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Frequency and temperature dependence of the electrical conductivity of $KTaO_3$; Li and $PbTiO_3$; La, Cu: Indication of a low temperature polaron mechanism

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ABSTRACT

Recently, the concept of polarons has again been at the focus of solid-state research, as it can constitute the basis for understanding the high-temperature superconductivity or the colossal magnetoresistance of materials. More than a decade ago there were some indications that polarons play an important role in explaining low temperature maxima in imaginary part of the dielectric constant $\varepsilon''(T)$ in ABO_3 perovskites. In the present work we report the ac electrical conductivities of $KTaO_3$; Li and $PbTiO_3$; La, Cu and their frequency and temperature dependence. The real part of the complex ac conductivity was found to follow the universal dielectric response $\sigma' \propto \nu^s$. A detailed theoretical analysis of the temperature dependence of the parameter s revealed that, at low temperatures, the tunnelling of small polarons is the dominating charge transport mechanism in ABO_3 perovskites.

1. Introduction

More than a decade ago dielectric properties at high and low temperatures in ABO_3 perovskites (more than 100 samples) were systematically studied [1,2]. In many pure and doped samples the low temperature (below 50 K) dielectric loss anomaly was observed. Dielectric spectra were described by the Arrhenius law with activation energies around 80 meV and attempt relaxation time τ_0 in the range of $10^{-13}-10^{-14}$ s. It was proposed that polaronic excitations are responsible for such behaviour of dipoles. $KTaO_3$, $KTaO_3$; Nb, and $KTaO_3$; Li, Fe have various properties ranging from quantum paraelectric to orientational glass and ferroelectric. Further, such low temperature dielectric losses with similar activation energies were observed in doped ceramics $BaTiO_3$ and $PbTiO_3$ [1,3]. The manifestation of Jahn-Teller polarons [4] was shown in $BaTiO_3$ crystals with EPR. Recently [5], on the basis of measurements of magnetic susceptibility and electrical conductivity in $BaTi_{1-x}Nb_xO_3$, it was shown that immobile spin-singlet small bi-polarons are formed in this system.

With one exception [3], the concept of polarons connected with the existence of low-temperature peaks in $\varepsilon''(T)$ has not been supported by theoretical analysis.

In the present work we analyze the frequency and temperature dependence of ac electrical conductivity in $KTaO_3$; 8% Li and $PbTiO_3$; 20% La, 8% Cu (abbreviated as PLTC(20,8)), for the first time using the theoretical model for small polarons, and determine the energy barriers for polarons, reduced polaron radius, attempt relaxation times and the density of polarons. Very probably it will be possible to analyze the ac conductivity in many other ABO_3 perovskites with anomalies in $\varepsilon''(T)$ at low temperatures, using the same method, thus supporting the polaronic concept proposed approximately 15 years ago.

Besides infrared excitation in optical conductivity [6,7], the fingerprint of polarons is usually connected with the temperature and frequency dependence of ac electrical conductivity [8–10].

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For many amorphous and crystal systems it has been shown that, besides the dc contribution of conductivity, σ_{dc}, the frequency dependent real part of complex ac conductivity, σ', follows the so-called universal dielectric response (UDR) [11], thus

$$\sigma' = \sigma_{dc} + Av^s. \quad (1)$$

Here, A is a temperature dependent constant, v is the measuring frequency, and s the frequency exponent, $s \leqslant 1$. Such behaviour has been deduced by several theoretical approaches from the microscopic transport properties, including hopping or tunnelling of the charge carriers through the energy barrier separating different localized states [12–15]. Different mechanisms, however, lead to different frequency dependence of the ac conductivity, i.e., to different temperature dependence of the UDR parameter s.

2. Experiment

$KTaO_3$; 8% Li mono-crystals were grown by spontaneous crystallization. The starting components were K_2CO_3 and Ta_2O_5 of high purity. $PbTiO_3$; La, Cu samples are labelled PLTC(Y,X) where Y denotes the amount (in %) of lanthanum ($Y = 100y$) and the second ($X = 100x$) the amount (in %) of copper. PLTC (20, 8) ceramic samples were prepared from very pure PbO, TiO_3, CuO, and La_2O_3 as starting materials with $y/2$ excess of PbO. Materials were sintered in an alumina crucible in a PbO rich atmosphere so that loss of Pb during sintering was minimized. Details of the sintering procedure have been described [16]. The colour of PLTC (20, 8) is brown. The composition was determined by chemical analysis and the homogeneity by X-ray powder analysis.

The complex dielectric constant $\varepsilon^*(v,T) = \varepsilon' - \varepsilon''$ was measured between 4.5 and 300 K in the frequency range of 0.3 Hz–1 MHz, using a Novocontrol Alpha High Resolution Dielectric Analyzer. The amplitude of the probing ac electric signal was 1 V/mm. The temperature was stabilized within ±0.1 K using an Oxford Instruments continuous flow cryostat. The real part of the complex ac conductivity $\sigma^* = \sigma' + \sigma''$ was calculated via $\sigma' = 2\pi v \varepsilon_0 \varepsilon''$, with ε_0 being the permittivity of the vacuum.

3. Results and discussion

The real part of the complex ac conductivity σ' of $KTaO_3$; 8% Li at various frequencies is shown as a function of inverse temperature (Fig. 1a). We observe $\sigma'(T)$ peaks at various temperatures below approximately 30 K, which move with increase in frequency to higher temperatures. Below 20 K, σ' is nearly temperature independent. Strongly frequency-dependent plateaus in the $\sigma'(T)$ data below 20 K suggest that hopping or tunnelling of localized charge carriers governs the electrical transport at lower temperatures [17]. The relaxation frequency determined from the peaks in $\sigma'(T)$ vs. reciprocal temperature follows the Arrhenius law $f = f_0 \exp(-\Delta U/T)$ (Fig. 2). The activation energy has the value $\Delta U = 76.1 \pm 0.4$ meV and f_0 the value $(2.6 \pm 0.3) \times 10^{11}$ s^{-1} ($\tau_0 = 1/(2\pi f_0) = 6.0 \times 10^{-13}$ s). Such behaviour is the result of the simple model [18,19].

The frequency dependence of σ' at different temperatures is presented in Fig. 3a. It is clearly evident that, at higher frequencies, the conductivity follows the UDR behaviour, $\sigma' \propto v^s$, while at lower frequencies the data shift away from this dependence due to the dc conductivity contribution. Thus, in one decade, the frequency range σ' could be described by Eq. (1).

The UDR parameter s, determined by linear fits as presented in the Fig. 3a, is shown in Fig. 4a as a function of temperature. It exhibits non-monotonous temperature behaviour, with a minimum at ≈ 25 K. Such behaviour is predicted by the tunnelling

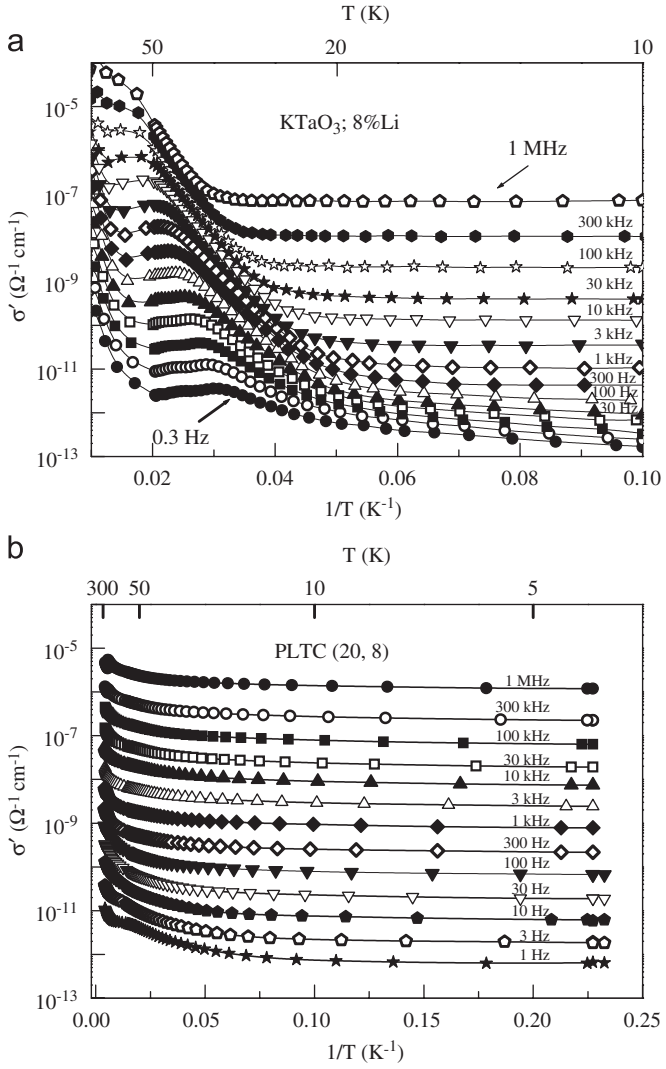

Fig. 1. The real part of the complex ac conductivity σ'. (a) In $KTaO_3$; 8% Li. Measured along the [1 0 0] crystallographic axis at several frequencies versus inverse temperature. (b) In PLTC (20, 8). Measured at seven frequencies, as a function of inverse temperature.

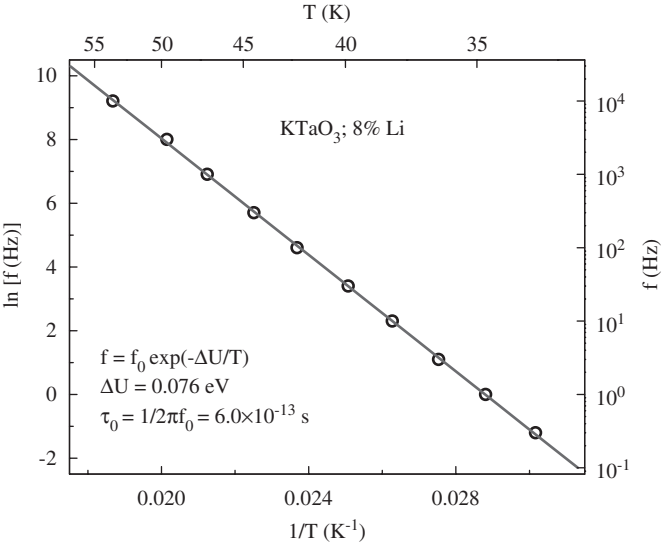

Fig. 2. Relaxation frequency determined from the peaks in σ' in Fig. 1a versus reciprocal temperature in $KTaO_3$; 8% Li.