

THE EFFECT OF METAL ION SUBSTITUTION ON THE DIELECTRIC DISPERSION IN $\text{NH}_2(\text{CH}_3)_2\text{Ga}_{1-x}\text{Cr}_x(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ CRYSTALS

V. Kapustianyk^{1,2}, S. Semak², Yu. Eliyashevskyy², S. Sereda^{1,3}

¹*Scientific-Technical and Educational Center of Low Temperature Studies, Ivan Franko National University of Lviv, 50, Drahomanov St., UA-79005, Lviv, Ukraine*

²*Department of Solid State Physics, Ivan Franko National University of Lviv, 50, Drahomanov St., UA-79005, Lviv, Ukraine*

³*Forschungszentrum Jülich, Institut für Energie- und Klimaforschung-Plasmaphysik, 52425, Jülich, Germany*

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The comparative study of the dielectric dispersion in the vicinity of the ferroelectric-ferroelastic phase transition in $\text{NH}_2(\text{CH}_3)_2\text{Ga}_{1-x}\text{Cr}_x(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($x = 0; 0.065$) crystals was performed. As it follows from the analysis of the temperature-frequency dependences of the dielectric permittivity and the Cole–Cole diagrams, the dielectric dispersion is connected with a critical slowing down of the dipole relaxation (fundamental dispersion) in the high frequency range and with the domain wall dynamics at lower frequencies of the measuring electric field. It has been shown that the metal ion substitution practically does not affect the temperatures of phase transitions but manifests itself in the parameters of the low frequency dielectric dispersion. The substitution of gallium with chromium is followed by an increase in the relaxation time, the activation energy and the half-width of the Gaussian, which describes the distribution of the relaxation times. This was explained by the fact that chromium ions, due to their larger sizes in comparison with gallium ions, cause local lattice deformations. The latter promote the formation of more massive dipole clusters in the vicinity of the ferroelectric phase transition.

Key words: dielectric dispersion, ferroelectric crystal, phase transition, chromium.

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I. INTRODUCTION

In recent time, $\text{NH}_2(\text{CH}_3)_2\text{Ga}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (DMA-GaS) ferroelectric crystals were studied using different experimental methods. Their crystal structure is built up of Ga cations coordinated by six water molecules, regular SO_4 tetrahedra and $[\text{NH}_2(\text{CH}_3)_2]^+$ (DMA) cations, all hydrogen bonded to a three dimensional framework [1]. It has been found that this crystal undergoes a first-order phase transition at $T_{c1} = 134$ K from ferroelastic ($T > T_{c1}$) to ferroelectric ($T < T_{c1}$) phases. This transition with the symmetry change $2/m \rightarrow m$ is associated with the ordering of the polar DMA cations in the ferroelectric phase [1].

On cooling, at $T_{c2} = 106$ K the crystal undergoes a second first-order phase transition with a large thermal hysteresis up to 12 K [2]. The ferroelectric phase in DMA-GaS lies within the temperature range from $T_{c1} = 136$ K to $T_{c2} = 119$ K in a heating run [3].

DMAGaS crystal is an isomorphous analogue to $\text{NH}_2(\text{CH}_3)_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (DMAAIS) [3, 4]. Therefore, one can suppose that the dielectric dispersion in DMA-GaS would be similar to that in DMAAIS crystals. The latter are characterized by the coexistence of the fundamental ferroelectric dispersion and the dispersion caused by the dynamics of domain walls at comparatively low frequencies of the measuring electric field [5]. Both relaxation processes significantly affect the dielectric properties of the ferroelectrics, so their research looks very

important. The dielectric relaxation of DMAGaS was studied in a wide frequency range in Ref. [2], although the low frequency dispersion connected with the domain walls dynamics still demands a more precise analysis.

Previous studies showed that substitution of aluminium with chromium in the isomorphous analogue — DMAAIS crystals — noticeably affects the phase transition temperature [6, 7]. Moreover, paper [8] reported a successful creation of the paramagnetic order in the initially diamagnetic DMAAIS crystal by such an isomorphous substitution of a metal ion. A large magnetoelectric (ME) coupling was successfully generated this way. Besides, the possibility to tune its sign changing the Cr content was demonstrated.

This paper presents the data concerning the effect of the metal ion substitution on the phase transitions and the low frequency dielectric dispersion in $\text{NH}_2(\text{CH}_3)_2\text{Ga}_{1-x}\text{Cr}_x(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($x = 0; 0.065$) (DMAGa_{1-x}Cr_xS) crystals. These investigations look very important, taking into account that the abovementioned solid solution also would be considered as potential multiferroics with the possible manifestation of the ME effects.

II. EXPERIMENTAL

Single DMAGa_{1-x}Cr_xS ($x = 0; 0.065$) crystals were grown from a water solution containing gallium sulfate, an excess of dimethylammonium sulfate and chromium



sulfate at the constant temperature of 303 K by the slow evaporation method. The molar ratio of $\text{Ga}^{3+}:\text{Cr}^{3+}$ for the solid solution with $x = 0.065$ was equal to 1:0.065. In order to avoid the influence of absorption water, the samples were annealed before the experiments at the temperatures higher than 320 K.

The real and imaginary parts of the dielectric permittivity were investigated using the traditional method of capacitor capacitance measurement.

The crystals were cut in a shape of plates perpendicular to the ferroelectric direction. The polished samples were covered with conducting silver paste electrodes. The measurements were carried out with Hewlett-Packard 4284A RLC-meter in the frequency range from 100 Hz to 1 MHz at the applied electric field not higher than 5 V cm^{-1} . The error in the measurements of the dielectric parameters did not exceed 1 %.

A programmable temperature controller UNIPAN 680 was used for the control of the sample's temperature,

which was measured by a copper-constantan thermocouple with an accuracy not worse than 0.1 K.

A special software application was developed based on the C programming language for the dielectric data analysis.

III. RESULTS AND DISCUSSION

The temperature dependences of the dielectric parameters for $\text{DMAGa}_{1-x}\text{Cr}_x\text{S}$ ($x = 0; 0.065$) crystals measured at the radio frequency range below 100 kHz (Fig. 1) show sharp anomalies of the dielectric permittivity and the dielectric loss tangent at T_{c1} temperature, characteristic of the ferroelectric phase transition. The jump-like anomalies were also observed at T_{c2} (ferroelectric-antiferroelectric phase transition) for both compared crystals. One can use these dependences for a precise determination of the phase transition temperatures.

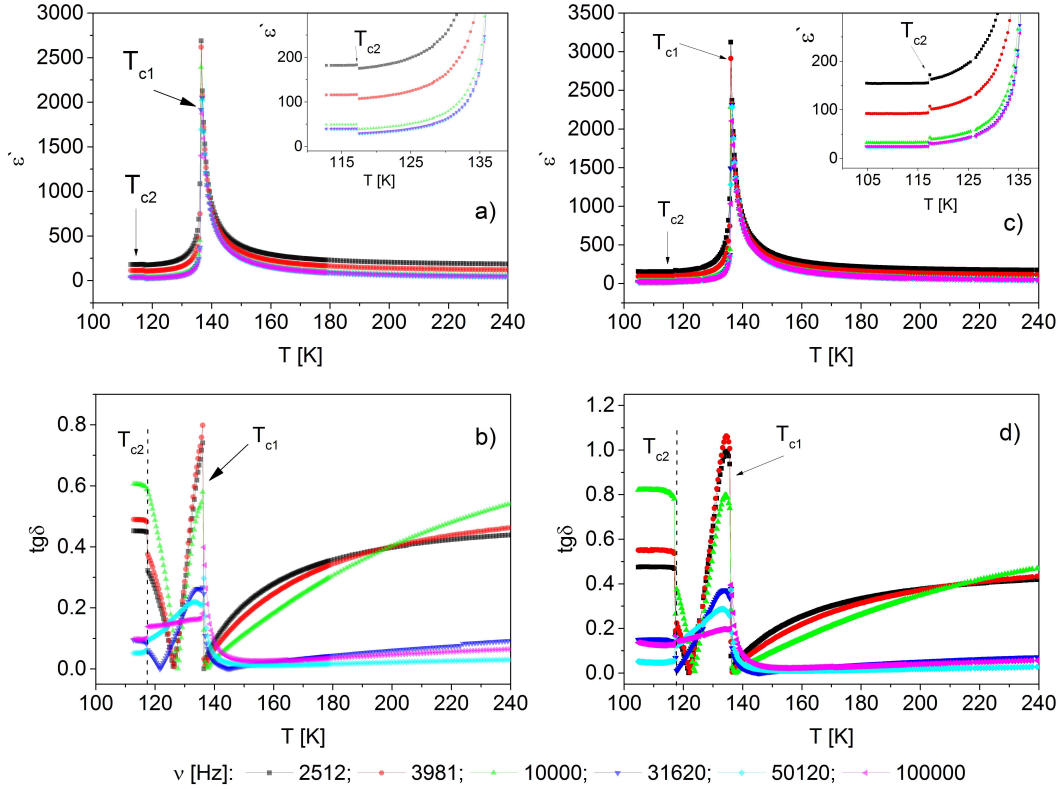


Fig. 1. Temperature dependences of the real part of the dielectric permittivity ϵ' (a, c) and the tangent of dielectric losses $\text{tg } \delta$ (b, d) for $\text{DMAGa}_{1-x}\text{Cr}_x\text{S}$ (a, b: $x = 0$; c, d: $x = 0.065$) measured at the different frequencies of measuring electric field at cooling. The insets present the anomalies of the dielectric permittivity in the vicinity of T_{c2} temperature.

As it is known, the introduction of chromium ions into the isostructural DMAAIS crystal was followed by a noticeable shift in the ferroelectric phase transition temperature [6, 9, 10]. In particular, T_{c1} temperature in the sample with 6.5% of chromium shifted toward higher temperatures in comparison with DMAAIS by 2.4 K. However, as it turned out in our studies, the similar substitution of gallium with chromium in DMAGaS practically did not

affect the temperatures of the phase transitions. Indeed, the temperatures of the phase transitions were found to be $T_{c1} = 136 \text{ K}$ and $T_{c2} = 117 \text{ K}$ (at cooling) both for DMAGaS and $\text{DMAGa}_{0.935}\text{Cr}_{0.065}\text{S}$ crystals. This is clearly illustrated by the temperature dependences of the dielectric parameters for initial and chromium doped DMAGaS crystals measured at the applied field frequency 1 kHz (Figure 2).

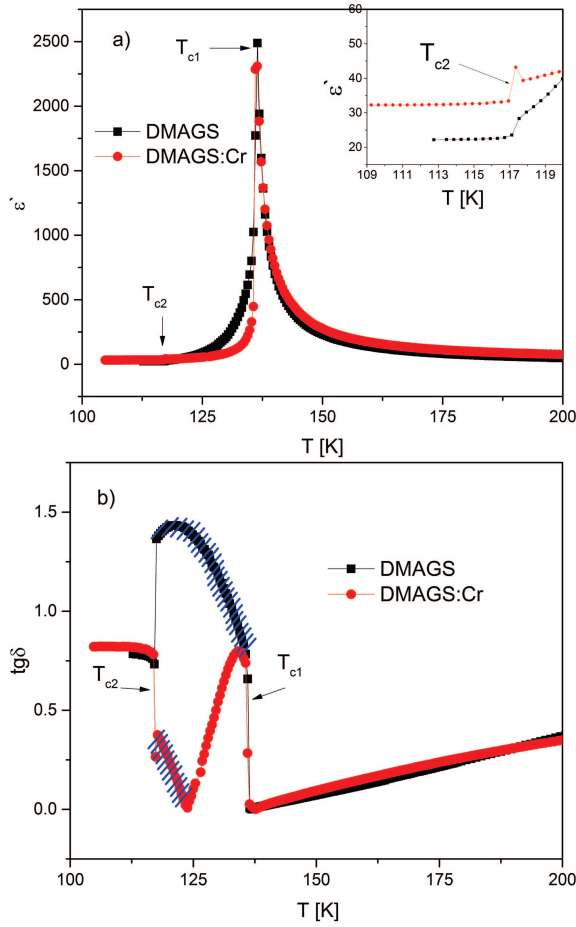


Fig. 2. Comparison of the temperature dependences of the real part of dielectric permittivity (a) and the dielectric loss tangent (b), obtained in a cooling run with applied field frequency 1 kHz for DMAGaS and DMAGa_{0.935}Cr_{0.065}S crystals.

The observed lack of chromium dopant influence on the phase transition temperatures may be explained by the closer sizes of Cr³⁺ and Ga³⁺ ions contrary to the case of Cr³⁺ and Al³⁺ pair [9].

Previous studies of the temperature dependence of the dielectric constant in DMAGaS crystal demonstrated the fulfillment of the Curie–Weiss law (1) above the ferroelectric phase transition up to 150 K [11]:

$$\chi = \frac{C_+}{T - \Theta}; \quad (\varepsilon = 1 + \chi), \quad (3.1)$$

where C_+ is the Curie–Weiss constant and Θ is the Curie–Weiss temperature.

Our analysis confirms that dielectric susceptibility also obeys this law for the chromium doped DMAGaS crystals in the paraelectric phase up to 170 K (Fig 3). Figure 3 clearly shows the deviation from the direct line of the inverse susceptibility temperature dependence at $T > 170$ K. This can be explained by a significant influence of the proton conductivity at higher temperatures, which also was observed in isostructural DMAAl_{1-x}Cr_xS crystals [6]. The behaviour of the temperature dependence of the inverse susceptibility in the vicinity of the

phase transition point T_{c1} confirms its first order contrary to the case of isostructural DMAAl_{1-x}Cr_xS crystal undergoing a second order ferroelectric phase transition [6, 9, 10]. Table 1 presents the Curie–Weiss law parameters for investigated DMAGa_{1-x}Cr_xS ($x = 0; 0.065$) crystals in comparison with the corresponding data obtained in [10] for DMAAl_{1-x}Cr_xS ($x = 0; 0.065; 0.2$). All obtained values of the Curie–Weiss constants $C_+ = (1500 \div 4200)$ K are typical of the order–disorder type phase transitions [12]. When the frequency of the measuring field is quite high for the manifestation of the domain wall dynamics (see Figs. 1a and 4a), the Curie–Weiss constants ratio C_+/C_- was found to be about 8, that is also characteristic of the first-order phase transition ($C_+/C_- |_{\text{DMAGa}_{0.935}\text{Cr}_{0.065}\text{S}} = 8.7$) [2].

	DMAGa _{1-x} Cr _x S		DMAAl _{1-x} Cr _x S*		
x	0	0.065	0	0.065	0.2
Θ , K	135.5	136.9	152	155.8	153.2
C_+ , K	3842	4112	2410	1528	4216
C_- , K	357	469	424	424	657

Table 1. Curie–Weiss law parameters for DMAGaS and DMAAlS doped with chromium in different concentration (the data marked with * are taken from [7]).

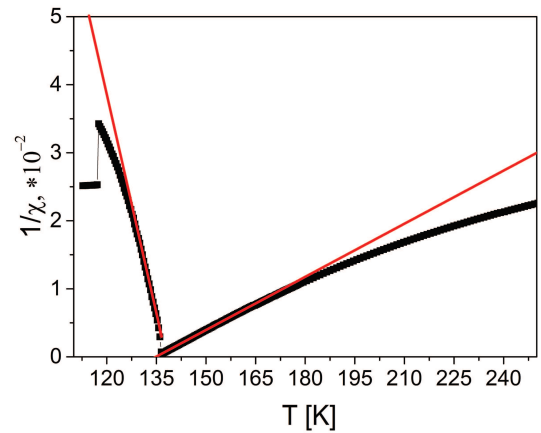


Fig. 3. The reverse susceptibility as a function of temperature obtained at 100 kHz for a DMAGa_{0.935}Cr_{0.065}S crystal.

The analysis of different relaxation processes in DMAGa_{0.935}Cr_{0.065}S could be performed by analogy with those observed in DMAGaS crystals [11]. Indeed, it has been shown that the Debye type dielectric dispersion occurred in the paraelectric phase ($T > T_{c1}$) of DMAGaS crystals in a very wide frequency range ($f = 100\text{Hz} \div 30$ MHz) and was related to the reorientational motion of dimethylammonium cations. A similar dispersion was observed in DMAGa_{0.935}Cr_{0.065}S crystal in a temperature range above T_{c1} (Fig. 1). First of all, it manifests itself clearly in the dielectric loss tangent temperature dependences (Figure 1b). When the temperature drops closer to the ferroelectric phase transition, a certain orientation of the DMA⁺ cation becomes more probable, that

leads to the transformation of the Debye dispersion into a ferroelectric fundamental dispersion, which in the case of $\text{DMAGa}_{0.935}\text{Cr}_{0.065}\text{S}$ crystal manifests itself at quite high frequencies beginning from 10 kHz. First of all, this concerns the temperature-frequency dependences of the dielectric loss tangent of $\text{DMAGa}_{1-x}\text{Cr}_x\text{S}$ crystals. Indeed, below the jump-like anomalies of this parameter observed at the phase transition point T_{c1} (Figs. 1b, 2b), one can observe comparatively wide peaks. Their intensity decreases and the half-width increases with increasing frequency, that is characteristic of the fundamental ferroelectric dispersion.

Beside these anomalies, in the investigated samples one can observe a part of the very wide maxima of $\tan \delta$ for different quite low frequencies within the ferroelectric phase. These wide maxima shift toward lower temperatures with a decrease of the measuring field frequency (Fig. 1b). Such a behaviour would be related to the domain walls dynamics. It is impossible to observe these broad maxima completely as in $\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$ because of the onset of the second phase transition T_{c2} [6]. As it follows from Figs. 1b, d and 2b the maxima corresponding to the domain wall dynamics in $\text{DMAGa}_{0.935}\text{Cr}_{0.065}\text{S}$

are considerably shifted to lower temperatures in comparison with those in the initial crystals (the corresponding region is shaded in blue). Such a shift would be considered as the most noticeable effect of the isomorphous substitution of the metal ions on the domain wall dynamics. The corresponding low frequency dispersion manifests itself also in the real part of the dielectric permittivity below T_{c1} but it is not so evident as for the imaginary part.

A similar dielectric dispersion has been observed in the crystals of the KDP family as well as in the initial (DMAAlS), deuterated (DMAAlSD) and chromium doped ($\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$) crystals and has been related to the dipole reversal within the domain walls in the AC field [13, 6]. Due to this fact, the domain walls can move and the reorientation of the corresponding dipoles enlarges the dielectric permittivity at the relatively low frequencies. When approaching a certain “freezing temperature” T_f , the dipoles are no longer easily removable and consequently the mobility of the domain walls vanishes, leading to an abrupt decrease of the electric permittivity [13].

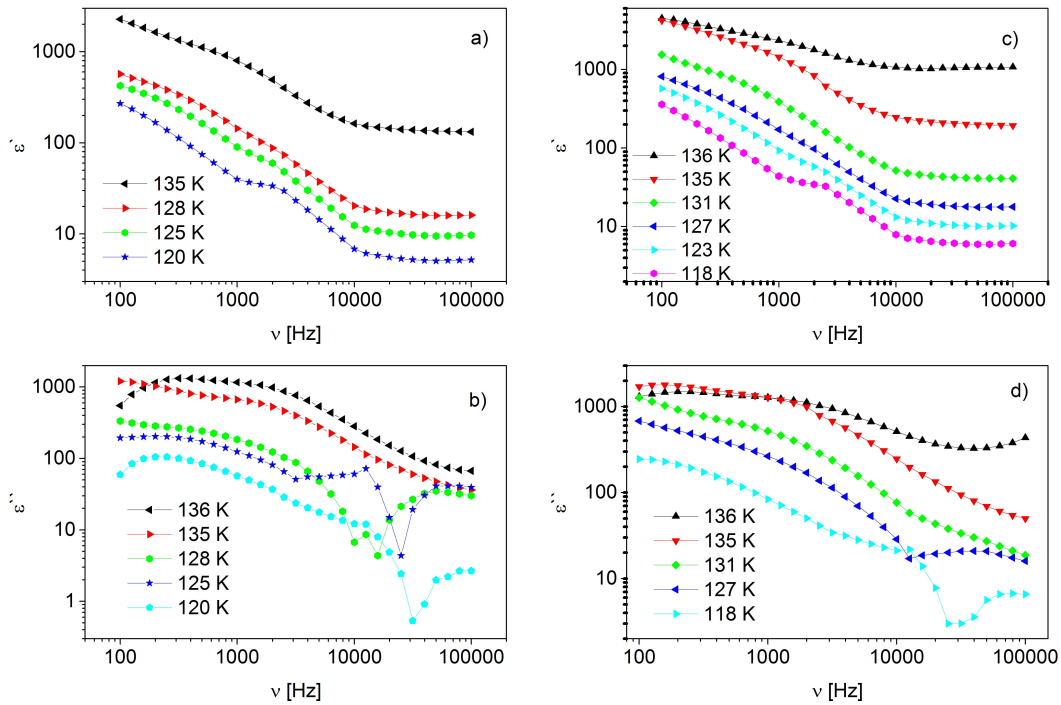


Fig. 4. Dispersion of the real and imaginary part of the dielectric permittivity in the ferroelectric phase of DMAGaS (a, b) and $\text{DMAGa}_{0.935}\text{Cr}_{0.065}\text{S}$ (c, d) crystals.

Figure 4 presents a comparison of the frequency dependences of ϵ' and ϵ'' for DMAGaS (a, b) and $\text{DMAGa}_{0.935}\text{Cr}_{0.065}\text{S}$ (c, d) crystals. The relaxation type dispersion associated with the motion of the domain walls similar to those in $\text{DMAAl}_{1-x}\text{Cr}_x\text{S}$ was found to be just below T_{c1} for both samples. Indeed, one can observe a step-like behaviour of the frequency dependence of ϵ' . At cooling, these steps shift to lower frequencies and be-

come lower in height. The frequency dependences of ϵ'' presented in a logarithmic scale (Fig. 4b) look as wide peaks shifting to the low-frequency region and becoming broader and lower at cooling. These data reflect a peculiar behaviour of the relaxation times whose distribution function is strongly temperature dependent. The considered dispersion in the measured frequency range disappears above T_{c1} . DMAAlS and deuterated (DMAAlSD)

crystals also were characterized by a similar behaviour [6]. Figure 4a, c clearly shows the two steps responsible for the two relaxation processes corresponding to the domain walls motion and fundamental ferroelectric dispersion. They are clearly separated by frequency at lower temperatures and overlap slightly below T_{c1} . Unfortunately, one can observe only a part of the first low-frequency step related to the domain walls motion since it was impossible to measure correctly the dielectric parameters at the frequencies lower than 100 Hz. This problem was connected with the manifestation of piezoelectric resonant phenomena and the harmonics of the electric net frequency 50 Hz.

It is necessary to note a very interesting feature characteristic of both compared crystals — the very sharp minima

on the temperature-frequency dependences of the dielectric loss tangent observed in the middle of the ferroelectric phase (Figs. 1b, d, Fig. 2b and Figs. 4 b, d). They reflect a very sharp transformation of the fundamental dispersion at higher frequencies into the dispersion connected with the domain walls dynamics. Such an abrupt change is explained by the fact that the same dipoles — DMA groups — are the basis of both types of dispersion. When the sample is cooled below T_{c1} , the arising polarization “dissolve” into the domains the clusters of DMA groups responsible for the critical slowing down of the relaxation process at the Curie point. It means that the domain dispersion arises “on account” of the fundamental ferroelectric one.

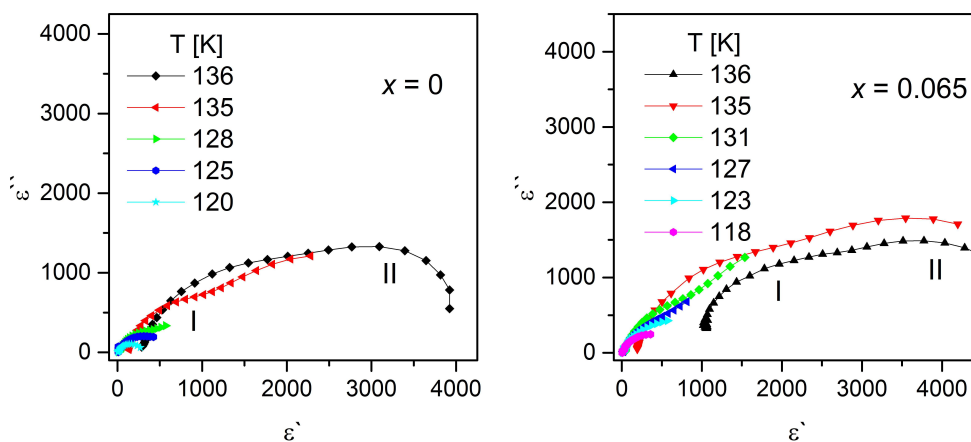


Fig. 5. The Cole–Cole diagrams for the ferroelectric phase of $\text{DMAGa}_{1-x}\text{Cr}_x\text{S}$ crystals obtained in the frequency range of $100 \text{ Hz} \div 1 \text{ MHz}$.

The analysis of the Cole–Cole diagrams provides additional information concerning the parameters and nature of the dielectric relaxation processes [14]. The corresponding diagrams for both initial and doped crystals are depicted in Fig. 5. In accordance with the above considerations, the diagrams obtained at temperatures 135 K and 136 K for both crystals are clearly divided into two parts: the part of distorted semicircle I, corresponding to the fundamental dielectric dispersion, and the low-frequency part II, connected with the domain walls dynamics. The relaxation process at higher frequencies (part I) is observed only in the vicinity of T_{c1} , since at the cooling of a sample below the Curie point, the corresponding relaxation time decreases due to the destruction of the correlated dipole clusters under the influence of growing polarization and a coercive field. At lower temperatures, one can observe only parts of a considerably distorted semicircle corresponding to the domain wall dynamics.

The phenomenological model, proposed by Kuramoto in [15] for the description of the complex dielectric permittivity, will be applied for the explanation of the domain wall dynamics in DMAGaS and

$\text{DMAGa}_{0.935}\text{Cr}_{0.065}\text{S}$ crystals. This model takes into account the normal distribution of the relaxation times and the activation energies of the relaxation process. The complex dielectric permittivity can be written in this case as [16]:

$$\varepsilon^*(\omega, t) = [\varepsilon_0(T) - \varepsilon_\infty(T)]\varepsilon_{\text{rel}}^*(\omega, t) + \varepsilon_\infty(T), \quad (3.2)$$

where ε_∞ and ε_0 are the values of the permittivity for the frequency of the measuring field tending to infinity and to zero respectively. The distribution $g(\tau, T)$ of the relaxation times τ has to be included into the relaxation part of the dielectric permittivity [6]:

$$\varepsilon_{\text{rel}}^*(\omega, t) = \int_0^\infty \frac{g(\tau, T)}{1 + i\omega\tau} \frac{d\tau}{\tau}. \quad (3.3)$$

The above mentioned normal distribution includes the temperature dependence of the relaxation time and the activation energies $f(E)$ of Vogel–Fulcher–Tammann (VFT) type and should be written as [6, 15]:

$$g(\tau, T) = \frac{T - T_0}{\sqrt{2\pi\sigma}} \exp \left\{ -\frac{[(T - T_0)(\ln \tau - \ln \tau_0) - E_0]^2}{2\sigma^2} \right\}, \quad (3.4)$$

where T_0 is the VFT temperature at which the relaxation time reaches infinity; τ_0 is the corresponding constant; σ is the half-width of the activation energy distribution.

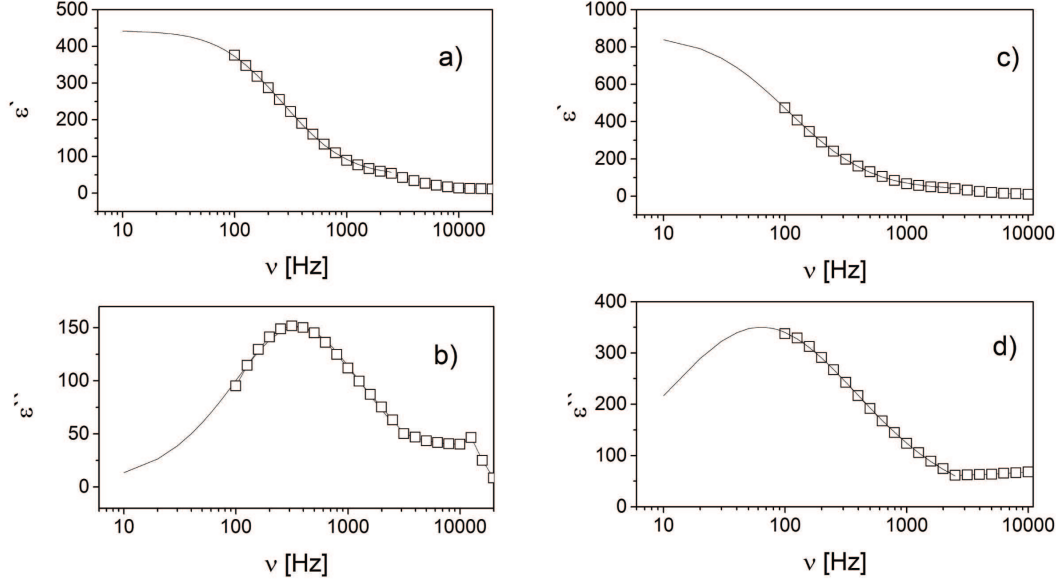


Fig. 6. Approximation of the frequency dependences of the real and imaginary parts of the dielectric permittivity using formulae (5-6) for DMAGaS crystal at $T = 125$ K (a and b respectively) and DMAGa_{0.935}Cr_{0.065}S crystal at $T = 121$ K (c and d). White square — experimental data, solid line — approximating curves.

On the basis of the abovementioned consideration, it is possible to obtain the relation for the complex permittivity, which could be found in [6, 15]. After the separation of the real and imaginary parts of this dielectric permittivity, we obtain the relations that could be used for the analytical description of the low frequency dielectric dispersion:

$$\varepsilon'(\omega, t) = \varepsilon_\infty(T) + B(T) \int_{-\infty}^{\infty} \frac{e^{-[C(T)x - D(T)]^2}}{1 + \omega^2 e^{2x}} dx, \quad (3.5)$$

$$\varepsilon''(\omega, t) = \omega B(T) \int_{-\infty}^{\infty} \frac{e^{-[C(T)x - D(T)]^2 + x}}{1 + \omega^2 e^{2x}} dx, \quad (3.6)$$

In these equations, the following designations were used:

$$B(T) = [\varepsilon_2(T) - \varepsilon_\infty(T)] \frac{T - T_0}{\sqrt{2\pi\sigma}}, \quad (3.7)$$

$$C(T) = \frac{T - T_0}{\sqrt{2\pi\sigma}}, \quad (3.8)$$

$$D(T) = \frac{(T - T_0) \ln \tau_0 + E_0}{\sqrt{2}\sigma}. \quad (3.9)$$

Using the described procedure and working out least-squares fits to the experimental data, one can obtain the important parameters for DMAGaS and DMAGa_{0.935}Cr_{0.065}S crystals such as the relaxation time at “infinite” temperature τ_0 , VFT temperature T_0 , mean value E_0 and variance σ for the distribution of activation energies (Table 2).

	σ , K	T_0 , K	τ_0 , s	E_0 , K
DMAGaS	9.1	100.4	$3.3 \cdot 10^{-6}$	216
DMAGa _{0.935} Cr _{0.065} S	23.5	76.8	$3.4 \cdot 10^{-5}$	332
DMAAIS*	10.3	116.0	$5.80 \cdot 10^{-7}$	62.8
DMAAl _{0.935} Cr _{0.065} S*	29.8	126.0	$1.07 \cdot 10^{-5}$	86.0
DMAAl _{0.8} Cr _{0.2} S*	23.5	113.1	$2.95 \cdot 10^{-5}$	98.4

Table 2. Parameters of the dielectric dispersion connected with motion of domain walls in DMAMe_{1-x}Cr_xS (Me = Al, Ga) crystals; data marked with * are taken from the paper [6].

The examples of the approximation of the real and imaginary parts of the dielectric permittivity using formulas (5) and (6) are depicted in Fig. 6 respectively — for

DMAGaS (a and b) and the crystal doped with chromium (c and d). The approximation curves (solid lines in Fig. 6) corresponding to a pure dielectric relaxation process connected with a domain walls dynamics fairly well coincide with the experimentally obtained frequency dependences for both crystals. Using the procedure of the

linear approximation of the parameters C and D temperature dependences, described in detail in [6], one can calculate the characteristic parameters of the domain walls dynamics for DMAGaS and DMAGa_{0.935}Cr_{0.065}S crystals (Table 2).

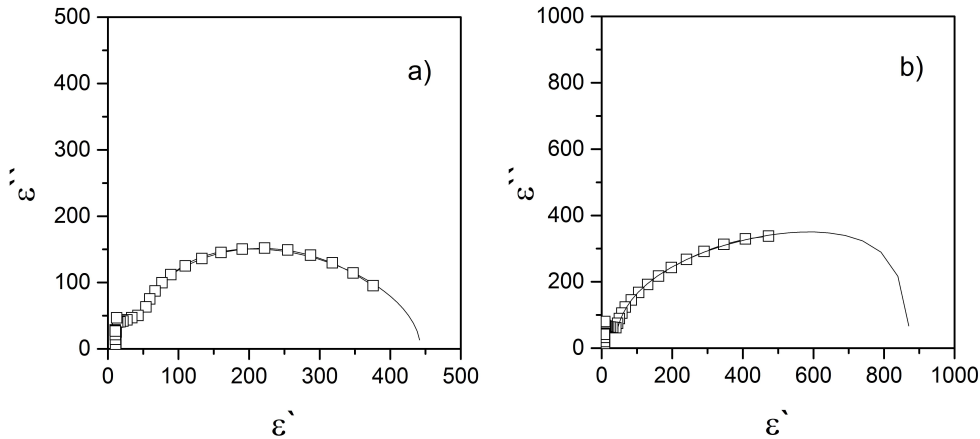


Fig. 7. The example of approximations of the Cole-Cole diagrams for DMAGaS crystal at $T = 125$ K (a) and DMAGa_{0.935}Cr_{0.065}S crystal at $T = 121$ K (b).

Using the above mentioned approach, one can obtain the approximation curves for the Cole-Cole diagrams corresponding to the pure dielectric relaxation process connected with the motion of domain walls (see Fig. 7 as an example). It is necessary to note that the experimental data and the approximation curves in Figs. 6 and 7 have to be self-consistent. These diagrams, similarly to the case of isostructural DMAAlS and DMAAl_{0.935}Cr_{0.065}S crystals, were found to be considerably asymmetric [6]. This fact confirms the adequacy of the suggestion concerning the distribution of the relaxation time and activation energies.

A comparison of the parameters of the dielectric relaxation process for DMAGa_{0.935}Cr_{0.065}S and DMAGaS crystals (see Table 2) shows that the solid solution with chromium is characterized by higher values of the relaxation time and activation energy and a wider distribution of the activation energy in comparison with DMAGaS crystals. This can be related to the fact that chromium ions, due to their larger sizes than gallium ions, can be considered as the sources of local lattice deformations, leading to the formation of more massive dipole clusters in the vicinity of the ferroelectric phase transition. This process is followed by an increase in the relaxation time and activation energy and a wider distribution of the activation energy. Besides, the temperature of the domain walls freezing decreases in the crystals doped with chromium. These results correlate well with the data presented in Fig. 2b. It is clearly seen that the metal ion substitution leads to the shift of the broad maxima characterizing the dispersion associated with the domain walls motion toward lower temperatures (the shaded region in Fig. 2b).

Comparing DMAGa_{1-x}Cr_xS and DMAAl_{1-x}Cr_xS, one can also note that the crystals with gallium are characterized by a more narrow distribution of the activation energies as well as the characteristic relaxation times. This result explains why these compounds are characterized by a sharper change of the dispersion type in the temperature-frequency dependences of $\tan \delta$ discussed above in comparison with the crystals with aluminium. In this respect, it is necessary to mention that the relaxation time of the fundamental dispersion $\tau = 2.17 \cdot 10^{-7}$ s determined for DMAGaS in [11] was found to be quite close to that characteristic of the domain dynamics (Table 2), which implies the observed tight coexistence of both types of dispersion in a very narrow frequency and temperature range.

IV. CONCLUSION

The effect of metal ion substitution on the phase transitions and dielectric dispersion in the frequency range of 100 Hz – 1 MHz in DMAGa_{1-x}Cr_xS crystals was investigated. It was shown that such a substitution practically doesn't affect the temperatures of both phase transitions limiting the ferroelectric phase, in contrast to the case of isostructural DMAAl_{1-x}Cr_xS crystals. This difference is explained by closer sizes of Cr³⁺ and Ga³⁺ ions contrary to the case of the Cr³⁺ and Al³⁺ pair.

On the basis of the performed investigations, one can conclude that DMAGa_{1-x}Cr_xS crystals in the ferroelectric phase are characterised by two types of dispersion – the fundamental ferroelectric one and the dispersion caused by the motion of domain walls. Besides, a high-

frequency Debye type dielectric relaxation was observed in the paraelectric phase. The low-frequency dispersion associated with the motion of the domain walls has been analysed in detail using the Kuramoto model [15].

It was established that the substitution of gallium for chromium substantially affects the parameters of the domain wall dynamics. In particular, it leads to an increase in the relaxation time, the activation energy and the half-width of the Gaussian, which describes the distribution

of the relaxation times. This was explained by the fact that chromium ions, due to their larger sizes in comparison with gallium ions, cause local lattice deformations. The latter promote formation of more massive dipole clusters in the vicinity of the ferroelectric phase transition. Besides, it has been found that the above mentioned metal ion substitution leads to a significant decrease of the temperature of the domain walls freezing.

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ВПЛИВ ЗАМІЩЕННЯ ЙОНА МЕТАЛУ НА ДІЕЛЕКТРИЧНУ ДИСПЕРСІЮ КРИСТАЛІВ $\text{NH}_2(\text{CH}_3)_2\text{Ga}_{1-x}\text{Cr}_x(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

В. Капустяник^{1,2}, С. Семак², Ю. Еліяшевський², С. Середя^{1,3}

¹ Науково-технічний і навчальний центр низькотемпературних досліджень, Львівський національний університет імені Івана Франка, вул. Драгоманова, 50, 79005, Львів

² Фізичний факультет, Львівський національний університет імені Івана Франка, вул. Драгоманова, 50, 79005, Львів

³ Науково-дослідницький центр Юліха, Інститут енергетики та кліматичних досліджень — Фізика плазми, 52425, Юліх, Німеччина

Досліджено дисперсію діелектричної проникності кристалів диметиламініметал сульфат гексагідрат $\text{NH}_2(\text{CH}_3)_2\text{Ga}_{1-x}\text{Cr}_x(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($x = 0; 0.065$) в околі сегнетоелектричного-сегнетоеластичного фазового переходу. На основі аналізу температурно-частотних залежностей діелектричної проникності та діаграм Коула-Коула зроблено висновок, що діелектрична дисперсія у високочастотному діапазоні зумовлена релаксацією диполів (фундаментальна дисперсія), а за нижчих частот — динамікою доменних стінок. Показано, що заміщення йона металу практично не впливає на температуру фазових переходів, але проявляється в параметрах низькочастотної діелектричної дисперсії. Заміщення галію на хром супроводжується збільшенням тривалості релаксації, енергії активації й півширини гаусіана, який описує розподіл часів релаксації. Це пояснюється тим, що йони хрому внаслідок їхніх більших розмірів порівняно з йонами галію викликають виникнення локальних деформацій кристалічної ґратки, які своєю чергою сприяють утворенню масивніших дипольних кластерів поблизу сегнетоелектричного фазового переходу.