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Low-temperature dielectric relaxation peaks involving proton tunneling in $Ba_{1-x}Nd_xCeO_3$

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An investigation of dielectric relaxation at relatively low-temperature (55–225 K) of the protonic conductor $Ba_{1-x}Nd_xCeO_3$, for $x=0.05$, has revealed a major dielectric relaxation peak, as well as an associated smaller peak, with characteristics that strongly suggest proton tunneling. In particular, the relaxation rate is almost constant between 55 and 85 K. The nature of the dipolar defect that can give rise to such a peak is considered. [S0163-1829(99)50630-9]

Due to the low mass of the hydrogen atom, tunneling by protons or by hydrogen atoms plays a role in the behavior of a wide range of systems.[1–4] These include the following: diffusion of hydrogen in metals,[3,5] O-H defects in Y and Nb metals,[6,7] the B-H complex in silicon,[8] hydrogen in polymers,[9] proton transfer in organic molecules, especially benzoic acid,[10,11] and ferroelectric-type materials known as ''hydrogen glasses.''[12]

The present study provides one of the most striking manifestations of quantum-mechanical tunneling of protons in a relatively simple system, showing a Debye-type relaxation peak whose relaxation time is almost temperature independent up to relatively high temperatures (~85 K), as well as a secondary smaller peak with similar characteristics. It involves the perovskite-structured oxide, $BaCeO_3$, which, when doped with lower-valent cations on the Ce^{4+} sites and heat treated in water vapor, is known to become an excellent protonic conductor.[13–15] The proton enters the lattice in the form of an OH^- ion occupying an O^{2-} site, and conduction occurs by proton transfer or hopping from one O^{2-} ion to a nearest neighboring one.[16] In the case of Nd^{3+} doping, the basic defects then present at low dopant concentrations are (in Kroger-Vink notation): Nd'_{Ce} and $OH^{\cdot}_{O}$. The present work investigates the low-temperature dielectric relaxation of a 5% Nd-doped sample of $BaCeO_3$ (i.e., $Ba_{0.95}Nd_{0.05}CeO_3$) following pretreatment in water vapor at 600 °C, which results in a proton uptake of close to 3 mol %. For this material, an activation energy for the protonic conductivity of 0.53 eV is observed at temperatures above 240 K; this energy is attributed to the hopping process.[14] This same material has been shown to display two anelastic relaxation peaks with activation energies of 0.51 and 0.63 eV, respectively.[17] These peaks, which also occur at relatively high temperatures, are attributed to variously *associated* defects. The fact that the peak heights increase with the Nd concentration faster than linearly supports this claim.

The electrical relaxation measurements are carried out using an ac bridge covering the frequency range 10 Hz to 100 kHz, and over the temperature range 55–235 K. Data for the conductivity, $\sigma(\omega)$, as a function of angular frequency in this range show steplike behavior suggestive of a relaxation process. Accordingly, we converted these data into ε'', the imaginary part of the complex dielectric constant, through the relaxation[18]

$$\varepsilon''=[\sigma(\omega)-\sigma(0)]/\varepsilon_0\omega, \tag{1}$$

where $\sigma(0)$ is the dc conductivity, extrapolated from higher temperatures, and ε_0 is the permittivity of vacuum. The results, given in Fig. 1, show the presence of a distinct Debye-like relaxation peak, with a second smaller peak at the high-frequency end for the lower temperatures. A striking feature of Fig. 1 is that the curves are nearly identical for the temperatures from 55 to 85 K, including both peaks. Unfortunately, the high-frequency side of the smaller peak is not visible because of the limiting range of the present equipment, and this peak also moves entirely out of range above ~135 K.

In addition to the peaks, these curves show a negative power-law type of variation at low frequencies suggestive of the well-known UDR (''universal dynamic response'') behavior.[18,19] Accordingly, we have carried out least-squares fitting of the data to the following equation:

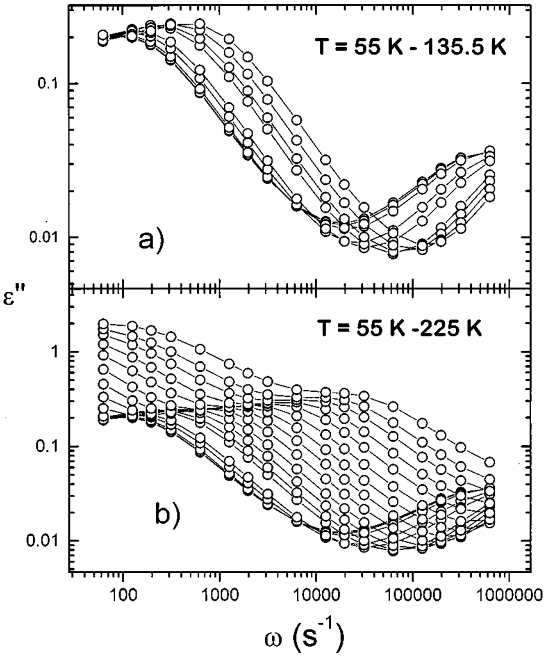

FIG. 1. Data for ε'' as a function of frequency: (a) the lower temperature curves, (b) the full range of measurements. The lines drawn are merely to connect the points.

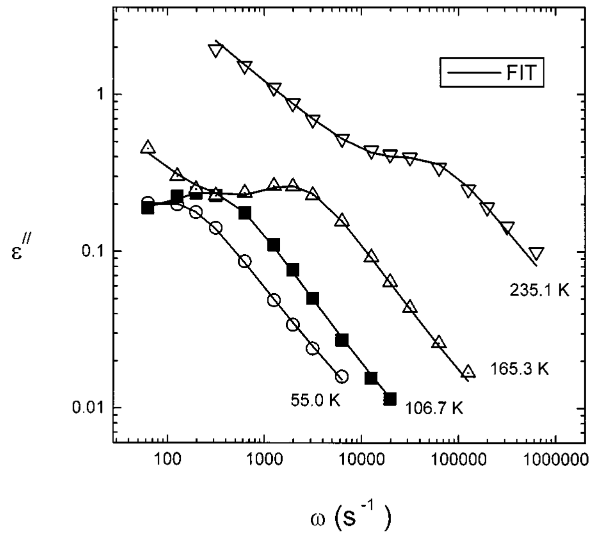

FIG. 2. Data of Fig. 1 at four temperatures fitted to Eq. (2) with parameters given in Table I.

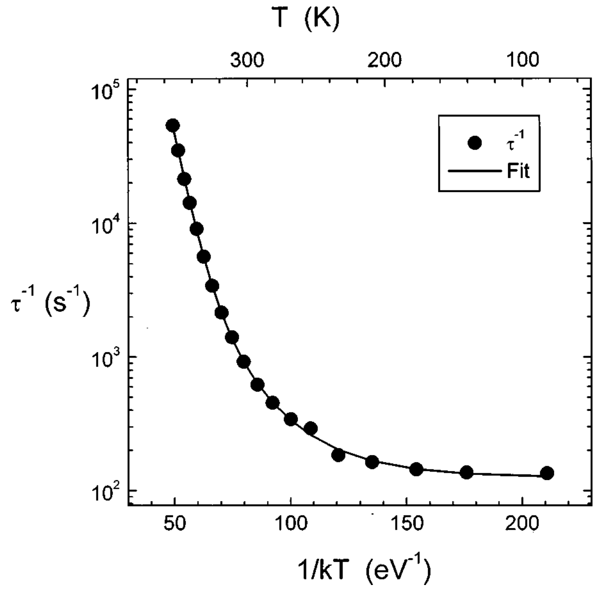

FIG. 3. Plot of relaxation rate τ^{-1} obtained from the peaks of Fig. 1, versus reciprocal temperature. The solid line is the fit to Eq. (3), with parameters given in the text.

$$\varepsilon''=A\omega^{-p}+(\delta\varepsilon)(\omega\tau)/(1+\omega^2\tau^2) \tag{2}$$

ignoring the smaller high-frequency peak. The exponent p is equal to $1-s$, where s is the power exponent of the conductivity in the UDR region, while the second term represents a Debye relaxation peak. Equation (2) gives a good fit to the data, as is shown in Fig. 2, and the parameters obtained from this fitting are listed in Table I. The fact that Eq. (2) fits as well as it does implies that our principal relaxation peak is close to a Debye peak. The results of Table I show that the peak magnitude $\delta\varepsilon$ varies only slowly, if at all, over most of the temperature range of the measurements (above 106 K). The values of the relaxation rate τ^{-1} are plotted vs reciprocal absolute temperature in Fig. 3; they show a striking near independence of temperature below about 85 K, which is, of course, suggestive of a tunneling process. Figure 3 is quite similar to the Arrhenius curves for other, more complex, systems, which involve proton transfer at low temperatures.[1,9,10] Finally, the parameter A of Eq. (2) varies with temperature in a manner similar to τ^{-1}.

Low-temperature Debye relaxation peaks have also been observed in other solid electrolytes that are *oxygen-ion* conductors, notably in CeO_2 doped with trivalent dopants, including Y^{3+}, Gd^{3+}, and Sc^{3+}, and in $CaTiO_3$ doped with Al^{3+}.[20–22] In these cases, the relaxation rate shows strictly classical Arrhenius behavior, involving activation energies well below those for diffusion or the dc ionic conductivities, but with preexponentials $\sim10^{12}$ to 10^{13} sec^{-1}, i.e., comparable to phonon frequencies. The low-temperature peaks in variously doped CeO_2 have been attributed to off-symmetry defect configurations that undergo limited ionic movements over small potential barriers.[21,23] To describe such processes, one invokes the well-known diagram of an asymmetric double-well potential, also known as a ‘‘two-level system,’’ with Δ as the asymmetry energy and V, the mean barrier height.[24] In the present case, where non-Arrhenius behavior is a manifestation of proton tunneling, we must therefore consider proton tunneling through, as well as hopping over, such a barrier. At the lowest temperatures, one expects coherent tunneling, that is, not assisted by phonons, involving a relaxation rate, τ^{-1}, independent of temperature. For a one-phonon process, τ^{-1} varies as $\coth(\Delta/2kT)$, which, for small Δ will not deviate much from a constant.[25] At higher temperatures, one may anticipate multiphonon assisted tunneling. A two-phonon process will asymptotically (at higher temperatures) obey a power law, e.g., T^7, depending on the type of potential.[25–27] Finally at higher temperatures, one may expect over-the-barrier hopping, giving an Arrhenius temperature dependence.

TABLE I. Results of the fitting to Eq. (2) for alternate temperatures. The exponent p is equal to 0.513.

T (K)	$\delta\varepsilon$	τ^{-1} (sec^{-1})	A (sec^{-1})^p
55.0	0.26	135	0.85
75.2	0.27	144	0.86
96.1	0.32	185	0.87
115.9	0.39	342	1.04
135.5	0.40	622	1.45
155.3	0.39	1407	2.55
175.3	0.37	3421	4.92
195	0.36	9096	9.93
214	0.39	21450	18.6
235.1	0.43	53700	42.0

To simplify the description, we have fitted data of Fig. 3 to the following relation:

$$\tau^{-1}=\tau^{-1}(0)+\alpha T^n+\nu_0\exp(-E/kT). \tag{3}$$

The results, given in Fig. 3, show an excellent fit to this rather crude function, indicating that all stages of tunneling behavior are present. The values obtained are: $n=5.3$, $\alpha=2.6\times10^{-9}$, $\tau^{-1}(0)=123$ sec^{-1}, and $E=0.20$ eV, while the low value of the preexponential, $\nu_0 \sim 10^9$ sec^{-1}, indicates that the classical range may not yet be reached at the highest temperatures of our measurements (~200 K). This is not surprising, since multiple phonon processes can give rise to Arrhenius expression for the transition rate with an anomalous preexponential.[25–28] For example, low values of the preexponential are observed for hydrogen diffusion in metals at low temperatures.[3,5]

The observation of a Debye relaxation peak means that a unique dipolar defect is involved. The central question is, then, what is that defect. Further information may be derived from the peak magnitude $\delta\varepsilon$, from which it is possible to estimate the concentration of contributing dipoles c_d. The classical relation involved is[29]

$$\delta\varepsilon = c_d \mu^2 / 3\varepsilon_0 v_0 kT \tag{4}$$

in which μ is the appropriate dipole moment, and v_0 is the volume of the unit cell ($=a^3$, where a is the lattice parameter). We choose the value $\delta\varepsilon = 0.42$ at 225 K to represent, most nearly, the classical range, and $\mu = ea/\sqrt{2}$, where e is the electronic charge, to obtain $c_d = 1.4 \times 10^{-3}$, or 0.14%. This value is considerably smaller than the dopant concentration of 5%, indicating that only special configurations of defects are involved.

Further experiments will be required in order to determine the defects responsible for the observed relaxation peaks. Three such experiments immediately come to mind. First, the peaks should be studied as a function of the Nd concentration, particularly going to lower concentrations. Second, study of the isotope effect, in which deuterons replaces protons, can be very enlightening.[1–3] Finally, to explore the second, smaller, peak more fully, measurements at higher frequencies will be required.

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