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Dielectric dispersion associated with the dc-electric-field-enforced ferroelectric phase transition in the pressure-induced antiferroelectric CsH_2PO_4

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The dc-electric-field dependence of the dielectric properties (complex permittivity and relaxation time) of the antiferroelectric CsH_2PO_4 was investigated at 4.5 kbar under various frequencies. The strong dielectric dispersion along the *b* axis associated with the field-enforced ferroelectric phase transition was observed. The slowing down of the relaxation time toward a critical electric field E_{cr}, which induces the forced transition to the ferroelectric phase, was observed. Although the dielectric dispersion strength is zero without an applied dc field E_d, with an increase in E_d it increases gradually, rapidly near E_{cr} in the antiferroelectric phase and decreases monotonically in the ferroelectric phase. The relaxation time of the order of 10^{-5} s near E_{cr} in the antiferroelectric phase for the field-enforced transition is extremely low in contrast to that of the order of 10^{-8} s near the transition temperature in the paraelectric phase for the paraelectric-ferroelectric phase transition.

In many ferroelectrics and antiferroelectrics, it is known that as the transition point for either the paraelectric-ferroelectric or paraelectric-antiferroelectric phase transition is approached, the dielectric relaxation time becomes longer, i.e., a critical slowing down of the dielectric relaxation time,[1] whereas little has been reported on the dielectric dispersion for the antiferroelectric-to-ferroelectric phase transition induced by a dc electric field. In antiferroelectrics, polarization–electric field *P*-*E* double hysteresis loops have been observed.[1] Critical electric fields of *P*-*E* double hysteresis loops, which cause the change from the antiferroelectric to the ferroelectric phase, have been reported to have large values. For example, in potassium dihydrogen phosphate (KDP)-type $NH_4H_2PO_4$, the ferroelectric phase has not been recognized to be induced by the application of an electric field.[2] Layered antiferroelectric cupric formate tetrahydrate has a large critical electric field of about 10 kV/cm at 3 °C below the transition temperature T_c.[3] Thus, dielectric properties such as the real ϵ_r' and imaginary parts ϵ_r'' of complex relative permittivity and the relaxation time τ associated with the field-enforced ferroelectric phase transition were hardly investigated. On the other hand, it has been known for cesium dihydrogen phosphate CsH_2PO_4 (abbreviated CDP)[4,5] that the change from the paraelectric-ferroelectric to the paraelectric-antiferroelectric phase transition is caused by pressure as small as ~3.3 kbar and in the pressure-induced antiferroelectric the critical electric field has a very small value of 0.42 kV/cm due to the one-dimensional nature characterized by the chainlike ordering of the hydrogen bond parallel to the ferroelectric *b* axis. The antiferroelectric structure has been considered as follows:[6-9] The structure is described as hydrogen-bonded layers (*b*-*c* planes). Interlayer interaction is weak and by an application of pressure, neighboring layers are polarized oppositely through an alternative reorientational ordering of PO_4^{-3} groups; antiferroelectric stacking of ferroelectric *b*-*c* planes is along the *a* axis. This phase is characterized by antiferroelectric order with hydrogen atoms at off-center positions in the bond along the *b* axis, and equal and opposite sublattice polarization, due to the atomic displacements of heavy atoms along the *b* axis, consistent with the hydrogen ordering as well as the behavior of the hydrogen bonds. Consequently, the change in dielectric properties with the field-enforced ferroelectric phase transition can be measured by using a material such as CDP.

On the other hand, one of the main factors which has prevented the use of ferroelectrics in switching devices is that these materials, unlike ferromagnetics, do not have a true coercive field.[10] In contrast to ferroelectrics, it has been pointed out in antiferroelectrics[11] that the transition between different ordered states might provide a fixed coercive field. It is important to clarify the dielectric properties such as ϵ_r', ϵ_r'', and τ associated with the field-enforced antiferroelectric-to-ferroelectric phase transition, from the points of view of fundamental interest and also of practical importance, for applications of switching devices.[12-14]

We investigated the dc-electric-field dependence of the complex permittivity under various frequencies accompanied by the dipole reversal for the field-enforced ferroelectric phase transition and clarified a slowing down of the dielectric relaxation time toward a critical electric field. In this Rapid Communication, the dc-electric-field dependence of the real and imaginary parts of complex permittivity and the relaxation time is presented and the slowing down of the dielectric relaxation time is shown.

Single crystals of CDP were grown from an aqueous solution by the slow evaporation method at room temperature.[15] A plate perpendicular to the ferroelectric *b* axis was cut out with a beryllium wire cutter from a single crystal and gold was evaporated on its surfaces to act as electrodes. Each sample was covered with a silicone varnish to protect it from moisture. The electrical capacitance and the dielectric loss tangent of the sample were measured in the frequency range from 1 to 100 kHz with a field smaller than 1 V/cm using an ac bridge. A Cu-Be high-pressure vessel with a 1:1 mixture of normal and isopentane as a pressure-transmitting fluid was used in order to apply the hydrostatic pressure to the sample. A detailed description of the high-pressure apparatus has been given elsewhere.[15] All of the dielectric data were gathered for increasing dc electric field after the temperature had been stabilized at temperatures below $-157\,^\circ\mathrm{C}$ at 4.5 kbar. CDP crystals were confirmed to be antiferroelectric below $-157\,^\circ\mathrm{C}$ at 4.5 kbar by the observation of P-E double hysteresis loops[15] (see the inset in Fig. 1).

Figure 1 shows the dc-electric-field dependence of the real part ϵ_r' of the complex relative permittivity [Fig. 1(a)] and the dielectric-loss tangent $\tan\delta$ [Fig. 1(b)] along the b axis of CDP at 4.5 kbar at $-170\,^\circ\mathrm{C}$ for various frequencies. The strong dielectric dispersion along the b axis is observed. The dc electric field is seen to have a marked effect on the dielectric relaxation in Figs. 1(a) and 1(b). With increasing dc electric field E_d, ϵ_r' increases gradually, rapidly with decreasing frequency f near a dc electric field E_{cr} of 1.04 kV/cm, and shows a dielectric anomaly at E_{cr}, which is independent of f, as seen as an inflection point on the ϵ_r' vs E_d curve in Fig. 1(a). After that, ϵ_r' shows a maximum at a dc electric field E_m, which approaches E_{cr} as f decreases. This E_{cr} corresponds to the critical electric field E_{cri} on the P-E double hysteresis loop by which the arrangement of polarizations can be changed from antiparallel to parallel.[15] E_{cri} was estimated to be about 1 kV/cm as the value of the field at the center of a loop for a 60-Hz ac field at $-170\,^\circ\mathrm{C}$ at 4.5 kbar.[15] Then, the antiferroelectric phase is at $E_d < E_{\mathrm{cr}}$ and the ferroelectric one is at $E_d > E_{\mathrm{cr}}$. With increasing E_d, $\tan\delta$ increases gradually, rapidly near E_{cr}, and also shows the dielectric anomaly at E_{cr} as seen as an inflection point on the $\tan\delta$ vs E_d curve in Fig. 1(b). After that, $\tan\delta$ also shows a maximum at E_d which is shifted toward E_{cr} with decreasing f. It is found from the results above that although the dielectric dispersion strength is zero without applied E_d, with increasing E_d it increases gradually, rapidly near E_{cr} in the antiferroelectric phase, and decreases monotonically in the ferroelectric one. The increase in ϵ_r' at low frequencies near E_{cr} in the antiferroelectric phase and its decrease in the ferroelectric one with an increase in E_d are due to the nonlinear and the saturation effects on P against E, respectively, as found phenomenologically from the slope of P against E on the P-E double hysteresis loop.[11,15,16] Figure 2 shows the dc electric field dependence of the dielectric relaxation time τ and its reciprocal $1/\tau$. τ is calculated as a reciprocal of the relaxation frequency which gives the maximum value of the imaginary part ϵ_r'' of the complex relative permittivity in the frequency characteristics of ϵ_r'' replotted from Fig. 1 under the given dc field. With increasing E_d, τ increases in the antiferroelectric phase at $E_d < E_{\mathrm{cr}}$ and decreases in the ferroelectric phase at $E_d > E_{\mathrm{cr}}$; and then a slowing down of the relaxation time toward E_{cr} is observed. Figures 3(a) and 3(b) show the Cole-Cole diagrams in the antiferroelectric and ferroelectric phase under various dc fields obtained by a replotting from Fig. 1. Data points $(\epsilon_r', \epsilon_r'')$ at the given dc field in the Cole-Cole diagram lie nearly on a circular arc, and the centers of all arcs lie on the straight line below the real axis. Thus, the frequency dependence

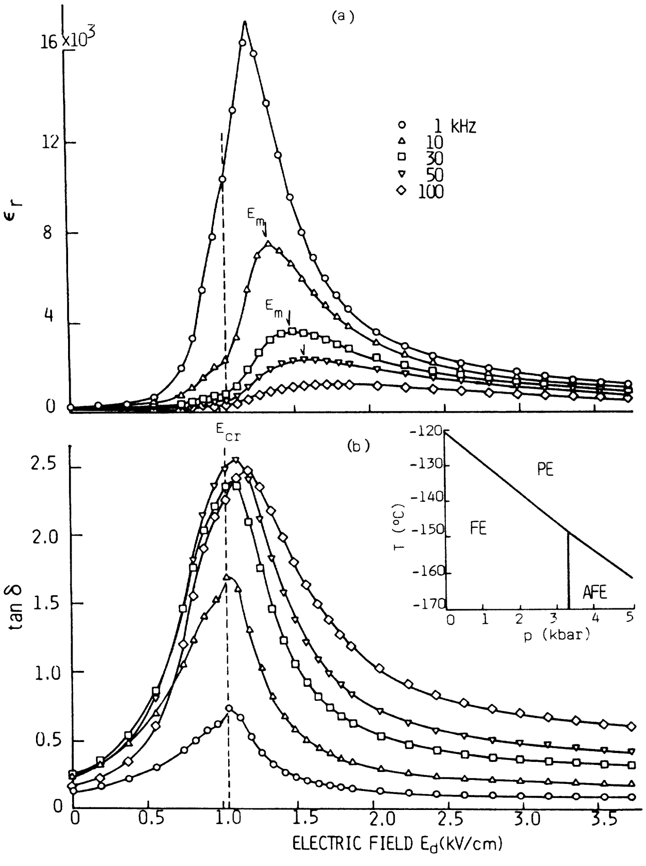

FIG. 1. dc-electric-field dependence of (a) the real part ϵ_r' of the complex relative permittivity and (b) the dielectric loss tangent $\tan\delta$ along the b axis of $\mathrm{CsH_2PO_4}$ at 4.5 kbar at $-170\,^\circ\mathrm{C}$ under various frequencies. The inset shows the pressure p vs temperature T phase diagram of $\mathrm{CsH_2PO_4}$ [paraelectric phase (PE), ferroelectric (FE), and antiferroelectric (AFE)] (Ref. 5).

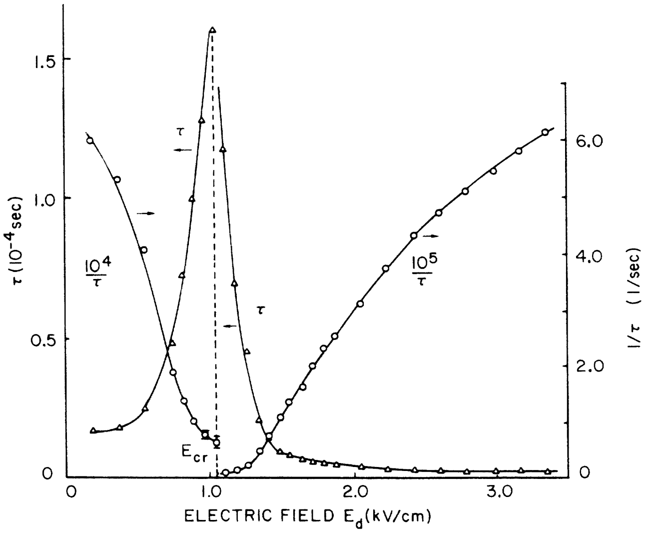

FIG. 2. dc-electric-field dependence of the dielectric relaxation time τ and its reciprocal of $\mathrm{CsH_2PO_4}$ at 4.5 kbar at $-170\,^\circ\mathrm{C}$.

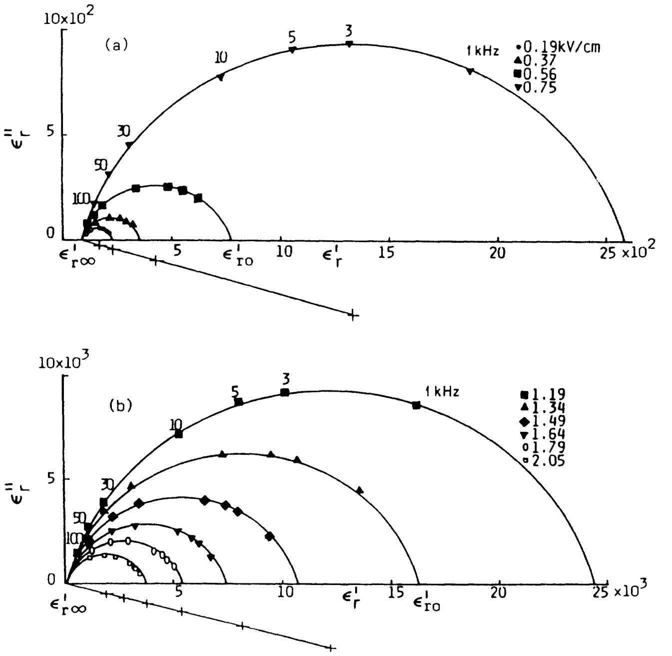

FIG. 3. Cole-Cole diagrams of CsH_2PO_4 (a) in the antiferroelectric and (b) in the ferroelectric phase under various dc fields at 4.5 kbar at $-170\,^{\circ}C$.

of ϵ'_r and ϵ''_r obey the Cole-Cole arc law.[17] Two intersections $(\epsilon'_{r0}, \epsilon'_{r\infty})$ between the real axis and a circular arc in Fig. 3 give the relative permittivity at zero frequency ϵ'_{r0} and the relative permittivity at infinitive frequency $\epsilon'_{r\infty}$. The circular arc gets larger in the antiferroelectric phase and smaller in the ferroelectric phase with increasing E_d. The parameter β, representing a measure of width of the distribution of dielectric relaxation times, is estimated to be about 0.85 in both phases. This indicates the dielectric dispersion of the polydispersive type.

In many ferroelectrics and antiferroelectrics, the dielectric relaxation time has been known to be proportional to the static relative permittivity.[18–20] Mason's theory has been applied to the dielectric dispersion of the relaxation type (the Debye dispersion),[18,21,22]

$$\tau = A(\epsilon'_{r0} - \epsilon'_{r\infty})\exp(\Delta U/kT)\,, \tag{1}$$

where k is the Boltzmann constant, ΔU the activation energy for the flipping motion of dipoles, and A the frequency factor. The ϵ'_r at higher frequencies tends to show a minimum at the field-enforced ferroelectric phase transition point E_{cr} [see Fig. 1(a)]. Judging from this[23] and the results mentioned above for τ and the dielectric dispersion strength $(\epsilon'_{r0} - \epsilon'_{r\infty})$ as a function of E_d, Eq. (1) may also be applicable to the dielectric dispersion associated with the field-enforced ferroelectric transition. Figure 4 shows the dc-electric-field dependence of the logarithmic values of $\tau/(\epsilon'_{r0} - \epsilon'_{r\infty})$ obtained by using values of ϵ'_{r0} and $\epsilon'_{r\infty}$ derived from the Cole-Cole diagram. It is seen from results in Fig. 4 that the linear relation between $\log_{10}[\tau/(\epsilon'_{r0} - \epsilon'_{r\infty})]$ and E_d holds in the antiferroelectric phase, except in the vicinity of E_{cr} in the ferroelectric phase. Therefore, from Eq. (1), relations of $\Delta U = \Delta U_0 \times [1 + a(E_{cr} - E_d)]$ in the antiferroelectric phase and $\Delta U = \Delta U_0[1 + a(E_d - E_{cr})]$ in the ferroelectric phase, where ΔU_0 and a are constants, are obtained. Values of ΔU_0 and a are estimated to be 0.15 eV and 0.19 $(kV/cm)^{-1}$ in the antiferroelectric phase and 0.10 eV and 0.02 $(kV/cm)^{-1}$ in the ferroelectric one, respectively, by making use of the slope of the $\log_{10}[\tau/(\epsilon'_{r0} - \epsilon'_{r\infty})]$ vs $1/T$ straight line under various dc fields. Values of A are estimated from Eq. (1) to be $1.0 \times 10^{15}\ s^{-1}$ and $0.2 \times 10^{15}\ s^{-1}$ in the antiferroelectric and in the ferroelectric phases, respectively. The dielectric relaxation time for the paraelectric-ferroelectric phase transition in CDP (Refs. 22 and 24) has been reported to be of the order of 10^{-8} s near the transition temperature T_c in the paraelectric phase. In contrast to this, the relaxation time for the field-enforced phase transition of the order of 10^{-5} s near E_{cr} in the antiferroelectric phase is extremely low.

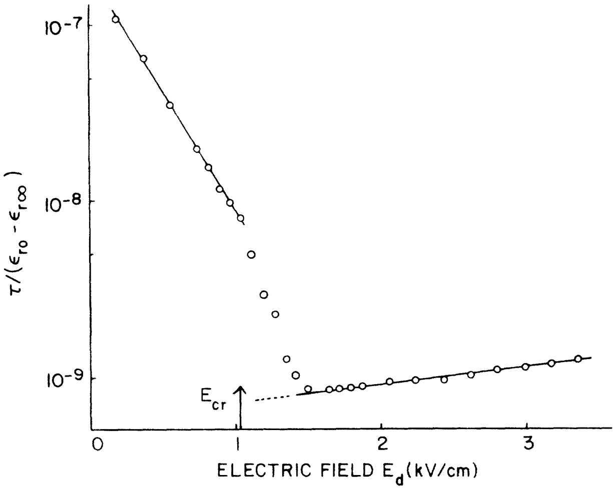

FIG. 4. dc-electric-field dependence of the logarithmic $[\tau/(\epsilon'_{r0} - \epsilon'_{r\infty})]$ for CsH_2PO_4 at 4.5 kbar at $-170\,^{\circ}C$.

In a process of dipole reversal for the field-enforced antiferroelectric-to-ferroelectric phase transition, the hydrogen atom changes its position to the other site and, accompanied by this ferroelectric reordering of b-chain hydrogens from antiferroelectric ordering, a reorientation of $PO_4{}^{-3}$ groups and the relative displacement of $PO_4{}^{-3}$ groups and Cs^{+1} ions responsible for the generation of polarization take place.[6–9] On the other hand, the following has been pointed out in such a material as CDP:[25] The hydrogen bonds which are of the double-well type with a low intermediate barrier, link molecular-ionic groups (e.g., $PO_4{}^{-3}$), with very strong local interactions between the protons and the molecular electronic wave functions, and very-long-range correlations, can easily develop in the networks formed by hydrogen-bonded molecular-ionic groups. These correlations indicate precursory development of the ferroelectric structure above T_c. If such correlations develop by an application of E_d in the pressure-induced antiferroelectric CDP, the crystal becomes a clusterlike structure near E_{cr} in the antiferroelectric phase. Thus, the slowing down of the relaxation time around E_{cr} may be due to the growth of a clusterlike structure with an increase in E_d. A more detailed study is now in progress.

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