# Point-defect contribution to the low-frequency dielectric response of LiTaO<sub>3</sub> at $T > T_c$

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The real and imaginary parts of the dielectric constant of LiTaO<sub>3</sub> have been measured from 20 Hz to 20 kHz at  $T > T_c$  under moderate oxygen partial pressures to prevent dielectric losses from becoming too high. A very large frequency-dependent contribution to the dielectric constant is observed, much higher than the normal ferroelectric contribution, which may be attributed to mobile charged point defects, presumably connected with the nonstoichiometry of the crystal. The data can be interpreted satisfactorily within the framework of a modified Debye model allowing for collective defect migration under the low-frequency ac field.

### I. INTRODUCTION

Lithium tantalate, like its isomorph, lithium niobate, rhombohedral  $R \, 3c$  at room temperature and  $R \, 3c$  at  $T > T_c$ , is a high-temperature ferroelectric material<sup>1</sup> with important technological applications due to its nonlinear optical and photorefractive properties.<sup>2</sup> Those properties are substantially affected by nonstoichiometry and defect structure. Considerable work has been devoted to studying the influence of point defects in these materials, especially in the niobate,<sup>3-7</sup> from which it has been concluded that singly ionized oxygen vacancies and lithium ions play important roles in their high-temperature transport properties.

Since near and above  $T_c$  the intrinsic (ferroelectric) dielectric constant of LiTaO<sub>3</sub> is very high, it may be expected that the strong local field acting on charged mobile defects produces noticeable effects on the low-frequency dielectric response of the crystal.

## **II. EXPERIMENT**

All measurements reported in this investigation were performed on a single-crystal sample of  $LiTaO_3$  of excellent optical quality donated to us by G. Samara of Sandia Laboratory. The sample was disk shaped, 9.6 mm in diameter, and 2.7 mm in thickness, with gold electrodes attached to the main surfaces perpendicular to the ferroelectric c axis. A high-temperature furnace, designed and built in our laboratory, allowed work under a controlled gas atmosphere (usually oxygen) at fixed temperature. The sample temperature was measured independently by a platinum-platinumrhodium(13%) thermocouple using a Fluke digital microvoltmeter, and remained constant to within  $\pm 0.1$  K for each series of measurements of  $\epsilon(\omega)$ . The real and imaginary parts of the dielectric constant were measured with an ESI-2100 video bridge from 20 Hz to 20 kHz, with a relative accuracy of 0.1%. For good reproducibility, the sample was given the same thermal treatment, keeping it for three hours at  $T \approx 1000$  K with the same partial oxygen pressure of 4 kP/cm<sup>2</sup>, before each frequency scan at each fixed temperature near and above  $T_c$ .

### III. RESULTS

Figure 1 shows a log-log plot of  $\epsilon'(\omega)$ , the real part of the dielectric constant, at various temperatures above  $T_c$  as a





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FIG. 2. Log-log plot of the imaginary part of the dielectric constant as a function of frequency at various temperatures  $T > T_c$  for LiTaO<sub>3</sub>. (× at 643 °C,  $\odot$  at 640.5 °C,  $\Delta$  at 635.5 °C, and  $\Box$  at 631 °C).

FREQUENCY (Hz)

function of frequency. It can be observed that from the lowest frequency at which we could measure, 20 Hz, up to frequencies in the range 100–1000 Hz, depending on the temperature of the measurements,  $\epsilon'(\omega)$  goes down with frequency closely as  $1/\omega^2$ , and then it continues going down much more slowly. The values for  $\epsilon'$  in the low-frequency side are truly enormous in comparison with what could be expected on the basis of normal ferroelectric Curie-Weiss behavior. The values for  $\epsilon'$  in the high-frequency side are roughly of the order of those to be expected for normal ferroelectric behavior. It can be concluded from those considerations that charges other than those associated with the

intrinsic ferroelectric dipoles are being pushed back and forth by the low-frequency field over considerable distances.

Figure 2 shows similar results for  $\epsilon''(\omega)$ , the imaginary part of the dielectric constant. In this case, however, the asymptotic frequency dependence at the low-frequency side goes like  $1/\omega$  instead of  $1/\omega^2$ . It may be noted that from  $\omega \approx 4000$  Hz onwards  $\epsilon''$  shows somewhat irregular behavior, especially for high temperatures, which might be connected with new activation mechanisms associated with different charges defects.

Finally, Fig. 3 shows a log-log plot of  $\epsilon''$  vs  $\epsilon'$  which clearly indicates an asymptotic tendency towards  $\epsilon'' \approx K (\epsilon')^{1/2}$ 



FIG. 3. Log-log plot of  $\epsilon''(\omega)$  vs  $\epsilon'(\omega)$  for LiTaO<sub>3</sub>. (T=640.5 °C.)

for large values of  $\epsilon'$  and  $\epsilon''',$  corresponding to low frequencies, and a departure from this behavior at the opposite side.

### **IV. DISCUSSION**

As stated above the observed results for  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$ at low frequencies may be interpreted in terms of the response of mobile charged defects, for instance, those associated with nonstoichiometry, such as ionized oxygen vacancies or lithium ions. Let us examine the possibility of modifying Debye's model<sup>8</sup> of reorientable permanent dipoles (which is the simplest description of "off center" point charges in double wells undergoing a relaxation process) allowing for the possibility of point-charge migration within a network of partially vacant potential wells in the lattice, all acting under the influence of a low-frequency field.

In the straight Debye model for a point charge in a symmetric double potential well (symmetric only, of course, under zero external field E) of height  $\phi$  and separation 2d, it is easy to show<sup>9</sup> that the differential equation governing the relaxation process is given by

$$\frac{dP_d(t)}{dt} = 2p_0 \left( \frac{Nq^2 d^2 E}{k_B T} - P_d(t) \right) \quad , \tag{1}$$

where  $P_d$  is the dipolar polarization per unit of volume (i.e., the contribution to the total polarization associated with the point charges in either one or the other well),  $p_0 = v \exp(-\phi/k_B T) \equiv 1/\tau$  is the jump probability per unit time for each charge, N is the number of point charges per unit volume, q is the magnitude of the charge, and  $E = E_0 \exp(i\omega t)$  is the external field, which should be substituted by the local field when it be appropriate. The stationary  $(t >> \tau)$  solution of Eq. (1) is, of course,

$$P_d(t) = Ned\left(\frac{(qdE_0/k_BT)}{1+i\omega\tau}\exp(i\omega t)\right) , \qquad (2)$$

which leads directly to Debye's expression for  $\epsilon(\omega)$ 

$$\epsilon(\omega) \equiv \epsilon'(\omega) - i \epsilon''(\omega) = \epsilon_{\infty} + \frac{A}{1 + \omega^2 \tau^2} - i \frac{A \,\omega \tau}{1 + \omega^2 \tau^2} \quad . \tag{3}$$

Let us consider the situation for n mobile point charges (or, equivalently, n mobile vacants) which can move, perhaps in zig-zag motion, through a network of periodic potential wells under the influence of a strong local field, which, making use of the Lorentz and Clausius-Mossotti relations, is related to the external field by

$$E_L = \frac{\epsilon_{\infty} + 2}{3}E \quad . \tag{4}$$

If the sample is sufficiently thick, each point charge (or each vacancy) can perform m jumps per half period of the low-frequency ac field, where m is given by

$$m \approx (p_0)(T/2) = \left(\frac{1}{2\tau}\right)(\pi/\omega) \approx 1/\omega\tau \quad . \tag{5}$$

[It may be noted that, strictly speaking, for a sample of thickness l,  $m \approx (1/\omega\tau)[1 - \frac{1}{2}(d/\omega\tau)/l]$ , for  $(1/\omega\tau) < (l/d)$ , and  $m \approx m_{\text{max}} = \frac{1}{2}(l/d)$ , for  $(1/\omega\tau) > (l/d)$ .]

Taking into account the expressions for m and  $E_L$ , Eq. (2)

becomes

$$P_{md}(t) = mnqd \left[ \frac{mqd \left(\epsilon_{\infty} + 2\right)/3k_B T}{1 + i\omega\tau} \exp(i\omega t) \right] , \qquad (6)$$

where  $P_{md}(t)$  now means the polarization associated with mobile charged defects. From this

$$\epsilon_{md}(\omega) = \epsilon_{md}(\omega) - i\epsilon_{md}(\omega)$$
$$= \epsilon_{\omega} + \frac{B}{\omega^2 \tau^2 (1 + \omega^2 \tau^2)} - i\frac{B}{\omega \tau (1 + \omega^2 \tau^2)} , \quad (7)$$

where

$$B = 4\pi nq^2 d^2 (\epsilon_{\infty} + 2)/3k_B T \tag{8}$$

and

$$\tau = \frac{1}{2p_0} \approx \frac{1}{2\nu} \exp(\phi/k_B T) \quad . \tag{9}$$

Then, for  $1 \gg \omega \tau \gg d/l$ ,

$$\epsilon'_{md}(\omega) \approx \epsilon_{\infty} + B/\omega^2 \tau$$

. . .

. .

and

$$\epsilon_{md}^{\prime\prime}(\omega) \approx B/\omega\tau \quad , \tag{10}$$

which show a frequency dependence analogous to the observed behavior for  $LiTaO_3$ , shown in Figs. 1 and 2.

Lithium vacancies, due to the controlled nonstoichiometry inherent in the growth process of LiTaO<sub>3</sub> crystals, are good candidates as possible mobile point-charge defects. We can use available data<sup>10</sup> to estimate *n* from Eq. (8) and then compare it with the relative number of Li<sup>+</sup> vacancies corresponding to the nonstoichiometry parameter x = 0.486, which determines the actual composition of  $x \operatorname{Li}_2O(1-x)\operatorname{Ta}_2O_5$ , leading to an estimated relative abundance of 2.8% Li<sup>+</sup> vacancies.

Using the data for  $T \approx 643$  °C, for which  $\epsilon_{\infty} \approx 1.2 \times 10^4$  at  $\nu \approx 500$  Hz and, from the lowest frequency data,  $B_{\text{expt}} \approx [\epsilon_{md}^{"}(\omega)]^2 / \epsilon_{md}^{'}(\omega) \approx 1.3 \times 10^4$  esu when  $[\epsilon_{md}^{"}(\omega)]^2 >> \epsilon_{\infty}$ ; and using d = 3.765 Å for the Li-Li distance in the lattice, and  $q = 4.8 \times 10^{-10}$  esu for the charge, we get, from Eq. (8),

$$n \approx \frac{B_{\text{expt}}}{4\pi q^2 d^2 (\epsilon_{\infty} + 2)/3k_B T} \approx 0.9 \times 10^{20} \text{ vacancies/cm}^3, \quad (11)$$

which is of the same order of

 $n \approx (2.8/100) V_c^{-1} \approx 1.48 \times 10^{20} \text{ vacancies/cm}^3$ 

determined from nonstoichiometry considerations. The agreement could be somewhat improved if one takes into account that a small number of Ta ions might be occupying Li positions, therefore lowering the resulting number of Li ions. This seems to be the case<sup>2</sup> for LiNbO<sub>3</sub>.

Another point to be checked is the temperature dependence of  $\tau$ , which is related to  $\phi$ , the height of the potential barrier, and to  $\nu(T)$ , which, because of the soft mode accompanying the transition, is presumably very pronounced. Equation (9) leads to

$$(2\pi/\tau)^2 = 4(2\pi\nu)^2 \exp(-2\phi/kT) \quad . \tag{12}$$

From our data, shown in Figs. 1 and 2 at various temperatures, one can get  $\tau(T) \approx \epsilon_{md}'(\omega)/\omega \epsilon_{md}'(\omega)$ , taking into account Eqs. (10) for  $\epsilon_{md}'(\omega) \gg \epsilon_{\infty}$ . The relaxation time obOn the other hand, from Raman scattering<sup>11</sup> data  $C_{\nu} \equiv (2\pi\nu)^2/\Delta T = 2.3 \times 10^{24} \text{ rad}^2/\text{s}^2 \text{ K}$ . Then from Eq. (12), one can estimate

$$\phi \approx \frac{1}{2} k_B T \ln(\nu \tau)^2 \approx \frac{1}{2} k_B T_c \ln(C_{\nu}/C_{\tau}) \approx 1.5 \text{ eV}$$
 (13)

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This value is not unreasonable for an ionic crystal, and is different from the activation energy required to get Frenkel pairs of thermal  $Li^+$  and  $O^{2-}$  vacancy centers.

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