Ferroelectric phase transitions in oxides of the persovskite family

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Anomalies have been found in the dielectric constant of $YBa_2Cu_3O_{6+x}$ which are similar to the anomalies which occur during phase transitions in ferroelectric and antiferroelectric materials of the $BaTiO_3$ type.

The discovery of high-temperature superconductivity has heightened interest in research on perovskite oxides. Since the complex oxides of the perovskite family exhibit well-expressed structural features in their dielectric properties, it is possible that ferroelectric and antiferroelectric phase transitions occur in them. It is thus worthwhile to study the dielectric properties of the oxides and possible ferroelectric and antiferroelectric states in them.

There are now several experimental results which support the suggestion that a ferroelectric (or antiferroelectric) order exists in 1–2–3 oxides (these results are briefly reviewed in Ref. 1). Judging from the results available, the ferroelectric order should be associated with dielectric domains which exist in the metallic matrix of the oxide. On the other hand, a heterophase structure of the $YBa_2Cu_3O_{7-x}$ type has been confirmed.[2–4] It was shown in Refs. 3 and 4 that domains with a lowered oxygen concentration are present in the crystal. Our purpose of the present study was accordingly to learn about the dielectric properties of $YBa_2Cu_3O_{7-x}$ with a lowered oxygen concentration.

The samples for the dielectric studies were prepared by pressing annealed powdered $YBa_2Cu_3O_{7-x}$ ($T_s \approx 90$ K) at a pressure of 2 kbar with an organic dielectric binder at 250–280 °C. The samples were disks 10 mm in diameter and 1 mm thick. The binder was the fluoroplastic FT-3M; the degree of filling was 40%. The dielectric constant of FT-3M is essentially independent of the temperature ($\epsilon \approx 2.5$ at 200 K and $\epsilon \approx 3.0$ at 370 K; Ref. 5). The pressing of the samples at 2 kbar, at temperatures at which oxygen begins to desorb from the crystal lattice, combined with the high gas permeability of the binder, which promotes a removal of oxygen from the ceramic grains, makes it possible to synthesize samples with a reduced oxygen concentration. There is no diamagnetic response. Electrodes were pressed into the end surfaces during the synthesis of the samples, so it was unnecessary to carry out an additional heat treatment in order to braze electrodes.

Figure 1 shows the temperature dependence of the dielectric constant. The shape here is characteristic of perovskite ferroelectrics and antiferroelectrics which undergo a second-order phase transition: Specifically, $\epsilon(T)$ goes through a maximum, above which the dependence $\epsilon^{-1}(T)$ obeys the Curie-Weiss law. There is no thermal hystere-

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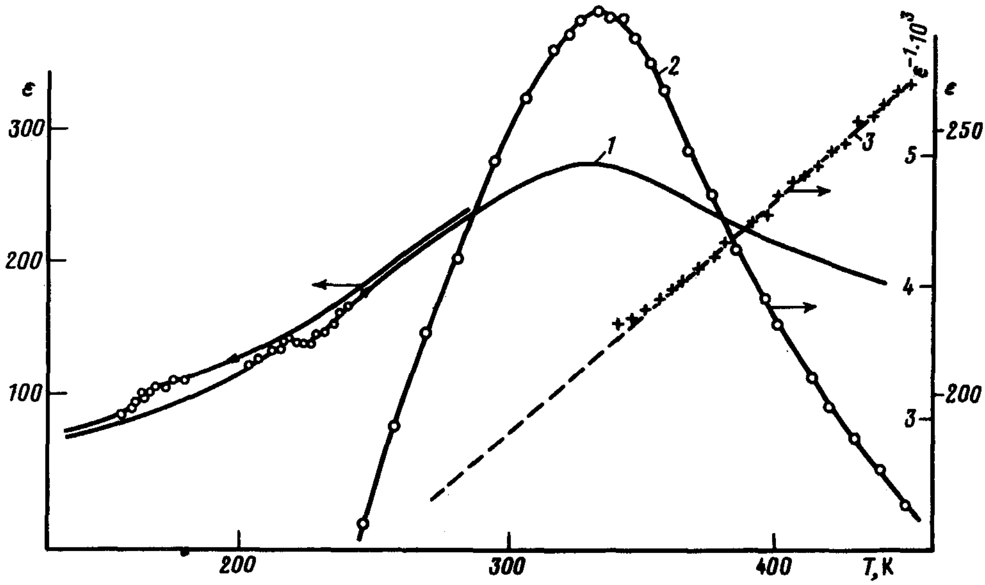

FIG. 1. Temperature dependence of the dielectric constant (1,2) (2—near ϵ_{max}) and of the reciprocal of the dielectric constant (3).

sis. The Curie-Weiss constant is approximately the same as the values of this constant in some well-studied ferroelectrics and antiferroelectrics with the perovskite structure: $PbHfO_3$, $PbTiO_3$, $PbZrO_3$ and $BaTiO_3$.

At lower temperatures we found an anomaly in the dielectric properties, which indicates a first-order phase transition. Specifically, heating causes a transition at 218 K, and cooling causes a transition at 167 K. Interestingly, the position of this anomaly coincides with those on the temperature dependence of other physical properties: the resistance in the form referred to by the Russian abbreviation PTKR,[6] the internal friction and attenuation of sound,[6,7] and positron annihilation.[8] Testardy *et al.*[9] have measured $\epsilon(T)$ for ceramic samples with an oxygen concentration close to 6.0 at temperatures below 290 K. There is a correlation between the temperature dependence of ϵ reported in Ref. 9 and that which we found. An anomaly on the $\epsilon(T)$ dependence at 220 K was also reported there.

Just as there are inclusions of a dielectric phase when there is a high oxygen concentration in a metallic matrix, there may be domains of a metallic phase at a low oxygen concentration in a dielectric (or semiconductor) matrix. In this case a barrier layer with a capacitance $\epsilon(T)/d$ (d is the thickness of the barrier layer) will arise at the interface. This question was discussed in detail in Ref. 10 for the ferroelectric $BaTiO_3$. In this case the temperature dependence $\epsilon(T)$ remains the same in nature, with structural features at the phase transition, including the Curie-Weiss law in the paraphase, but with a renormalized Curie-Weiss constant.

In summary, this study has revealed anomalies in the dielectric properties of the Y–Ba–Cu–O system which may be associated with transitions to dipole-ordered states.

The Curie-Weiss constant, on the order of 10^5, suggests that there is a displacive phase transition. (The Curie-Weiss constant for the other known type of ferroelectric or antiferroelectric phase transition, the order-disorder type, is two orders of magnitude smaller.)

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