

Phase Transitions and Fundamental Ferroelectric Dispersion in DMAAl_{1-x}Cr_xS Crystals

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This paper presents the results of investigations of the temperature dependence of heat capacity and dielectric dispersion in the vicinity of ferroelectric-ferroelastic phase transition of dimethylammonium metal sulphate hexahydrate crystals DMAAl_{1-x}Cr_xS. In particular, it is shown that the isomorphous substitution of metal ion noticeably changes the temperature of phase transition and parameters of the fundamental ferroelectric dispersion observed around T_{c1} . These changes are explained in terms of clusters sizes and dynamics in the framework of order-disorder type phase transition mechanism.

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1. Introduction

In recent time the ferroelectric crystals NH₂(CH₃)₂Al(SO₄)₂ · 6H₂O (DMAAS) and related materials are widely studied using different experimental methods. The crystal structure of DMAAS [1, 2] is built up of Al cations coordinated by six water molecules, regular SO₄ tetrahedra and [NH₂(CH₃)₂]⁺ (DMA) cations, all hydrogen bonded to a three-dimensional framework. It has been found that this crystal possesses a second order phase transition at temperature $T_{c1} = 152$ K [3] from ferroelastic ($T > T_{c1}$) to ferroelectric ($T < T_{c1}$) phases. This phase transition is of the order-disorder type with a symmetry change $2/m \rightarrow m$. The transition is connected with ordering of the polar DMA cations which execute hindered rotations around their C-C direction in the paraelectric phase and order only in the spatio-temporal average in the ferroelectric phase [4]. Besides, it was shown that at lower temperatures ($T < T_1$) also the antiferroelectric phase would be realized [2, 5]. In [3, 6] the anomalies of the dielectric and optical parameters at $T_{c2} = 110.5$ K and $T_1 = 75$ K were considered as the limits of the region of ferroelectric and antiferroelectric phase coexistence.

Previous studies showed that partial substitution of aluminium with chromium affects the phase transition temperature of DMAAS crystals. In particular, in comparison with the pure DMAAS the phase transition temperature T_{c1} in the crystal doped with Cr³⁺ (6.5%) is shifted toward higher temperatures by 2.6 K [7].

This paper is devoted to the more detailed study of the partial isomorphous substitution of metal ion on the temperature of phase transition and parameters of the fundamental ferroelectric dispersion in DMAAl_{1-x}Cr_xS solid solutions.

2. Experiment

Single crystals of NH₂(CH₃)₂Al_{1-x}Cr_x(SO₄)₂ · 6H₂O (DMAAl_{1-x}Cr_xS) were grown from the water solution containing the metal sulfate in a stoichiometric ratio and excess of dimethylammonium sulfate at a constant temperature of 303 K by slow evaporation method. The samples with $x = 0, 0.065,$ and 0.2 were grown. The concentration of chromium in each sample was additionally estimated using energy dispersive X-ray analyzer available in REMMA 102-02 electronic scanning microscope.

To avoid the influence of absorption water the samples were annealed before the experiments at the temperatures higher than 320 K.

The measurements of the real part of dielectric permittivity and conductivity were carried out using traditional method of capacitor capacitance measurement. The samples were cut as a plate perpendicular to the ferroelectric direction. The conducting silver paste electrodes were applied on the previously polished samples. The capacitance was measured using automated setup based on LCR-meter HIOKI 3522-50 LCF HiTester in a wide frequency range with an amplitude of 10 V m⁻¹. The dielectric parameters were measured with an accuracy of nearly 1%.

The nitrogen vapor flow cryostat with UNIPAN 680 temperature control system was used for the dielectric measurements. The temperature was stabilized with an accuracy not worse than 5×10^{-3} K.

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DSC measurements were carried out using a Perkin-Elmer TMA-7 calorimeter with rates ranging from 10 to 20 K min⁻¹.

3. Results and discussion

The temperature dependences of the dielectric permittivity ε' and tangent of dielectric losses $\tan \delta$ are very useful for the precise determination of the phase transition temperatures in the samples with different chromium concentration (Fig. 1). Indeed, both these parameters

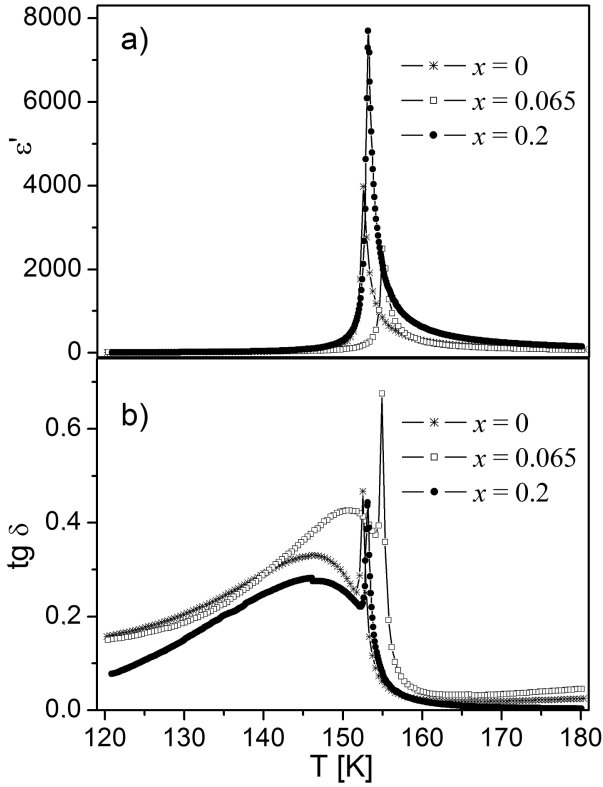


Fig. 1. Temperature dependences of the dielectric permittivity ε' (a) and tangent of dielectric losses $\tan \delta$ (b) for $\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$ with different Cr concentration measured along the ferroelectric axis at 100 kHz in a cooling mode.

manifest sharp anomalies at the temperature T_{c1} characteristic of proper ferroelectric phase transition for all investigated crystals. The temperatures of phase transition for the samples with different concentration of chromium are presented in Table I.

In comparison with the pure DMAAS the phase transition temperature T_{c1} in the sample with $x = 0.065$ was shifted toward higher temperatures by 2.4 K. Otherwise, increase of chromium concentration to $x = 0.2$ leads to the shift of this temperature toward lower temperatures. The temperature of phase transition in $\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$ with $x = 0.2$ is very close to the corresponding temperature of “pure” crystal.

The obtained data concerning the shift of the phase transition temperatures are confirmed by the results of

TABLE I

The temperatures of ferroelectric phase transition and temperatures of crystal decay for $\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$.

Chromium concentration x	0	0.065	0.2
Temperatures of phase transitions [K]			
dielectric data	152.5	154.9	153.1
data of DSC	152.8	154.7	153.7
Decay temperatures [K]			
data of DSC	403.8	417.3	408.6

DSC measurements (Fig. 2). They fairly well correlate with the data obtained on the basis of dielectric study. The temperatures of phase transitions obtained using both these methods were found to be very close in corresponding crystals, especially when to take into account that dielectric and calorimetric measurements cannot be performed at the same electric, heat and some other conditions.

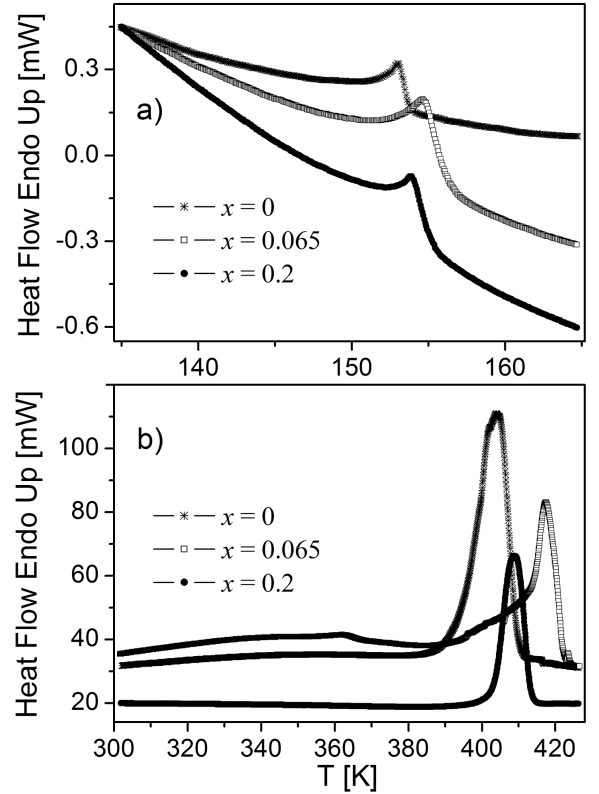


Fig. 2. Temperature dependences of heat capacity of $\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$ in vicinity of the ferroelectric phase transition (a) and crystal decay temperature (b) (heating).

The heat capacity measurements unambiguously point to second order character of this transformation at any composition. Besides, the calorimetric data testifies that dependence of the crystal decay temperature on the chromium content looks very similar to the behaviour

TABLE II

Curie–Weiss parameters and values of the relaxation time for DMAAl_{1-x}Cr_xS with different concentration of chromium.

Parameters	Chromium concentration x		
	0	0.065	0.2
Θ [K]	152	155.8	153.2
C_+ [K]	2410	1528	4216
C_- [K]	424	424	657
τ_0^+ [s K]	2.49×10^{-7}	3.15×10^{-7}	2.25×10^{-7}
τ_0^- [s K]	6.01×10^{-8}	7.96×10^{-8}	7.81×10^{-8}

of T_{c1} . Indeed, introduction of Cr³⁺ is followed by considerable shift of decay temperature toward higher values, although the shift was found to be larger for the sample with lower concentration of chromium (see Table I).

The nontrivial dependence of the ferroelectric phase transitions temperatures on the chromium concentration can be explained as follows. In the case of comparatively low concentration ($x = 0.065$) there arise the conditions leading to formation of more massive dipole clusters in the vicinity of ferroelectric phase transition. It is obvious that the chromium ions can be considered as the embryo during the formation of such clusters. Exactly this factor should be considered as a basic in the detected growth of the phase transition temperature in comparison with the pure DMAAS. However, increase of the chromium concentration causes multiplication of the mentioned embryos. This process is followed by fragmentation of the clusters and the corresponding decrease of T_{c1} . The formation of clusters' embryos is caused by the fact that the chromium ions, participating in formation of more strong Cr–O bonds in the crystal structure in comparison with Al–O ones, create the sources of the local electric field. Its turn causes a reorientation of the neighboring dipoles (DMA groups). This effect has an impact not only on the phase transition temperature but also on the fundamental ferroelectric dispersion and, besides, on the thickness of domain walls and hence their dynamics. The corresponding wide maxima on the temperature dependences of $\tan \delta$ (Fig. 1b) observed below T_{c1} would be considered as a characteristic manifestation of the latter. The detailed analysis of the low frequency dielectric dispersion connected with the domain dynamics will be presented elsewhere.

At the same time, one can conclude that the temperature dependence of the susceptibility at quite high frequency (Fig. 1) obeys the law of Curie–Weiss in the paraelectric (+) and ferroelectric (–) phases in the vicinity of the ferroelectric phase transition in DMAAl_{1-x}Cr_xS crystals with different concentration of chromium

$$\chi_{\pm} = \pm \frac{C}{T - \Theta}, \quad (1)$$

where Θ — the Curie–Weiss temperature, C — the Curie–Weiss constant, T — temperature.

The parameters of the Curie–Weiss law calculated by formula 1 are presented in Table II. These parameters in all cases are consistent with typical values for the ferroelectric phase transitions of ordering type [8].

Analyzing dispersion of the dielectric parameters of DMAAl_{1-x}Cr_xS ($x = 0.2$) (Fig. 3), we can see that at higher frequencies of the measuring field starting from $f = 1$ MHz the temperature dependences of ϵ' show a sharp minimum at T_{c1} instead of a clear peak usually observed in the ferroelectric substances at lower frequencies (Fig. 1a). The minimum becomes broader and deeper with increase of frequency. Simultaneously both shoulders of ϵ' are shifted away from the transition point. It is also interesting to note that the tangent of dielectric losses $\tan \delta$ shows maxima at T_{c1} . Such a behaviour of the

dielectric parameters is characteristic of “order-disorder” type ferroelectric phase transitions and is related to a critical slowing down (paraelectric phase) and respectively speeding up (ferroelectric phase) of the dipole (order parameter) relaxation time. The very similar behaviour were found to be for the samples with $x = 0$ and 0.065 [7, 9]. The observed phenomenon is directly connected with increase of the relaxation time τ in the vicinity of the phase transition according to equation [9]:

$$\frac{1}{\tau} = \frac{T - \Theta}{\tau_0}, \quad (2)$$

where Θ denotes the Curie–Weiss temperature for ϵ' and τ_0 is considered as the temperature parameter of relaxation time.

The dispersive equation for $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ in this case may be obtained from the Debye equation

$$\epsilon^*(\omega, T) = \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau} + \epsilon_{\infty}. \quad (3)$$

Taking into account that $\epsilon_0 - \epsilon_{\infty} = C/(T - \Theta)$ and relation (2):

$$\epsilon^*(\omega, T) = \frac{C}{T - \Theta + i\omega\tau_0} + \epsilon_{\infty}. \quad (4)$$

In Eqs. (2)–(4) ϵ_{∞} denotes the high frequency limit and ϵ_0 is the permittivity obtained by static measurements.

According to (4) the temperature maximum of ϵ' in the region of dispersion is observed at

$$T_{\max} = \Theta \pm \omega\tau_0. \quad (5)$$

As it follows from the obtained experimental results (Fig. 3) $\Theta = 153.2$ K, both for the ferroelectric and the initial phase of the DMAAl_{1-x}Cr_xS ($x = 0.2$), i.e. the phase transition is of second order. Thus using the available data concerning the frequency shift of the corresponding ϵ' -maxima and Eq. (5) one could calculate τ_0^{\pm} (where “+” corresponds to the paraelectric phase and “–” — to the ferroelectric phase, respectively)

$$\tau_0 = \pm \frac{T_{\max} - \Theta}{\omega}. \quad (6)$$

The calculated values of corresponding relaxation time for all investigated crystals are presented in Table II. The highest values are found to be for the case of DMAAl_{1-x}Cr_xS ($x = 0.065$) crystals [7]. This result correlates with the highest values of the transition temperature for the considered sample. Under such

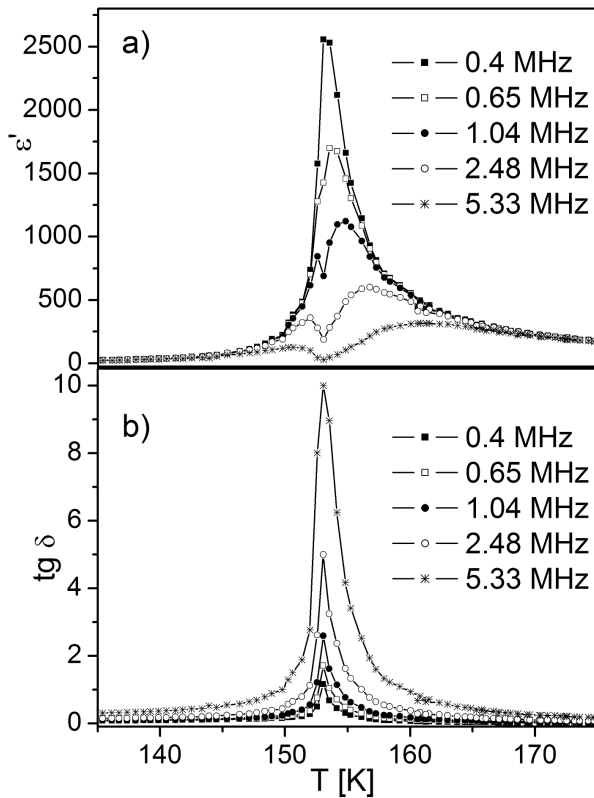


Fig. 3. Temperature dependences of the dielectric permittivity ϵ' (a) and tangent of dielectric losses $\text{tg } \delta$ (b) for $\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$ ($x = 0.2$) measured along the ferroelectric axis at different frequencies of measuring electric field.

circumstances one can conclude that in this case the chromium ions at comparatively low concentration cause formation of the larger dipole clusters in vicinity of the ferroelectric phase transition. At the same time, the samples with a higher concentrations of Cr^{3+} ($x = 0.2$) and pure crystal are characterized by smaller temperature parameters of the relaxation time that imply the lower temperatures of phase transitions.

4. Conclusions

In result of performed investigations of the dielectric and calorimetric properties of $\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$ crystals it has been shown that partial isomorphous substitution of the metal ion leads to the noticeable change of the ferroelectric phase transition and thermal decay temperatures and the relaxation time of the thermal dipole relaxation with a critical slowing-down at T_{c1} . The highest values of these parameters were found to be for the case of lower chromium concentration ($x = 0.065$). In the corresponding samples the chromium ions generate arising of the sources of local electric field leading to formation of more massive dipole clusters in the vicinity of ferroelectric phase transition. Increasing the chromium concentration causes multiplication of the cluster's embryos and fragmentation of the clusters and the corresponding

decrease both of the temperature parameter of relaxation time and phase transition temperature T_{c1} that in this case become close to those in the pure DMAAS crystal.

$\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$ crystals become more thermally stable due to the substitution of Al ions by Cr that is caused by more strong Cr–O bonds in comparison with Al–O ones [1]. At the same time, the nontrivial dependence of the decay temperature on the chromium concentration testifies that interaction of the metal–water octahedra with dimethylammonium groups carrying a dipole moment plays an important role in the observed effect.

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