# Dielectric anomalies above the glass transition in the mixed K1-x(NH4)xH2PO4 crystals

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# DIELECTRIC ANOMALIES ABOVE THE GLASS TRANSITION IN THE MIXED $K_{1-x}(NH_4)_xH_2PO_4$ CRYSTALS

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Abstract The temperature dependences of the complex dielectric constant have been measured in the mixed $K_{1-x}(NH_4)_xH_2PO_4$ crystals at frequencies 10Hz-100kHz. For ammonium concentrations $0.3 \leq x \leq 0.6$ pronounced dielectric anomalies in c-direction has been detected in the temperature range 200-260K. It was found that in this temperature range the dielectric relaxation dispersion is changed dramatically.

## INTRODUCTION

In the last years experimental studies of the mixed $K_{1-x}(NH_4)_xH_2PO_4$ (KADP) crystals have been done[1-5] to found the glass properties similar to those observed in $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) and other mixed crystals[6-8]. The results of these investigations point out that mixed KADP crystals exhibit a proton glass behavior for $0.23 \lesssim x \lesssim 0.6$[3,5]. The analysis of the dielectric data given in the literature usually refers to the low-temperature region (T <200K). However the recent dielectric measurements of the KADP (x=0.6) showed the pronounced anomalies of the temperature dependences of the complex dielectric constant $\varepsilon_c' + i\varepsilon_c''$ near 240K except the low-temperature anomalies at the glass transition $T_g$=23K[6,7].

In the present paper in order to clarify the general features of the high-temperature anomalies in the mixed KADP crystals we measured the temperature dependences of $\varepsilon_c' + i\varepsilon_c''$ for the compositions with x=0.3, 0.5, 0.6 and 1.0 in the temperature range 100-400K.

## THE EXPERIMENTAL

The KADP single crystals investigated in this study were grown by slow cooling of the aqueous solutions with ammonium concentrations X=0,5, 0,6, 0,65 and 1,0. The ammonium concentrations in crystals x determinated from the relationship between X and x [3] and x is 0,3, 0,5, 0,6 and 1,0 respectively.

The experiments were performed on the plates 0,7 x x 0,7 x 0,08 $cm^3$ of the c-cut. The conducting silver paint was used as electrodes. The sample was inserted into vacuum (dry air) cryostat and temperature was controlled by copper-constantan thermocouple. The complex dielectric constant $\varepsilon_c' + i\varepsilon_c''$ have been measured by Ando Electric TR - 10C and General Electric 1616 bridges in frequency range 10Hz - 100kHz.

## RESULTS AND DISCUSSION

The temperature dependencies of $\varepsilon_c'$ are shown in Fig.1,2, for the different ammonium concentrations and some charecteristic frequencies. For high frequencies ($\nu \geqslant 10kHz$) the pure ADP shows the apparent Curie - Weiss behavior from the phase transition temperature up to 370K. The Curie constant C is $7 \cdot 10^3$K. The frequency dispersion which occurs at T 310K, leads to the deviation of the low-frequency dielectric constant from a Curie-Weiss law (Fig.1). The $\varepsilon_c'(T)$ dependences of the mixed KADP crystals have the same general behavior and obey the Curie-Weiss law only below 220K. The values of C are $(4.8 + 5.2)\ 10^3$K for different compositions. The strong dielectric dispersion occurs just above 220K. Furthemore, on cooling the inverse dielectric constant $1/\varepsilon_c'$ shows the broad minimum near $T_m$=240K for KADP (x=0,5, x=0,6) and near $T_m$=250K for KADP (x=0,3) (Fig.1,2). On heating the observed dielectric anomalies are more pronounced that on cooling and are shifted to the high

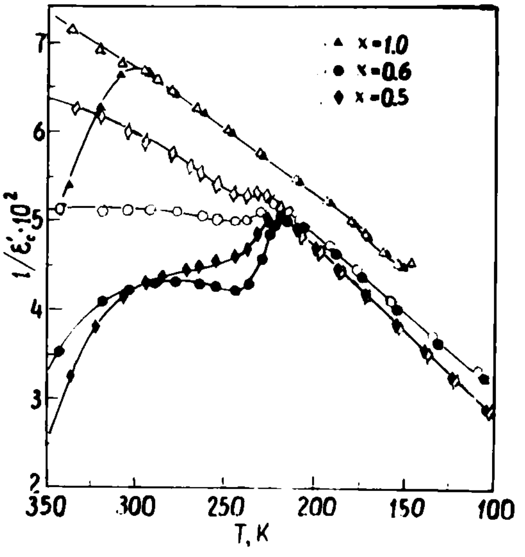


FIGURE 1 The temperature dependences of the inverse dielectric constant for mixed KADP crystals. The open symbols correspond to the frequency 10kHz, the closed symbols correspond to the frequency 30Hz.

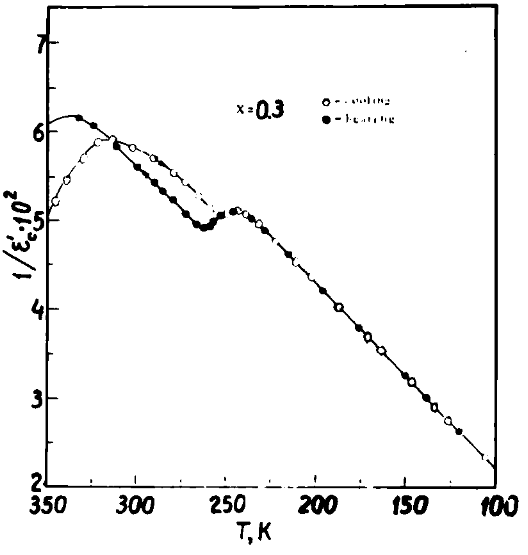


FIGURE 2 The temperature dependences of the inverse dielectric constant for KADP (x=0,3) at the frequency 30Hz.

temperatures (Fig.2). The amplitude of these anomalies decreases with increasing the frequency.

For sufficiently high temperatures the dielectric data can be analysed in the terms of Cole-Cole plots (Fig.3,4). In these figures the dielectric loss $\mathcal{E}_c''$ was determined as

$$\mathcal{E}_c''(\nu,T) = \frac{\sigma(\nu,T) - \sigma_{dc}(T)}{2\pi\nu} \qquad (1)$$

where $\sigma_{dc}$ is dc conductivity. At $T \geqslant 250K$ the mixed crystals show two well separated relaxation modes. The low-frequency mode is related to dc conductivity[4]. Figure 3 demonstrates the decreasing of the relaxation intensity of this mode when dc conductivity as grown KADP (x=0,6) decreased about 30 % after annealing. It should be noted that in our frequency window the low--frequency dispersion process disappears at $T > T_m$.

The high frequency relaxation mode is observed for the mixed crystals only. At $T > T_m$ this mode is characterised by a broad distribution of the relaxation times and can be described by the Cole-Cole equation

$$\mathcal{E}_c' + i\mathcal{E}_c'' = \mathcal{E}_\infty + \frac{\mathcal{E}_0^c - \mathcal{E}_\infty^c}{(1 + i2\pi\nu\tau)^{1-\alpha}} \qquad (2)$$

where does not depend practically on temperature (Fig. 3) up to $T \simeq T_m$.

In the vicinity of $T_m$ the relaxation dispersion is changed dramatically and below $T_m$ can be described by the equation

$$\mathcal{E}_c' + i\mathcal{E}_c'' = \mathcal{E}_\infty + \mathcal{E}''(i\omega\tau)^\gamma \qquad (3)$$

where $\gamma \approx 0,6$. The high frequency relaxation is sensitive to the sample history. Figure 4 shows irreversible decreasing of the relaxation intensity after heating and cooling of the "virgin" sample. This fact suggests a close analogy of KADP with real glasses.

Summarizing these results we can tentatively relate the anomalous dielectric behavior of the mixed KADP

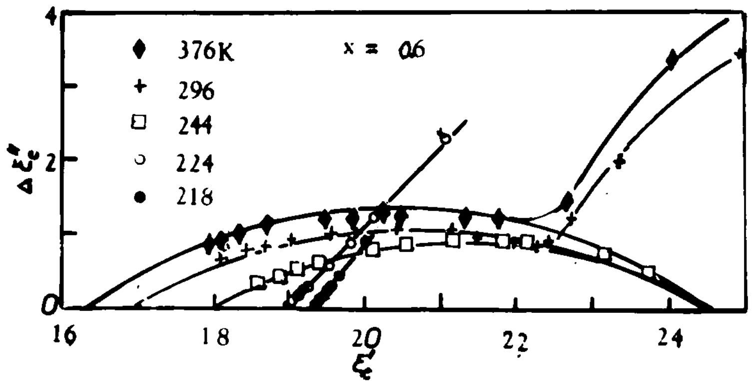


FIGURE 3 Cole-Cole representation of the complex dielectric constant for KADP (x=0,6) at different temperatures.

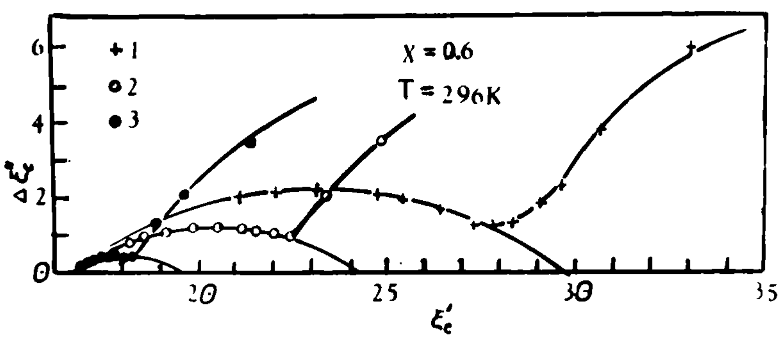


FIGURE 4 Cole-Cole representation of the complex dielectric constant for KADP (x=0,6) at room temperature 1-the "virgin" sample; 2-after the heating of the "virgin" sample; 3-after three cooling cycles.

crystals with rearrangement and orientational freezing of $NH_4$ groups at $T \leqslant T_m$.

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