

High dielectric permittivity of ceramic and single-crystal $\text{PrBa}_2\text{Cu}_3\text{O}_x$

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(Received 31 July 1992; revised manuscript received 10 November 1992)

A study of the dielectric response as a function of frequency (10^2 – 10^6 Hz) and temperature (4.2–300 K) in ceramic and *c*-axis-oriented single-crystal samples of $\text{PrBa}_2\text{Cu}_3\text{O}_x$ reveals dielectric constants $> 10^3$ at low frequencies in both cases but in different temperature regimes. High-frequency (0.2–20 GHz) measurements of the ceramic sample at room temperature show a loss peak and suggest a relaxation process for the polarization mechanism with characteristic time $\tau = 0.5 \times 10^{-9}$ s, which is near the electrical diffusivity time. For the single crystal the large polarizability results from a thermally activated process with an activation energy of 0.28 eV and an attempt frequency ω_0 of about 10^9 Hz at 300 K. Our results show that the high dielectric constant may be a common feature of the 1:2:3-structure oxide family, and that the previously discovered ordering of the Cu spins at $T \sim 300$ K in $\text{PrBa}_2\text{Cu}_3\text{O}_x$ may be accompanied by near ferroelectric polarizability.

Since the discovery of high- T_c superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_x$ there have been extensive studies of its physical properties. Recent measurements of the dielectric response in the nonsuperconducting phase of $\text{YBa}_2\text{Cu}_3\text{O}_x$ show a large, temperature and frequency dependent, dielectric constant.¹ The substitution of Y by the rare-earth element Pr suppresses superconductivity, while maintaining the original orthorhombic structure of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_x$.² We report measurements of the dielectric constant for a ceramic sample and a single crystal of $\text{PrBa}_2\text{Cu}_3\text{O}_x$ that also show a high dielectric constant with a strong frequency and temperature dependence. We find further evidence that the large polarizability for the single crystal may be associated with the transition leading to Cu spin ordering.

The ceramic sample of $\text{PrBa}_2\text{Cu}_3\text{O}_x$ was made using powder obtained from an oxalate coprecipitation process using nonaqueous solvents.³ The powder was then pressed into a disk-shaped pellet using a force of approximately 20 000 lb/in² ($\sim 1.38 \times 10^8$ Pa) and annealed in flowing oxygen for 2 h at 920°C and then for 2 h at 500°C followed by furnace cooling at room temperature at a rate of 1°/min. The resulting sample had a 1.756 cm diameter, 0.255 cm thickness, and a density of about 92.4% of the theoretical value for $\text{PrBa}_2\text{Cu}_3\text{O}_7$. Characterization by x-ray diffraction showed a predominantly single phase orthorhombic structure with less than 1% impurity phases and lattice parameters $a = 3.9501$ Å, $b = 3.8681$ Å, and $c = 11.7172$ Å, which closely agree

with previous published results.⁴

The single crystal of $\text{PrBa}_2\text{Cu}_3\text{O}_x$ was prepared using the BaCO_3/CuO flux method and had approximate dimensions of 1.5 mm \times 2 mm \times 0.23 mm. Details about the method of crystal growth are described elsewhere.⁵ Energy dispersion analysis indicated the ratio of 1:2:3 for Pr:Ba:Cu. The x-ray-diffraction pattern showed the single-crystal nature of the sample. From our lattice parameters ($a = 3.9320$ Å, b undetermined, $c = 11.75 \pm 0.05$ Å) and the relation $x = 78.77 - 6.153c$ (Ref. 6) we obtained an approximate oxygen content ≤ 6.6 . The crystal had two large surfaces that were within 5° of being parallel. X-ray diffraction indicated that one of these surfaces were nearly normal (to within 1°) to the *c* axis.

The real (ϵ'_r) and imaginary (ϵ''_r) parts of the complex dielectric constant relative to the permittivity of free space for the frequency range 100 Hz–1 MHz were determined from impedance measurements and a sample model of a capacitor and resistor in parallel. The data were collected at different temperatures (4.2–300 K). Ultrasonically soldered indium-tin electrodes were used for the ceramic sample and silver paint electrodes were used for the two large surfaces of the single crystal. High-frequency measurements (0.2–20 GHz) were made on the ceramic sample at room temperature without using electrodes.

The high-frequency data were taken with the HP8507A probe, which determines ϵ'_r and ϵ''_r (the real and imaginary relative dielectric constants) from the

reflected impedance of a sample located in the fringe fields of an open ended coaxial structure. The performance characteristics of the HP85070A probe show a typical uncertainty $\sim \pm 0.05$ for $\epsilon'_r \sim 10^2$ from 0.2 to > 10 GHz with the uncertainty increasing at the lower frequencies for smaller ϵ'_r . Uncertainties in the loss tangent ($= \epsilon''_r / \epsilon'_r$) are $\sim \pm 0.05$ with the same frequency restrictions. The use of this probe is limited by the frequency condition $F < 140 \text{ GHz} / \sqrt{|\epsilon_r^*|}$, where ϵ_r^* is the complex relative dielectric constant. An operational limitation on the probe for solids with high dielectric constant comes from roughness of the sample/probe interface. We spent considerable time improving this mating and determining the reproducibility of the data through multiple measurements under different mechanical loading and sample polishing. Once the measurement procedure was optimized, we found that data to be reproducible to $\sim \pm 20\%$.

The dc electrical conductivity for the single crystal with an applied electric field within 5° of the c axis was of the order of $10^{-3} (\Omega \text{ m})^{-1}$ at room temperature, while the ceramic sample had a value of the order of $10^2 (\Omega \text{ m})^{-1}$ at room temperature. This difference could be due to their difference in oxygen concentration.

Measurements of the real part of the dielectric constant (ϵ'_r) and the conductivity ($\sigma = \omega \epsilon_0 \epsilon''_r$, where ϵ_0 is the permittivity of free space and ϵ''_r is the imaginary component of the dielectric constant) as a function of frequency at temperatures below 64 K for the ceramic sample are shown in Fig. 1. Due to its high electrical conductivity at higher temperatures, measurements were only possible at low temperatures, where the dissipation

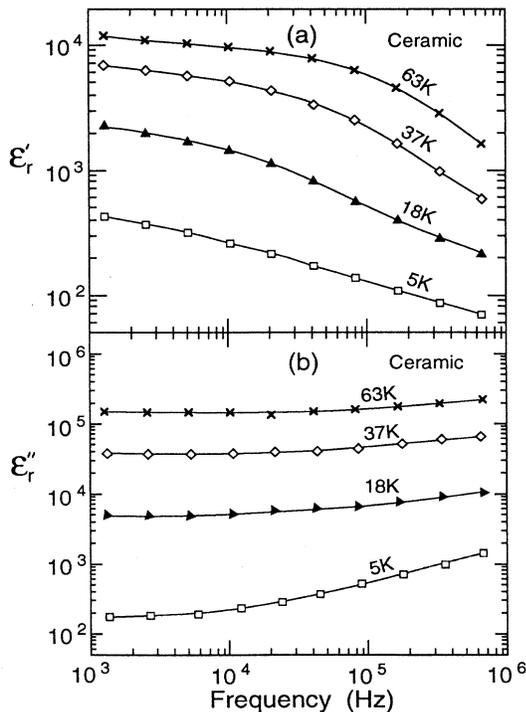


FIG. 1. Real part of the dielectric constant (a) and electrical conductivity (b) vs frequency for the ceramic sample.

factor ($D = \epsilon''_r / \epsilon'_r$) was small. Note the high and strongly temperature-dependent values of the dielectric constant ($\epsilon'_r > 40$) at low temperatures for all frequencies measured.

The conductivity plot shows an increase in the conductivity value as the frequency increases. The dc electrical conductivity at 63 K is $0.12 (\Omega \text{ m})^{-1}$, which is close to the σ value at low frequencies shown in Fig. 1. Similar results were obtained for the other temperatures measured.

The relaxation behavior in ϵ'_r and the nonconstant behavior in σ with frequency for the data of Fig. 1 indicate a failure in modeling the sample as a resistor and capacitor in parallel, and that the polarization is accompanied by dissipation that might be modeled as a series resistor. We have an insufficient frequency regime to carry out this analysis for the ceramic sample, but its application for the single-crystal results will be discussed later.

The high-frequency dielectric response for the ceramic sample at 300 K is given in Fig. 2. The imaginary component ϵ''_r was not measured above 10^{10} Hz due to instrumental limitations. The value of ϵ'_r changes from 1300 to about 50 through the microwave frequency region ($0.2 \rightarrow 10$ GHz). This drop in ϵ'_r is accompanied by a loss peak in ϵ''_r , suggesting a relaxation process for the polarization mechanism with a relaxation time of about 0.5×10^{-9} s, which corresponds approximately to the dc electrical diffusivity time. This corresponds to the inverse frequency ω_r at which the real current is equal in magnitude to the displacement current, $\epsilon_0 \epsilon'_r \rho \omega_r = 1$, where ρ is the dc resistivity of the ceramic sample and ϵ'_r is the relative static dielectric constant, obtaining in this case a frequency $\omega_r \sim 3 \times 10^9$ Hz. This relaxation observed in ϵ'_r and ϵ''_r indicates a new mechanism contributing to the polarization and having a series damping possibly due to real electrical currents being dissipated by the low-frequency resistance.

Our measurements on the single crystal $\text{Pr}_1\text{Ba}_2\text{Cu}_3\text{O}_x$

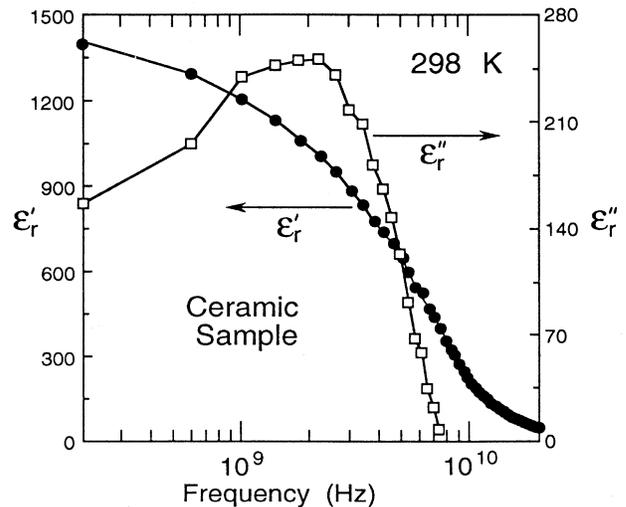


FIG. 2. Real and imaginary dielectric constant at 298 K vs frequency for the ceramic sample.

demonstrate that this large dielectric constant is a property of the material itself and not just a result of the sintering process and inhomogeneity of the ceramic sample. These measurements are accompanied by an uncertainty (about 20%) arising from the dimensions of the crystal and the irregularity of its shape. In addition, the electroded faces were not completely parallel ($< 5^\circ$).

Figure 3 shows the dc current density J as a function of the electric field E applied within 5° of the c axis for the single crystal of $\text{PrBa}_2\text{Cu}_3\text{O}_x$ at two different temperatures. A non-Ohmic behavior can be noted, which becomes more pronounced with the decrease in temperature and resulting in an increase in the resistivity. This strong electric-field dependence and nonlinearity of the conduction mechanism has also been found in the non-superconducting polycrystalline samples of $\text{YBa}_2\text{Cu}_3\text{O}_x$.¹ Since the resistivity of the $\text{PrBa}_2\text{Cu}_3\text{O}_x$ single crystal had a strong electric-field dependence above $E = 10^3$ V/m, we restricted our measurements of the dielectric response to an applied voltage of 0.01 V ($E \sim 45$ V/m) in order to obtain a dielectric response that would be field independent.

Figure 4 shows the frequency dependent ϵ'_r and σ for the single crystal for E fields along the c axis of symmetry (to within $< 5^\circ$). As the frequency increases beyond 10^6 Hz, ϵ'_r tends to a limiting value of about 20 for all temperatures. At lower frequencies, however, ϵ'_r is $> 10^3$ at the higher temperatures. Note also that from 154 to 6 K there is not much change in the value of ϵ'_r . The conductivity σ tends to the dc value as the frequency decreases. The conductivity was too small to be measured for temperatures lower than 160 K.

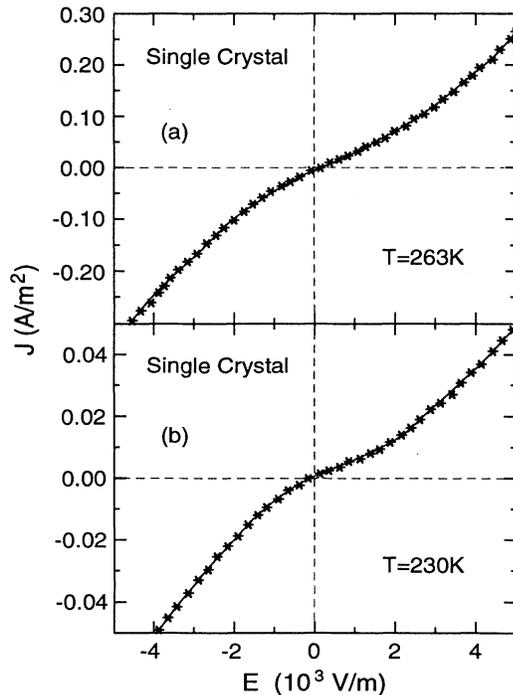


FIG. 3. Current density J vs electric field E at temperatures 263 K (a) and 230 K (b) for the single-crystal sample.

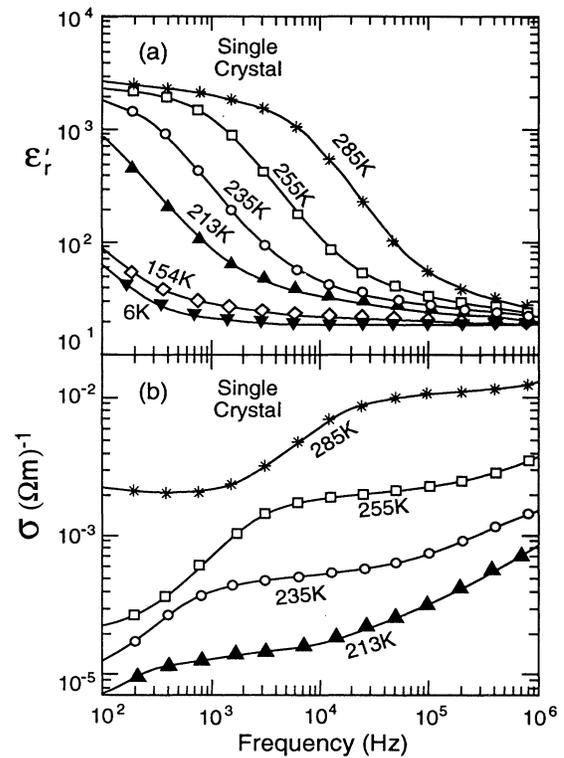


FIG. 4. Real part of the dielectric constant (a) and electrical conductivity (b) vs frequency for the single-crystal sample.

A thermally activated process for the electric polarization in the behavior of both ϵ'_r and σ as a function of frequency (see Fig. 4) was observed in the single crystal. The frequency dependence of the dielectric response can be represented by the Cole-Cole relaxation process⁷ whose complex permittivity is given by

$$\epsilon_r^* = \epsilon'_{r_\infty} + \frac{\epsilon'_s - \epsilon'_{r_\infty}}{1 + (i\omega\tau_m)^{1-\alpha}}, \quad (1)$$

where ϵ'_s and ϵ'_{r_∞} are the low-frequency and high-frequency limit dielectric constants, respectively, τ_m is the most probable relaxation time, and α is an empirical constant with values between 0 and 1, and is a measure of an assumed symmetric logarithmic distribution of the relaxation times. The case $\alpha=0$ corresponds to the Debye model that has a single relaxation time. We have found from regression analysis of the data for Eq. (1) that the polarization mechanism for the single crystal $\text{PrBa}_2\text{Cu}_3\text{O}_x$ follows this Cole-Cole behavior, with a mean α value of 0.15 ± 0.03 .

This relaxation time τ_m is also found to be given by the Arrhenius relation

$$\tau_m = \tau_{m_0} e^{E/kT}, \quad (2)$$

where E is the activation energy, T is the temperature, and τ_{m_0} is the attempt time over the limited temperature range of 213–285 K [Fig. 5(a)]. The activation energy E was found to be 0.28 eV for the single crystal in the tem-

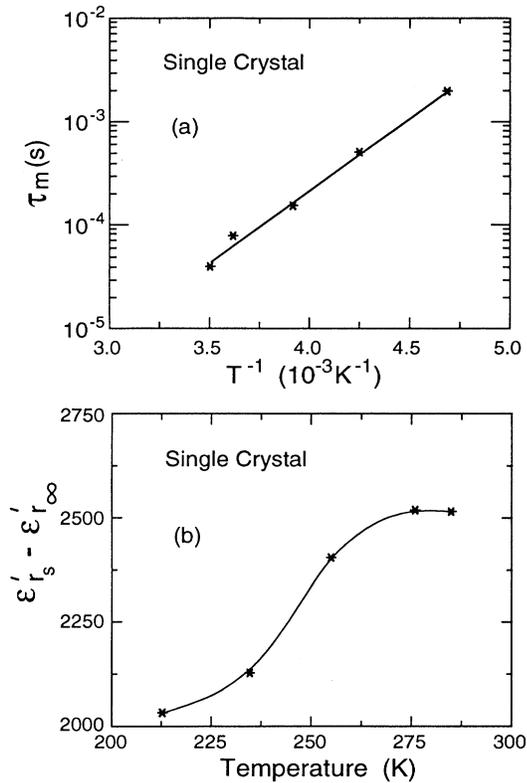


FIG. 5. (a) The relaxation time τ_m vs inverse temperature T^{-1} for the single-crystal sample. The points are determined by using the Cole-Cole fit for the experimental data, (b) the strength of the polarization mechanism $\epsilon'_s - \epsilon'_\infty$ using the Cole-Cole fit vs temperature.

perature range between 195–295 K. The attempt frequency $\omega_{m_0} = 1/\tau_{m_0}$ was found to be 1.63×10^9 Hz. This is close to the frequency at which a relaxation peak was found in the ceramic sample (Fig. 2) but no inference from this equality can be drawn with certainty at this time. This frequency is also very low compared to phonon frequencies sometimes found responsible for polarization mechanisms.⁸

The strength of the single-crystal polarization mechanism, $\epsilon'_s - \epsilon'_\infty$, obtained from the fit of the data to Eq. (1) is plotted against temperature in Fig. 5(b). There appears to be a flattening at approximately 280 K. This temperature correlates with that for the antiferromagnetic ordering of the Cu moments within the Cu-O planes and chains. Measurements on polycrystalline samples⁹ show that the Néel temperatures for this magnetic ordering in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ and the oxygen deficient $\text{PrBa}_2\text{Cu}_3\text{O}_6$ are ap-

proximately 285 and 385 K, respectively. Recent neutron-scattering data on single crystals¹⁰ display a higher temperature for the ordering of Cu moments along the planes and a temperature ordering along planes and chains strongly dependent on the oxygen concentration. For the oxygen deficient single crystal $\text{PrBa}_2\text{Cu}_3\text{O}_x$ the ordering of chain and plane Cu moments occurs at about 280–300 K.

Note also that there is only a 20% decrease in this relaxation strength on cooling from 280 to 213 K. However, even if this process were to continue with sizable strength for temperatures below 200 K, measurements of the dielectric response would become nearly impossible at low temperatures due to the exponential growth of the relaxation time on cooling. At 90 K (close to the temperature where $\text{YBa}_2\text{Cu}_3\text{O}_x$ becomes a superconductor), for example, it would take about 2×10^6 s (530 h) to achieve the quasistatic equilibrium condition for electrical polarization using extrapolated behavior from Fig. 5(a). Thus the weak dielectric response measured in the single crystal from 155 to 5 K may reflect only the high-frequency response governed by ϵ'_∞ .

To summarize, we have found a high dielectric constant for a polycrystalline sample of $\text{PrBa}_2\text{Cu}_3\text{O}_x$ in the frequency range of 10^3 – 10^6 Hz and at low temperatures. The dielectric response in the microwave frequency range (0.2–20 GHz) at room temperature shows a relaxation process with a relaxation time of 0.5×10^{-9} s. Measurements on a single crystal of $\text{PrBa}_2\text{Cu}_3\text{O}_x$ with E field along the c axis ($< 5^\circ$) exhibit also a high dielectric constant for the frequency region of 10^2 – 10^6 Hz at different temperatures, showing that this large dielectric constant is a property of the material itself. The dielectric response of the $\text{PrBa}_2\text{Cu}_3\text{O}_x$ single crystal is accompanied by a strong thermally activated polarization mechanism with an activation energy of 0.28 eV and a long relaxation time. It is this process that is responsible for the high dielectric constant at low frequencies of this material. A saturation of the strength of this polarization mechanism at about 280 K may be related to the transition leading to Cu-moment magnetic ordering in $\text{PrBa}_2\text{Cu}_3\text{O}_x$.

The authors wish to thank Tom Fellers for the SEM analysis of the ceramic sample, Jorge Bolivar for assistance in the ceramic sample preparation, William Jenks and Pedro Schlottman for general assistance, and the FSU MARTECH Program for their financial and technical support. Two of the authors (G.C. and J.O.) wish to acknowledge support provided by the National High Magnetic Field Laboratory and NSF Cooperative Agreement No. DMR-9016241.

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