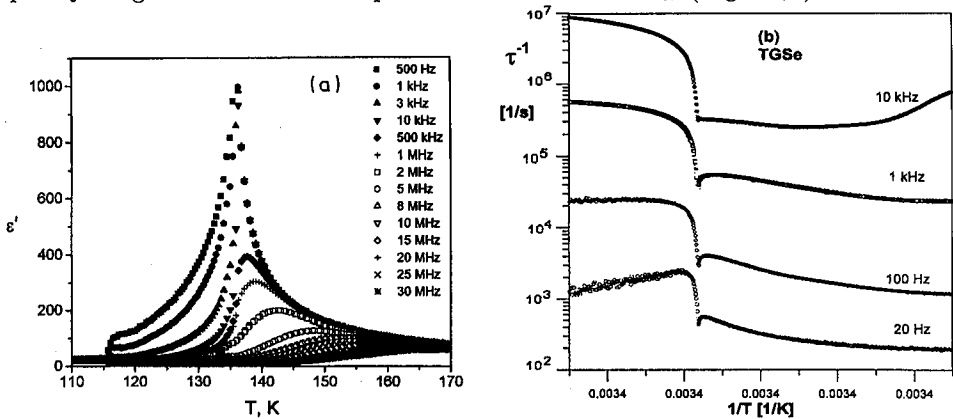


Fig. 1. Temperature dependence of the real (a) and imaginary (b) part of dielectric constant in DMAGaS crystal.

imum value of permittivity reaches 1500 at T_{c1} at the frequency of 100 Hz. In the paraelectric phase the dispersion can be described by Cole–Cole formula (1) with a single relaxation time τ

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_c - \epsilon_\infty}{1 + (i\omega\tau)^\beta}. \quad (1)$$

The dispersion begins at low frequencies (about 100 kHz) in the paraelectric phase. In this phase the maximum value of the electric permittivity shifts toward higher temperatures with increasing frequency of the measuring field. There is no clear minimum of the electric permittivity at T_{c1} for the higher frequencies and it confirms the first-order character of the phase transition. On the other hand, the shift of maximum of the electric permittivity towards higher frequencies testifies for critical slowing-down process of polarization in this crystal.

The results of ϵ' and ϵ'' measurements allowed us to construct the Cole–Cole diagrams presented for some chosen temperatures in Fig. 2. The obtained diagrams are typical semicircles with β parameter practically equal to 1 and we deal with a single relaxational process. We did not observe any additional contribution to permittivity and dispersion as it was presented in [3].

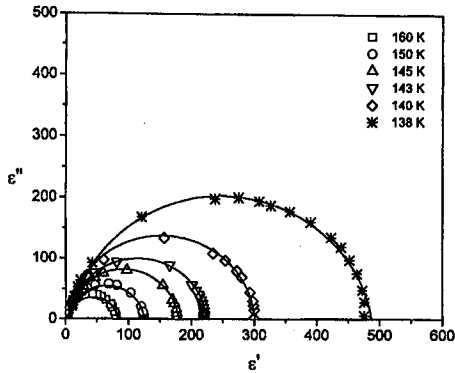


Fig. 2. The Cole-Cole plot for chosen temperatures above T_{c1} in DMAGaS crystal.

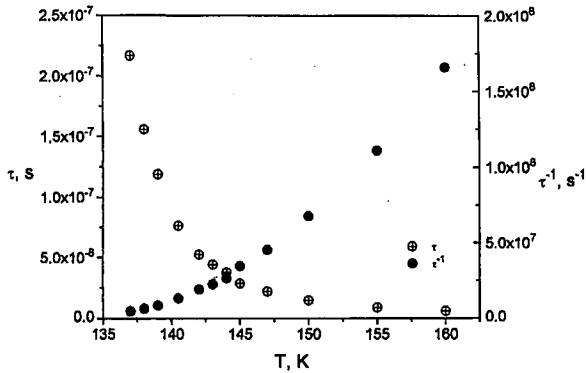


Fig. 3. Temperature dependence of the relaxation time and the reciprocal of the relaxation time in DMAGaS crystal.

The temperature dependence of the relaxation time τ obtained from Cole-Cole diagrams is shown in Fig. 3. The maximum value of the relaxation time (τ) reaches 2.17×10^{-7} s at the T_{c1} . It is twice higher than it was obtained in [3]. Figure 3 shows also the temperature dependence of the reciprocal relaxation time. The deviation of the dependence from the Curie-Weiss law is clearly seen.

According to a modified molecular field approximation in the case of the order-disorder type of the first-order phase transition the relaxation time varies in the paraelectric phase and its temperature dependence is described by a formula [8]:

$$\tau = \frac{h}{k_B} \frac{1}{T - T_0} \exp \frac{\Delta F}{k_B T}, \quad (2)$$

where k_B and h are Boltzmann's and Planck's constants, respectively, ΔF — the activation free energy of an electric dipole. However, the results of the measurements do not fulfil Eq. (2) just above T_{c1} (1–1.5 K).

Using the experimental data (Fig. 4) we obtained the activation free energy ΔF equal to 0.087 eV. This value is similar to that observed in [3].

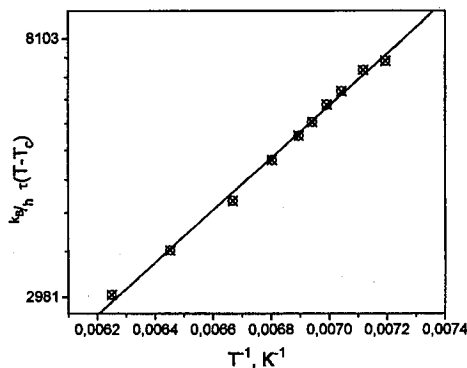


Fig. 4. The experimental data for obtaining the activation energy of an electric dipole.

Below T_{c1} an additional relaxational process related to the domain wall contribution to the permittivity is observed. The relaxation frequency of this process, which is rather diffused, is much lower in comparison with the dipolar dispersion observed in paraelectric phase and it is not analysed in the present studies.

Basing on the presented results one can state:

1. the phase transition is of order-disorder type and it is connected with ordering of dimethylammonium cations;
2. one relaxation process of Cole-Cole type related to reorientational motion of dimethylammonium cations was observed with $\beta \approx 1$;
3. the value of the relaxation time reaches $\tau = 2.17 \times 10^{-7}$ s at the T_{c1} . The estimated activation energy $\Delta F = 0.087$ eV;
4. the domain contribution to permittivity in ferroelectric phase is observed.

This work was supported by the Committee for Scientific Research grant 2016/W/IFD/1997.

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