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The ferroelectric and proton glass coexistence region in $K_{0.77}(NH_4)_{0.23}H_2AsO_4$ detected by complex permittivity measurements

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Abstract. This paper reports results of the studies on complex permittivity $\epsilon^* = \epsilon' - i\epsilon''$ in a mixed $K_{0.77}(NH_4)_{0.23}H_2AsO_4$ crystal. Measurements along the crystallographic a axis have clearly indicated the coexistence of the ferroelectric state and proton glass state in this crystal. The temperature dependence of ϵ'_a shows a maximum at $T_c = 61$ K, indicating a ferroelectric transition, while the dispersion of ϵ'_a and ϵ''_a below $T = 40$ K satisfies the Vogel-Fulcher equation with the parameters $T_0 = 8.3$ K, $E_c = 183.5$ K and $\nu_c = 1.65 \times 10^{11}$ Hz, which proves the presence of the proton glass state. Analysis of the shape of the temperature dependence of dielectric losses $\epsilon''_c(\nu, T)$ observed in the measurements along the ferroelectric c axis revealed the presence of another process of relaxation apart from that related to the freezing of ferroelectric domain wall motion known for KDP type crystals. The two relaxation processes are also described by the Vogel-Fulcher equation with the parameters $T_{01} = 34$ K, $E_{c1} = 7.7$ K and $\nu_{c1} = 6.8 \times 10^5$ Hz for one of them and for the other $T_{02} = 20.5$ K, $E_{c2} = 13.4$ K and $\nu_{c2} = 5.6 \times 10^6$ Hz. Our results prove the coexistence of the ferroelectric and proton glass states in the $K_{0.77}(NH_4)_{0.23}H_2AsO_4$ crystal, and the occurrence of different kinds of cluster of local ordering (proton glass and relaxor clusters) and ferroelectric domains.

1. Introduction

The proton glass state was discovered by Courtens [1] in 1982 in mixed $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) crystals, composed of ferroelectric RbH_2PO_4 (RDP) and antiferroelectric $NH_4H_2PO_4$ (ADP). The presence of this state, characterized by the disappearance of long-range order and the existence of short-range order within clusters [2], has also been shown for the isomorphous arsenate crystal $Rb_{1-x}(NH_4)_xH_2AsO_4$ (RADA) by Trybuła *et al* [3–6] and confirmed by other authors [7, 8]. The presence of this state was also reported for the deuterated forms DRADP [9, 10] and DRADA [11, 12]. Recently much attention has been paid to investigation of the coexistence of the glass and ordered states [6, 12], which is expected to contribute to explaining the phenomena leading to the formation of the proton glass state.

This work has been undertaken to study the region of coexistence of the ferroelectric state and proton glass state in a $K_{0.77}(NH_4)_{0.23}H_2AsO_4$ (KADA-23) crystal.

2. Experimental method

The crystal studied in this work was grown from an aqueous solution of KH_2AsO_4 (KDA) and $NH_4H_2AsO_4$ (ADA) in a 77/23 ratio, by the slow evaporation method. From this

monocrystal of $K_{0.77}(NH_4)_{0.23}H_2AsO_4$, the samples to be studied were cut out along the crystallographic a axis and along the ferroelectric c axis of the crystal. The size of the sample cut out along the a axis was $2.57 \times 8.52 \times 1.05$ mm, whereas the size of that cut along the c axis was $2.56 \times 2.81 \times 0.6$ mm. The polished surfaces of the samples were coated with graphite electrodes. The measurements of the complex permittivity $\epsilon^* = \epsilon' - i\epsilon''$ were performed between 3.4 K and 300 K in the Leybold He flow cryostat, with frequency varied from 200 Hz to 100 kHz using a *RLC* 1689M General Radio bridge and a 6425 Wayne Kerr analyser. The temperature of the studied samples was measured by a Lake Shore Cryotronic DT-500 Si diode thermometer.

3. Results

The temperature dependence of the real part of the permittivity ϵ'_a measured along the a axis is shown in figure 1. At ambient temperature the value of ϵ'_a was about 66. With decreasing temperature of the sample ϵ'_a monotonically increased. Figure 1(a) presents the temperature dependence of ϵ'_a in the range from 3.4 K to 120 K. At $T_c = 61$ K the real part of the permittivity reaches a clear maximum $\epsilon'_a = 152.7$, indicating a phase transition to the ferroelectric phase. For temperatures below 40 K, a dispersion of ϵ'_a characteristic of the proton glass state was observed for five different frequencies (figure 1(b)). Figure 2 presents the temperature dependence of ϵ'_c measured along the ferroelectric c axis. At 300 K $\epsilon'_c = 20$ and with decreasing temperature of the sample, as is the case of measurements along the a axis, ϵ'_c values increase following the Curie–Weiss law:

$$(\epsilon'_c - \epsilon'_{\infty})^{-1} = C^{-1}(T - T_{CW}) \quad (1)$$

where C is the Curie–Weiss constant and T_{CW} is the Curie–Weiss temperature. The values of these parameters were found to be $C = 2185.4$ K and $T_{CW} = 58.9$ K. Deviation from the Curie–Weiss law was observed at 67 K, whereas below 61 K dispersion of ϵ'_c began (figure 2(b)). The temperature dependence of the inverse of the real part of the permittivity, described by (1), is shown in figure 3. In figures 2(a) and 3 the Curie–Weiss dependence is marked with a solid line.

The temperature dependence of the imaginary part of the permittivity measured along the a axis, shown in figure 4 for a few frequencies, revealed below 40 K a dispersion characteristic for proton glass. These dependences were approximated by a Gaussian shape, according to the equation

$$\epsilon''_a(\nu, T) = A(\nu) \exp\{-[T - T_g(\nu)]^2/2\Delta^2\} \quad (2)$$

where $T_g(\nu)$ is the temperature at which ϵ''_a reaches a maximum value for a given frequency, and 2Δ is the width of the Gaussian curve. From the T_g values obtained in this way for all frequencies of the measuring electric field we could determine the Vogel–Fulcher dependence for this relaxation process:

$$\nu = \nu_c \exp(-E_c/(T_g - T_0)) \quad (3)$$

where T_0 is the Vogel–Fulcher temperature at which the system is completely frozen, E_c is the activation energy needed for reorientation of electric dipoles in a cluster, and ν_c is the cut-off frequency. The best fit was obtained for the following values of these parameters: $T_0 = 8.3$ K; $E_c = 183.5$ K; $\nu_c = 1.65 \times 10^{11}$ Hz. The Vogel–Fulcher

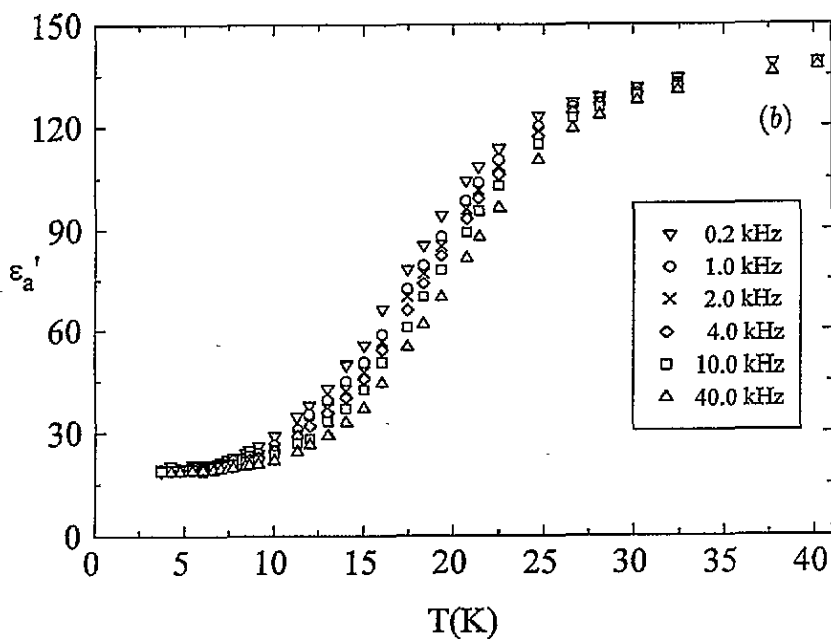
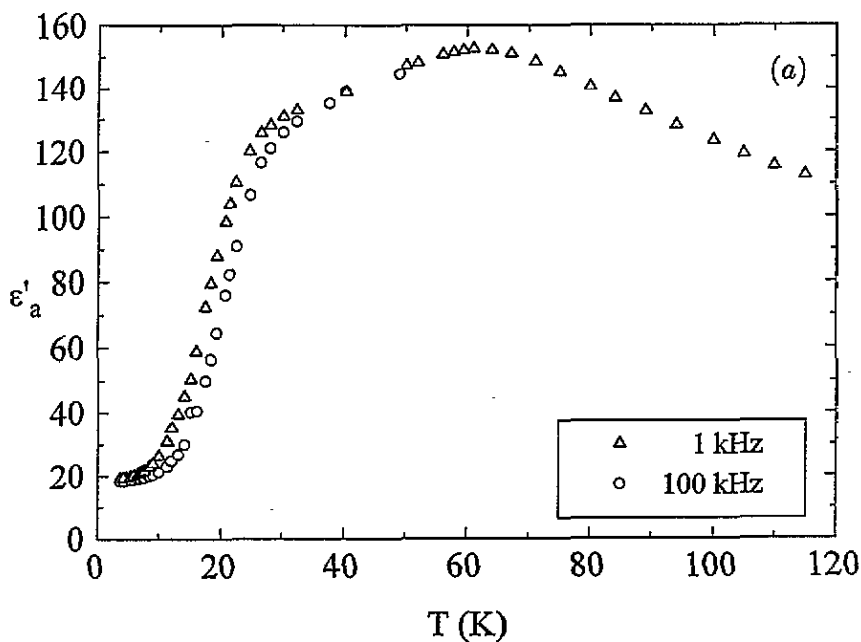


Figure 1. The temperature dependence of ϵ'_a for $K_{0.77}(NH_4)_{0.23}H_2AsO_4$: (a) $\epsilon'_a(T)$ in the temperature range from 3.4 K to 120 K; (b) the dispersion of ϵ'_a .

dependence for the measurements along the a axis is shown in figure 5. The character of the temperature dependence of ϵ''_c measured along the ferroelectric c axis is much more complex. Figure 6 presents the dependences for a few frequencies. Assuming a Gaussian

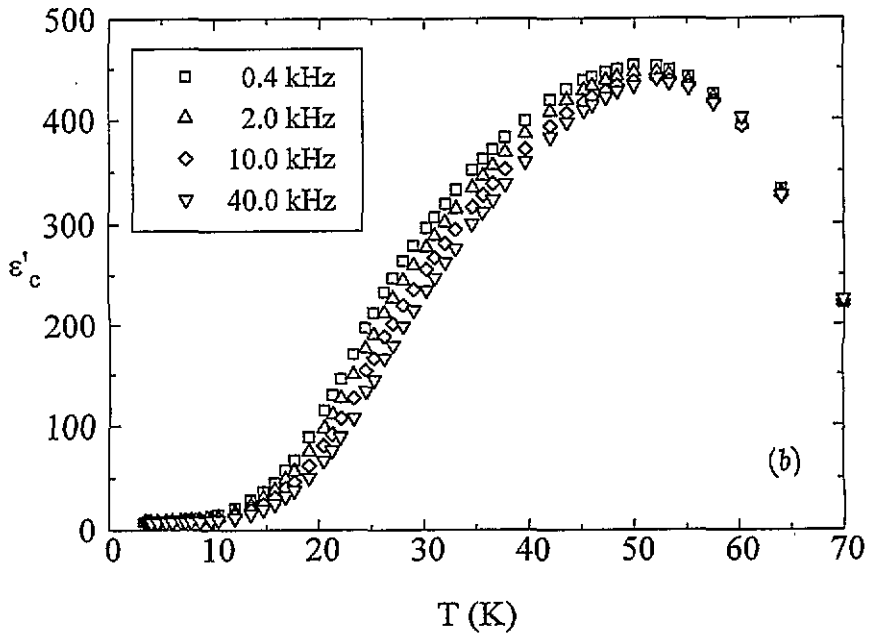
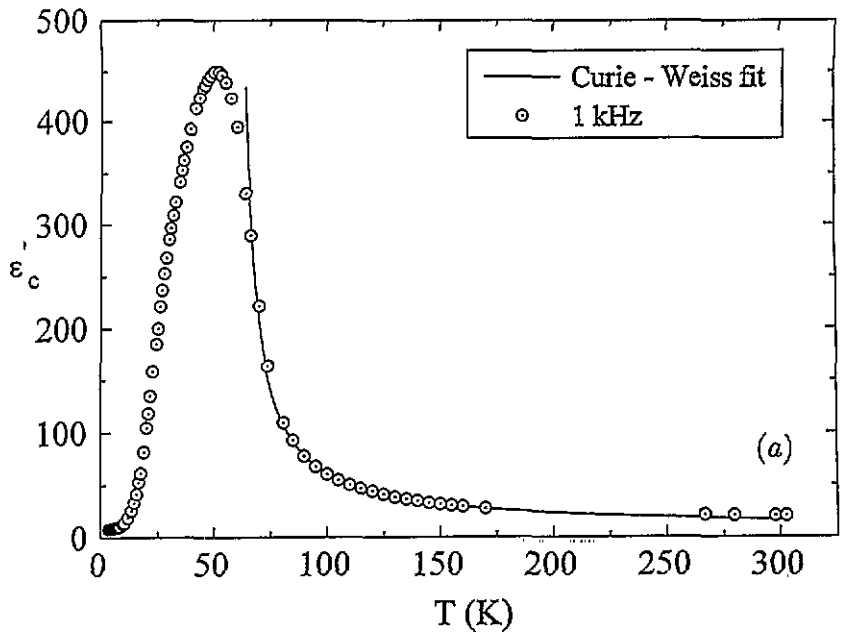


Figure 2. The temperature dependence of ϵ'_c for the measurements along the ferroelectric c axis for $K_{0.77}(\text{NH}_4)_{0.23}\text{H}_2\text{AsO}_4$: (a) $\epsilon'_c(T)$ for an electric field frequency of 1 kHz; (b) the dispersion of ϵ'_c in the temperature range from 10 K to 61 K.

shape of the temperature dependence of ϵ''_c and the existence of two relaxation mechanisms the experimental curve was approximated by the following equation (the solid lines in

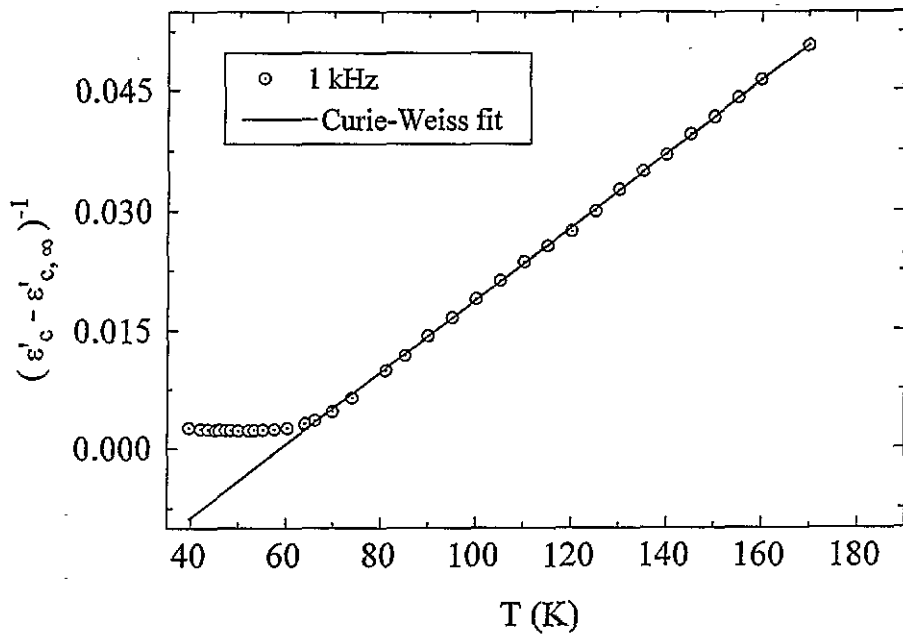


Figure 3. The Curie-Weiss dependence in $K_{0.77}(NH_4)_{0.23}H_2AsO_4$ for the measurements along the ferroelectric c axis.

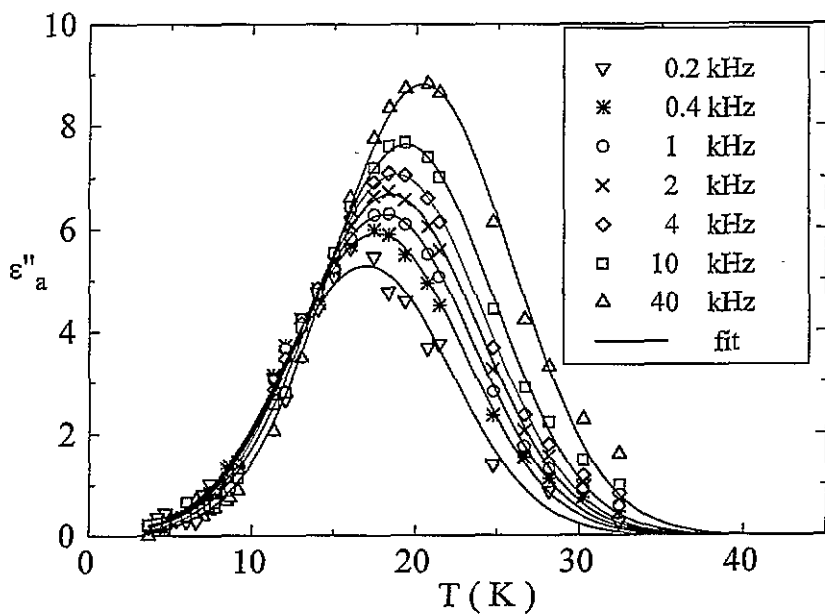


Figure 4. The temperature dependence of ϵ''_a in $K_{0.77}(NH_4)_{0.23}H_2AsO_4$ for a few frequencies of electric measuring field.

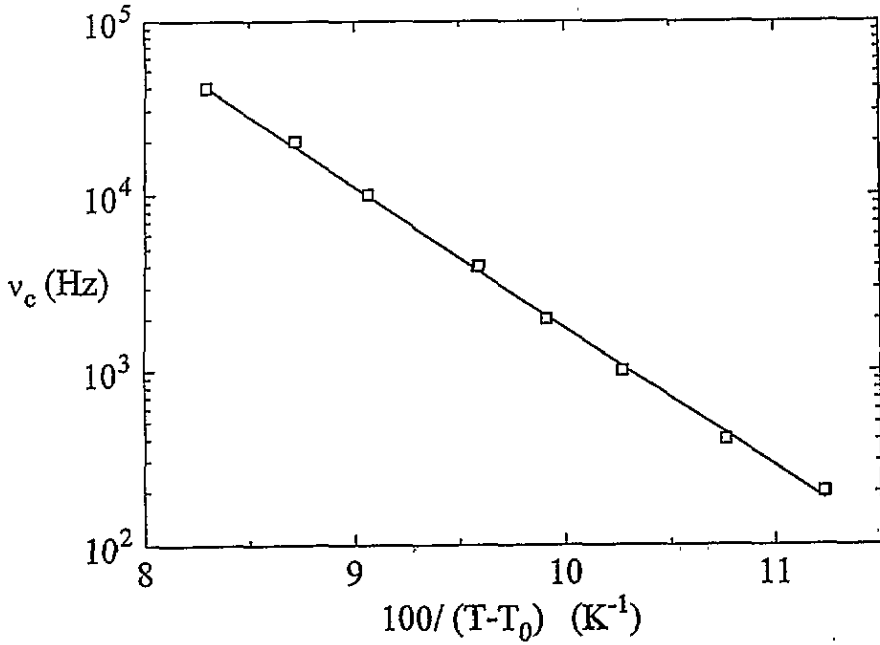


Figure 5. The Vogel-Fulcher dependence for the relaxation region along the a axis of $K_{0.77}(NH_4)_{0.23}H_2AsO_4$.

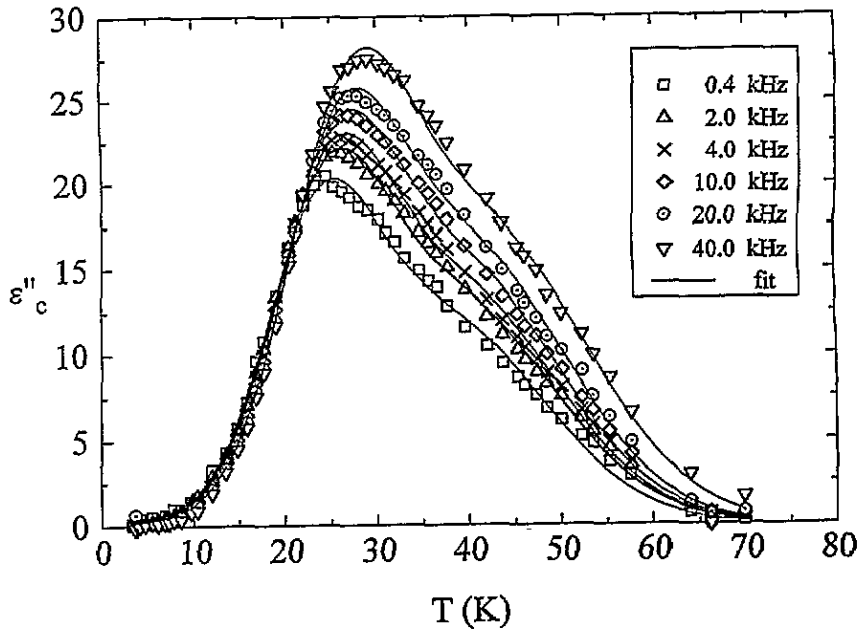


Figure 6. The temperature dependences of ϵ''_c along the ferroelectric c axis for a few frequencies of the electric measuring field in $K_{0.77}(NH_4)_{0.23}H_2AsO_4$.

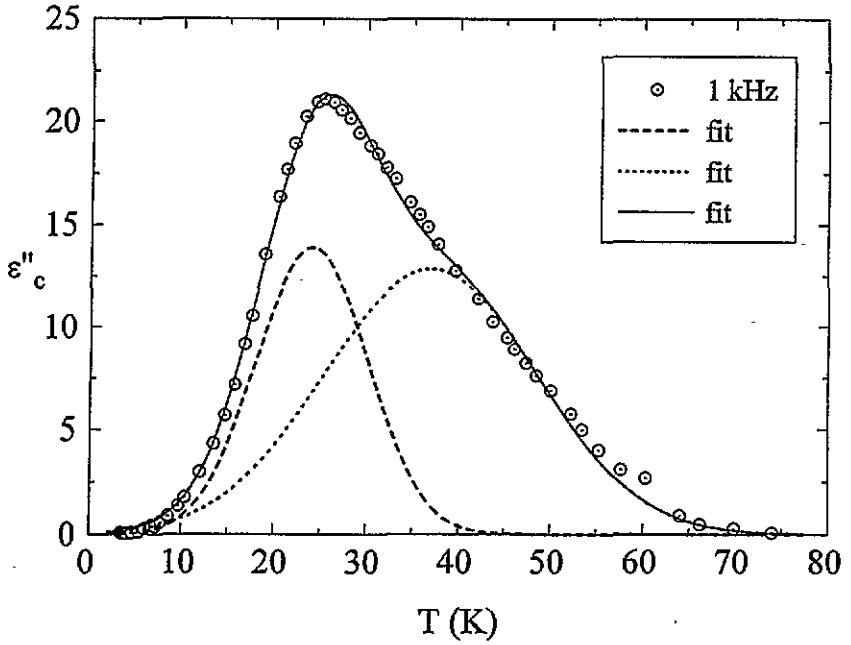


Figure 7. The fit of the experimental course of $\varepsilon''_c(T)$ for 1 kHz by (4). The sum of the courses marked by the broken and dotted lines gives the solid line course. The existence of two regions of relaxation is clearly visible.

figure 6):

$$\varepsilon''(T) = A[\exp[-(T - T_{gI})^2/2\Delta_I^2]] + B[\exp[-(T - T_{gII})^2/2\Delta_{II}^2]] \quad (4)$$

where A and B are the amplitudes of the Gaussian curves, $2\Delta_I$ and $2\Delta_{II}$ are their widths, and T_{gI} and T_{gII} are the temperatures at which ε''_c reaches a maximum. Figure 7 presents the course of the temperature dependence of ε''_c for a frequency of 1 kHz. The solid line represents the fit according to (4) while the dotted and the broken lines illustrate a decomposition of $\varepsilon''_c(T)$ into two Gaussian curves. For each of the studied frequencies we obtained a similar course of $\varepsilon''_c(T)$. The character of these courses indicates the existence of two different relaxation mechanisms, each described by a Vogel-Fulcher dependence. The relaxation occurring at higher temperatures (the dotted line in figure 7) is related to the freezing of the motion of ferroelectric domain walls and the best fit to (3) was obtained for the parameters $T_{01} = 34$ K, $E_{c1} = 7.7$ K and $\nu_{c1} = 6.8 \times 10^5$ Hz (figure 8). The other relaxation process (the broken line in figure 7) is also described by (3) but for different parameters: $T_{02} = 20.5$ K; $E_{c2} = 13.4$ K; $\nu_{c2} = 5.6 \times 10^6$ Hz (figure 9).

4. Discussion and conclusion

The results of temperature measurements of complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ in a mixed $K_{0.77}(NH_4)_{0.23}H_2AsO_4$ crystal along the a and the ferroelectric c axes prove the coexistence of the ferroelectric and the proton glass states in this crystal. This phenomenon has been also observed in RADA mixed crystals [6, 7]. In RADA [6] the coexistence on the ferroelectric

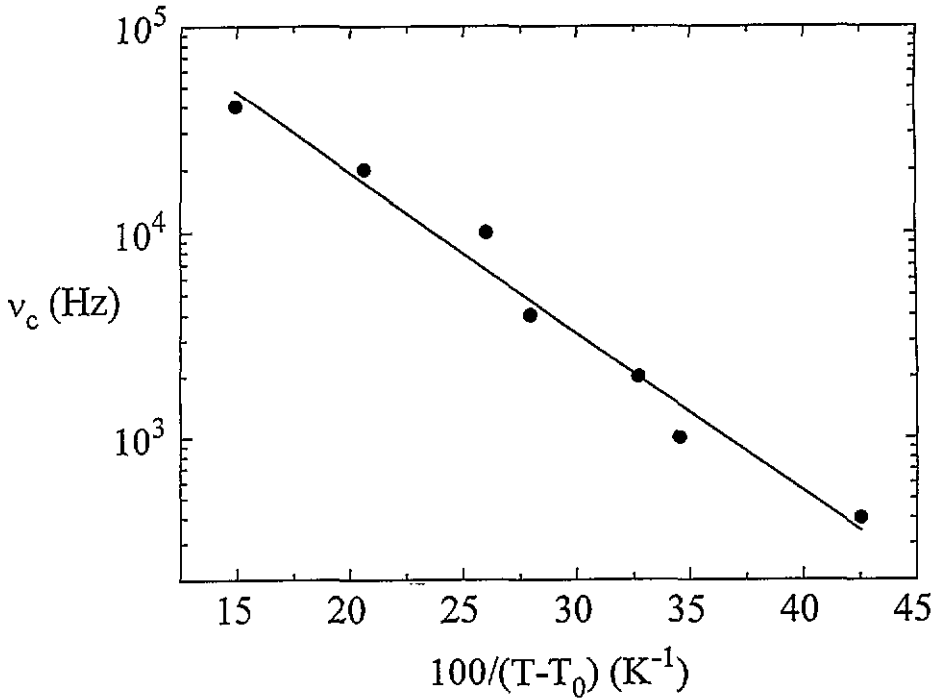


Figure 8. The Vogel-Fulcher dependence for the relaxation region marked by the dotted line in figure 7 for the measurements along the c axis of $K_{0.77}(NH_4)_{0.23}H_2AsO_4$.

side of the phase diagram ends for ammonium concentration $x \cong 0.15$, while for the studied KADA crystal the coexistence is clearly detected for $x = 0.23$. This suggests that the range of the glass state occurrence in KADA is narrower than for RADA.

The temperature dependences of the imaginary part of permittivity ϵ'' measured along the a and c axes are different. Analysis of the measurement along the a axis proved the presence of proton glass. The temperature dependence of $\epsilon''_a(T)$ was approximated by a Gaussian curve, which permitted determination of the parameters of the Vogel-Fulcher equation: $T_0 = 8.3$ K; $E_c = 183.5$ K; $\nu_c = 1.65 \times 10^{11}$ Hz. A comparison of these parameters with those obtained by Trybuła *et al* [13] for KADA with $x = 0.4$ ($T_0 = 5.4$ K; $E_c = 409$ K; $\nu_c = 2.5 \times 10^{13}$ Hz) shows that in KADA with $x = 0.23$ the clusters are greater than for KADA with $x = 0.4$, as expected, because KADA-23 has coexistence of ferroelectric and proton glass phases while KADA-40 only exhibits the proton glass phase.

Analysis of the temperature course of dielectric loss $\epsilon''_c(\nu, T)$ observed in measurements along the ferroelectric c axis revealed the presence of another process of relaxation different from that related to the freezing of ferroelectric domains. The two processes of relaxation are described by the Vogel-Fulcher equation but with different parameters: $T_{01} = 34$ K; $E_{c1} = 7.7$ K; $\nu_{c1} = 6.8 \times 10^5$ Hz and $T_{02} = 20.5$ K; $E_{c2} = 13.4$ K; $\nu_{c2} = 45.6 \times 10^6$ Hz. As these parameters are significantly different from those obtained from the measurements along the a axis, we have concluded that there are three different relaxation regions corresponding to clusters of different size: from the smallest ones (proton glass with parameters $T_0 = 8.3$ K, $E_c = 183.5$ K, $\nu_c = 1.65 \times 10^{11}$ Hz) through 'relaxor' for the parameters $T_{02} = 20.5$ K, $E_{c2} = 13.4$ K, $\nu_{c2} = 5.6 \times 10^6$ Hz to ferroelectric domains ($T_{01} = 34$ K; $E_{c1} = 7.7$ K; $\nu_{c1} = 6.8 \times 10^5$ Hz). The larger the cluster the lower the frequency of dipole reorientation in

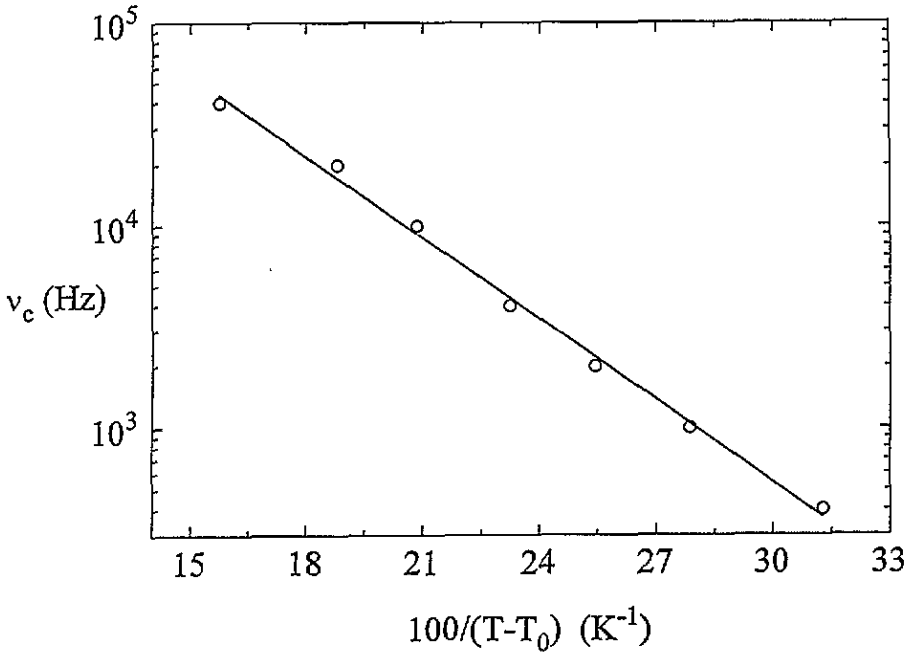


Figure 9. The Vogel-Fulcher dependence for the relaxation region marked by the broken line in figure 7 for the measurements along the c axis of $\text{K}_{0.77}(\text{NH}_4)_{0.23}\text{H}_2\text{AsO}_4$.

the cluster, the lower the activation energy of the process and the higher the Vogel-Fulcher temperature T_0 at which the dipoles are completely frozen in the cluster. A similar effect of the occurrence of two different relaxation mechanisms has been recently observed in deuterated DRADA, $x = 0.39, 0.46$ [12, 14] in the region of coexistence of the antiferroelectric and proton glass states.

In conclusion we can say that our measurements of complex permittivity $\epsilon^* = \epsilon' - i\epsilon''$ in a mixed $\text{K}_{0.77}(\text{NH}_4)_{0.23}\text{H}_2\text{AsO}_4$ crystal along the a and c axes prove the coexistence of the ferroelectric and the proton glass state in the crystal, and the occurrence of different kinds of cluster of local ordering (proton glass and relaxor clusters) and ferroelectric domains.

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