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Origin of low-frequency dielectric dispersion in KH_2PO_4 and RbH_2PO_4 ferroelectric crystals

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We have measured the low-frequency dielectric dispersions in KH_2PO_4 and RbH_2PO_4 crystals. In the paraelectric phase both crystals were observed to be free of dielectric dispersion in the low-frequency region concerned. However, both of them exhibited the low-frequency dielectric dispersion in the ferroelectric phase. Our study of the temperature-dependent dielectric relaxation in the ferroelectric phase supports that the major part of the low-frequency dielectric dispersion observed should be originated from the domain wall relaxations rather than the heat diffusion central peak of recent reports. [S0163-1829(99)04221-6]

I. INTRODUCTION

Low-frequency dynamics of the central peak in the ferroelectric crystals was a great concern of many research workers.[1–4] The central peak anomaly has origins from both intrinsic effects of phase transition dynamics and extrinsic effects associated with defects.

Very recently Chaves *et al.*[5] and Araujo *et al.*[6] reported their low-frequency dielectric dispersion as due to the heat diffusion central peak. Fally, Schranz, and Havlik[7] applied a phenomenological Landau theory to this heat diffusion central peak problem and predicted the possible temperature dependence of the low-frequency dielectric dispersion due to the heat diffusion central peak in the ferroelectric KH_2PO_4 (KDP) crystal. This possibility of the central peak study by use of low-frequency dielectric measurements should be well received as the most convenient and precise experimental study of the central peak dynamics in the ferroelectric crystals in parallel with the low-frequency elastic constant measurements of the central peak dispersion in the ferroelastic crystals.[8–12]

However, in the KH_2PO_4 crystal undergoing the ferroelectric phase transition at $T_C = 123$ K the domain wall mobility remains very large until temperature is lowered to 90 K, when we observe domain wall freezing and dielectric dispersion.[13,14] Paul, Albers, and Muser[15] observed the low-frequency dielectric dispersions in the KH_2PO_4 crystal at $T = 123$ and 90 K, which was attributed to the domain wall motion. We presented a Comment[16] that the low-frequency dielectric dispersions in the KH_2PO_4 crystal should be attributed to the domain wall freezing in accordance with Paul, Albers, and Muser.[15] Since the same claims of the heat diffusion central peak for the KH_2PO_4 crystal are more recent[6] than our Comment[16] we want to present our full data of experimental measurements on the low-frequency dielectric dispersion in both KH_2PO_4 and RbH_2PO_4 (RDP) crystals and provide more clear evidence for our claim that the observations do not agree with the theoretical predictions of the heat diffusion central peak contribution to the dielectric susceptibility[7] arguing that the low-frequency dielectric dispersions observed are not from the heat diffusion central peak contribution but from the domain wall contributions.[15,16]

II. HEAT DIFFUSION CENTRAL PEAK AND DOMAIN WALL MOTION

We want to pinpoint the difference in the temperature dependence of the low-frequency dielectric dispersion between the two cases of the central peak dispersion and the domain wall relaxation. Adiabatic susceptibility ϵ_{ij}^S and isothermal susceptibility ϵ_{ij}^T are related by the following thermodynamic equations:[5,17]

$$\epsilon_{ij}^S = \left(\frac{\partial D_i}{\partial E_j}\right)_S = \left(\frac{\partial D_i}{\partial E_j}\right)_T + \left(\frac{\partial D_i}{\partial T}\right)_E \left(\frac{\partial T}{\partial E_j}\right)_S$$

$$= \epsilon_{ij}^T + \left(\frac{\partial D_i}{\partial T}\right)_E \left(\frac{\partial T}{\partial E_j}\right)_S , \tag{1}$$

since we have

$$\left(\frac{\partial S}{\partial T}\right)_E = \frac{C^E}{T}, \tag{2}$$

$$\left(\frac{\partial D_i}{\partial T}\right)_E = p_i^E , \tag{3}$$

where C^E stands for specific heat and p^E pyroelectric coefficient.

We obtain

$$\epsilon_{ij}^S - \epsilon_{ij}^T = -\frac{(p_i^E)^2 T}{C^E}. \tag{4}$$

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Experimental conditions lead to the approximations that ϵ_{ij}^T corresponds to the low-frequency limit below the domain wall relaxation frequency while ϵ_{ij}^S corresponds to the high-frequency limit well above the domain wall relaxation frequency.[17]

In general we can write

$$\epsilon_{ij}(\omega)=\epsilon_{ij}^S+(\epsilon_{ij}^T-\epsilon_{ij}^S)Y(\omega), \tag{5}$$

where $Y(\omega)$, the response function, represents the dispersion. For a Debye relaxor we obtain[17]

$$Y_D(\omega)=\frac{1}{1+i\omega\tau}. \tag{6}$$

Chaves *et al.*[5] obtained for a system in contact with a heat bath

$$Y_C(\omega)=\left[\frac{1-\exp[-(1-i)\sqrt{\xi}]}{(1-i)\sqrt{\xi}}\right], \tag{7}$$

where $\xi=(\omega l^2/2D)$ and $D=\kappa/C^E$ thermal diffusivity.

Fally, Schranz, and Havlik[7] elaborated the theory in terms of a more general Landau free energy density and heat diffusion equation to derive

$$Y_F(\omega)=\frac{(1-i)[\Psi^+(\xi)-\Psi^-(\xi)]}{\pi\sqrt{\xi}}, \tag{8}$$

where

$$\Psi^{\pm}=\Psi\left[\frac{1}{2}\left(1\pm\frac{1+i}{\pi}\sqrt{\xi}\right)\right], \tag{9}$$

$$\Psi(z)=\frac{1}{F(z)}\frac{dF(z)}{dz}, \tag{10}$$

$$F(z)=\frac{d}{dz}\ln(z!). \tag{11}$$

From Eqs. (4) and (5) we can see that the heat diffusion central peak has a temperature dependence determined by those of heat capacity C^E and pyroelectric coefficient p^E. The dielectric strength $\Delta\epsilon$ will increase with increasing p^E and the characteristic response time τ will be divergent as temperature approaches the transition temperature T_c^-. That is, the relevant temperature of the central peak anomaly is $T_c^-=123$ K in KDP.

On the other hand, the domain wall freezing occurs at $T_f^+\simeq 90$ K, when the relaxation time tends to infinity. The dielectric strength $\Delta\epsilon$ in the case of the heat diffusion central peak will increase with increasing p^E as temperature approaches T_c^- but it will decrease in the case of the domain wall motion with decreasing domain wall mobility as temperature approaches T_f^+. We can thus make a distinction between the central peak dielectric anomaly and the domain wall dielectric contributions by observing the temperature dependence of the low-frequency dielectric dispersions.

III. EXPERIMENT

Both KH_2PO_4 and RbH_2PO_4 were recrystalized twice before making the saturated solutions in the deionized distilled water at 30 °C. The single crystals grown from the aqueous saturated solution were cut for the *c*-axis plate and vacuum deposition of aluminum electrodes was made in the thin film coating chamber. Our samples have the same dimensions of the previous report[16] as 7 mm×6 mm×1 mm for KDP and 6 mm×4 mm×0.9 mm for RDP, respectively. Sample temperature was controlled in the closed cycle helium refrigerator (APD, Displex) by use of a silicon diode sensor and a temperature control system (Lake Shore, 330). Temperature stability better than ±0.02 K for over one hour was required since it took one hour for the low-frequency dielectric measurement at one fixed temperature and a slight change in temperature caused a large change of dielectric constant in the neighborhood of the ferroelectric transition. It required the use of a diffusion pump with the helium refrigerator for better vacuum and better temperature stability. In the low frequency region (10 mHz–100 kHz) a capacitance bridge method was used employing the digital lock-in amplifier (EG&G, DSP 7260) with the standard capacitor (MultiCap) of value 1.0 μF as determined by the sample capacitance of about 1 nF in the temperature region concerned.

The internal oscillator of the lock-in amplifier supplies a sine wave signal of $1\,V_{\rm rms}$ across the sample and the standard capacitor in series. The output signal is derived from the standard capacitor and fed into the differential input of the lock-in the amplifier,

$$V_{\rm out}^*=\frac{C_{\rm sample}^*}{(C_{\rm standard}+C_{\rm sample}^*)}V_{\rm in}, \tag{12}$$

where $V_{\rm in}$ stands for the input voltage, $V_{\rm out}^*$ the signal detection at the lock-in amplifier, $C_{\rm sample}^*$ proportional to the dielectric constant of the sample, and $C_{\rm standard}$ capacitance of the standard capacitor. We obtain $V_{\rm out}\simeq 1.0$ mV for the case of $C_{\rm sample}\simeq 1.0$ nF near the ferroelectric transition temperature and expect $V_{\rm out}\simeq 10$ μV at temperatures far from the transition temperature with $C_{\rm standard}\simeq 1.0$ μF. The lock-in amplifier time constant is set nominally at $1/2\pi f_c$ where f_c is given by the -3 dB frequency of the low pass filter. For example, when we want to measure signals at 1 Hz, we expect an ideal case harmonic noise at 2 Hz so that we may take $1/2\pi f_c\simeq 200$ msec for the time constant and choose the gain slope at 24 dB/oct to obtain clean data of a good signal to noise ratio. However, in the real situations of many other noises depending on the experimental environments we have to set the time constant on the trial and error basis. Furthermore, with the RC type filter we need the equilibration time as long as about 5 times the time constant to obtain the saturated stable value of signal output. Our experience suggests a time constant of 100 sec for the DSP lock-in detection of signals at 10 mHz. Chaves and co-workers[5,6] used both oscilloscope and lock-in amplifier to measure the dielectric constants of KH_2PO_4 crystal where the imaginary part $\epsilon''(\omega)$ was missing. Our digital signal processing (DSP) lock-in amplifier system should be much better in phase sensitivity so that the superior precision measurement of ours

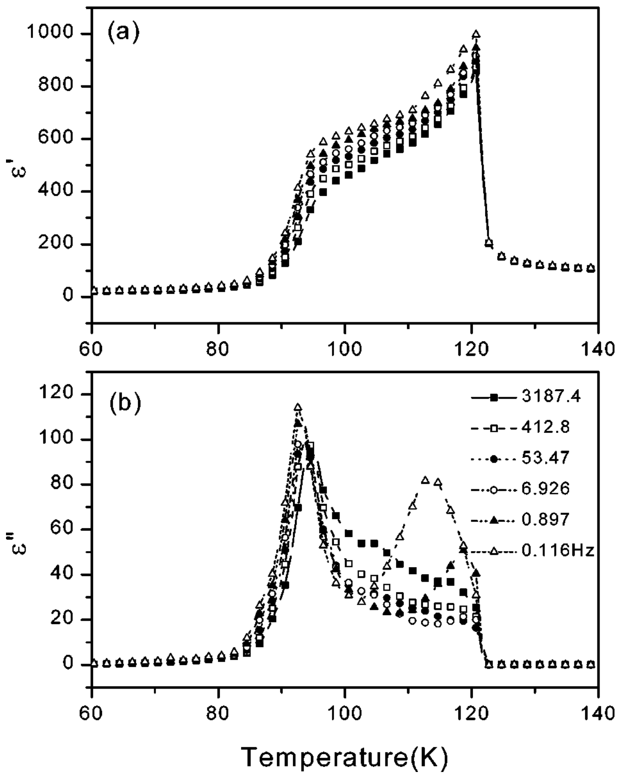

FIG. 1. (a) Re(ϵ') and (b) Im(ϵ'') parts of dielectric constant in the KH_2PO_4 crystal measured as a function of temperature at several selected frequencies. Frequency notations are the same for both (a) real and (b) imaginary parts.

made it possible to obtain the very small imaginary part $\epsilon''(\omega)$ as well as the real part $\epsilon'(\omega)$ in the KH_2PO_4 crystal.

IV. RESULTS AND DISCUSSION

In Fig. 1 we have shown the temperature-dependent dielectric constants at several probe frequencies in the temperature range of 140 to 60 K. The peak at 123 K represents the ferroelectric transition of KDP crystal and the plateau shoulder in the ferroelectric phase represents the large domain wall contribution to the dielectric constant. The rapid drop of the dielectric constant ϵ' with decreasing temperature below 90 K corresponds to the domain wall freezing. Dielectric dispersion can be seen to appear only after the ferroelectric transition, where the real part ϵ' is observed to increase with decreasing probe frequency in the low-frequency region of our measurement. The imaginary part ϵ'' shows a peak of domain wall freezing with lower peak temperatures at lower frequencies. At very low frequencies of 0.897 and 0.116 Hz another broad peak of ϵ'' below $T_c^- \simeq 123$ K is observed, where the peak temperature at 0.116 Hz is lower, that is, further away from T_c, than the peak temperature at 0.897 Hz.

When different relaxations are overlapping with each other the dielectric dispersions are more easily observable in the imaginary part as distinct peaks whereas the overlapping plateaus of real part dispersions in the Debye type relaxation system make it difficult to distinguish between different components. We therefore measured both the real part ϵ' and the imaginary part ϵ'' to study more details of the dielectric

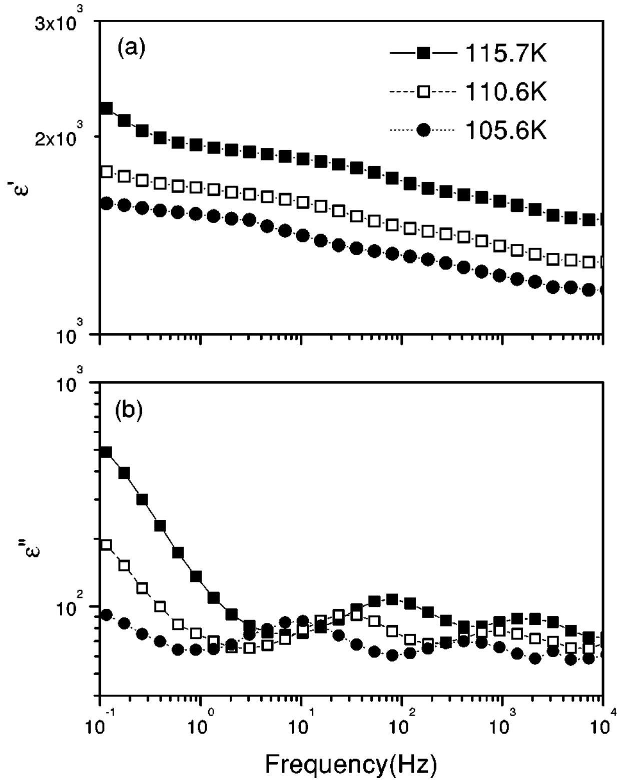

FIG. 2. (a) Re(ϵ') and (b) Im(ϵ'') parts of dielectric constant dependence on frequency in KH_2PO_4 crystal measured at three different temperatures.

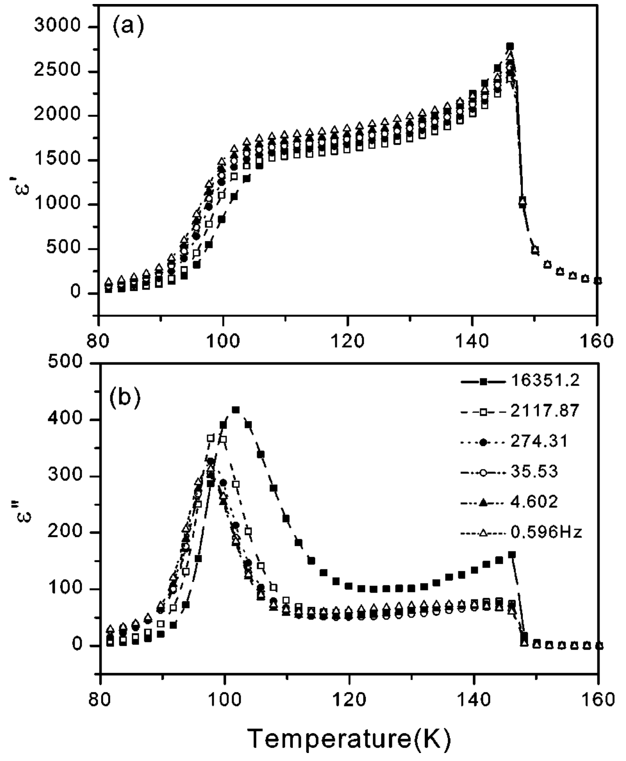

FIG. 3. (a) Re(ϵ') and (b) Im(ϵ'') parts of dielectric constant in the RbH_2PO_4 crystal measured as a function of temperature at several selected frequencies.

dispersion in KDP crystal as shown in Fig. 2 where the frequency dependence of ϵ'' in the low-frequency region was depicted at three different temperatures. Thus the low-frequency dielectric dispersion of KDP crystal should have at least three distinctive components[15,16] in contrast to the single dispersion assumption,[5,6] where they failed to distinguish between three components of their real part ϵ' data. This dielectric dispersion curve composed of three components cannot obviously be best fitted by a single Debye relaxation, and they assumed a more complex single dispersion of the heat diffusion central peak. As can be seen from Fig. 2(b) the three ralaxation peaks tend to shift to lower frequencies toward the central zero with decreasing temperature, that is, at temperatures further away from $T_c = 123$ K. This observation of relaxation frequency dependence on temperature is in disparity with the theoretical prediction for the heat diffusion central peak.[7]

In Fig. 3 we have shown the dielectric constant dependence on temperature for RbH_2PO_4 crystal at a few selected frequencies in the same low-frequency region concerned as for KDP crystal. In both Figs. 1(a) and 3(a) we can see that the dielectric constant difference $\Delta\epsilon$ between the high-frequency measurements and the low-frequency measurements remains nearly independent of temperature in the whole region of temperature from T_c^- to T_f^+, which is also in disparity with the theoretical behavior of $\Delta\epsilon(T)$ for the heat diffusion central peak.[7] All the observations above suggest that the low-frequency dielectric dispersion reported as due to the heat diffusion central peak[5,6] should be ascribed to the domain wall contributions.[13–16]

V. CONCLUSION

The temperature-dependent dielectric dispersion in KDP and RDP crystals observed in the low frequency region below 10 kHz is not a single dispersion of the heat diffusion central peak[5,6] but a composite dispersion including at least three different relaxational modes associated with the domain wall motion.[15,16] This criterion against the single dispersion assumption could be derived from the improved precision measurements in the low-frequency region by use of the DSP lock-in amplifier system, and extended temperature range from above T_c to below T_f.

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