# Infrared spectra and second-harmonic generation in barium strontium titanate and lead zirconate-titanate thin films: "Polaron" artifacts

J. F. Scott, <sup>a),b)</sup> A. Q. Jiang,<sup>a)</sup> S. A. T. Redfern, Ming Zhang, and M. Dawber<sup>a)</sup> Department of Earth Sciences, Cambridge University, Cambridge CB2 3EQ, United Kingdom

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We report infrared absorption spectroscopy and second-harmonic generation data for barium strontium titanate (BST) and lead zirconate-titanate (PZT) ceramic films in the  $3000-5500 \text{ cm}^{-1}$  region. Second-harmonic generation experiments give temperature dependences in accord with oxygen vacancy cluster theory [S. A. Prosandeev, Sov. Phys. JETP **83**, 747 (1996); S. A. Prosandeev, V. S. Vikhnin, and S. Kapphan, Integr. Ferroelectr. **32**, 1047 (2001); J. Phys. Condens. Matter **14**, 4407 (2002)]. A percolation model of vacancy ordering is discussed. The present work shows that earlier data interpreted as polaron spectra in these films were actually artifacts due to interference in the optical apparatus used [B. Guettler, U. Bismayer, P. Groves, and E. Salje, Semicond. Sci. Technol. **10**, 245 (1950]; more recent "polaron" spectra in WO<sub>3</sub> films may also be artifacts [L. Berggren, A. Azens, and G. A. Niklasson, J. Appl. Phys. **90**, 1860 (2001)]. Numerical estimates of the polaron mass  $m^{**} = 16 m_e$  in SrTiO<sub>3</sub> and BST help prove that dielectric data in strontium titanate interpreted as bipolarons [A. Levstik *et al.*, Appl. Phys. Lett. **81**, 4046 (2002)] are also artifacts. © *2003 American Institute of Physics*. [DOI: 10.1063/1.1596715]

# I. INTRODUCTION

The role of polarons in strontium titanate (SrTiO<sub>3</sub>) and its isomorphic mixed crystals with Ba-substitution [barium strontium titanate (BST)] is of interest in understanding its low-temperature properties, including the fact that it (SrTiO<sub>3</sub>) has a relatively high superconducting temperature (~0.25 K) in the form of a slightly oxygen-deficient *n*-type superconductor (~ $n = 10^{19}$  cm<sup>-3</sup>), and that  $T_c$  does not vary monotonically with *n*. This has suggested that it is not a Bardeen–Cooper–Schrieffer system and that bipolarons may play a role in the superconductivity. The notion that bipolarons may be the ground state for superconductivity remains contentious, especially in the case of YBCO.<sup>1,2</sup>

In addition, the role of oxygen vacancies in ferroelectric perovskite oxides is thought to be important in fatigue<sup>3-6</sup> and in long-term degradation<sup>7-13</sup> (time-dependent dielectric breakdown) when these materials are used in thin-film form as switching devices (memories); the latter effect is equally important in high-dielectric paraelectrics such as BST  $(Ba_xSr_{1-x}TiO_3)$ . Earlier studies on lead zirconate titanate (PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> or PZT) showed strong infrared absorption<sup>14</sup> in the  $4000 \text{ cm}^{-1}$  region, attributed (incorrectly, as we show later) to self-trapped polarons at oxygen vacancy sites; but no studies were done as functions of vacancy concentration or temperature. In the present article, we do both and show that these spectra are artifacts. Thus, in the first part of the article, we devote considerable space to a careful refutation of polaron interpretations of infrared data on ferroelectric films. In the second part of the article, we report (nominally forbidden) second-harmonic generation (SHG) in both donor- and acceptor-doped BST as functions of vacancy concentration and temperature; the SHG intensity data I(T) satisfy the oxygen-vacancy-cluster model of Prosandeev *et al.*<sup>15,16</sup>

## **II. INFRARED DATA**

#### A. Sample preparation and experimental setup

The doped and undoped  $Ba_{0.7} Sr_{0.3} TiO_3$  thin films were grown on 4 in. platinum-coated Si wafers via chemical solution deposition, using a propionate-based solution. For further processing details, see Hasenkox *et al.*<sup>17</sup> The dopants were added to be compensational: i.e., Mn was added to go on Ti sites and La on Ba/Sr sites, taking into account the charge compensation by cation vacancies. The single-phase BST films were ~ 300 nm thick and exhibited a polycrystalline structure with columnar morphology. A BST thin film sample and several PZT samples from J. Cuchiaro at Symetrix were also studied as comparisons.

The relationship between macroscopic high-temperature electrical characteristics, oxygen vacancies in undoped and acceptor-doped SrTiO<sub>3</sub> and BaTiO<sub>3</sub> crystals and bulk ceramics has been explained by the point defect chemistry model introduced by Smyth and co-workers.<sup>18</sup> The most detailed survey of donor-doped bulk systems was given by Moos and Härdtl.<sup>19</sup> Modifications to the conventional defect chemistry model have been proposed by Nowotny and Rekas.<sup>20</sup> The impact of grain boundaries on the defect chemistry of perovskite-type titanates has been revealed by Hagenbeck *et al.* as well as M. Vollmann *et al.*,<sup>21</sup> while the phase separation and formation of extended defects on perovskite surfaces has been investigated in detail by Szot *et al.*<sup>22</sup>

For titanate thin films, the first comprehensive study has been published by Hofman *et al.*<sup>23</sup> Recently, it has been found by Ohly<sup>24</sup> that the high-temperature properties of BST thin films differ distinctively from the bulk properties and

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Electronic man. jscopp@csc.cam.ac.ak

indicate that the conventional defect chemistry model perhaps may not apply to thin films.<sup>17</sup> (Note, that Ohly's work is compatible with our x-ray photoemission (XPS) data,<sup>25</sup> and it may explain the observations by Shanthi and Sarma, to be discussed in a later section, that each oxygen vacancy in SrTiO<sub>3-x</sub> contributes not 2.0 electrons to the conduction band but for x>9% contributes only 0.5 *e*.)

The mobility of electronic carriers in alkaline earth titanates has been studied by Choi *et al.*<sup>26</sup> and by Moos and Härdtl.<sup>27</sup>

In the present article, we complement those studies by determining the effect of donor/acceptor doping and temperature on oxygen vacancies microscopically through their SHG intensity.

Bruker IFS 113v and Bruker IFS 66v spectrometers were used to record infrared spectra. The 113v spectrometer was used for low-temperature measurements, whereas a microscope attached to the 66v spectrometer was used to measure spectra at room temperature and at high temperatures. Globar lamps, Hg Cd Te detectors and KBr beam splitters were chosen for measurements in between 650 and  $6000 \,\mathrm{cm}^{-1}$ and tungsten lamps and CaF2 beam splitters were chosen for measurement between 4000 and  $8500 \,\mathrm{cm}^{-1}$ . For hightemperature measurements, the samples were heated under Ar atmosphere in a heating stage which was coupled with quartz windows and a water-cooling system. Lowtemperature spectra were measured with the samples mounted inside a closed-cycle Leybold cryostat equipped with KRS5 windows. The substrates (double-polished Si wafers) and Au mirrors were used as references. The experimental results showed that the use of the Si wafer or Au mirror did not lead to significant spectral variations in the near-infrared region. Single-beam reflectance spectra of the references and the samples were recorded with an instrumental resolution of  $4 \text{ cm}^{-1}$  in normal (for the microscope) or near normal (for the 113v spectrometer) incident condition, and the resultant spectra were calculated with  $\log_{10}(I_{\text{sample}}/I_{\text{reference}})$ , where *I* is the single-beam reflectance intensity.

#### **B.** General spectral characteristics

# 1. Line shapes and peak energies expected for polarons in perovskite oxides

The absorption spectrum  $\sigma(\omega)$  for small polarons is expected to be symmetric (unlike asymmetric absorption peaks for large polarons) and approximately Gaussian. However, our spectral data (Fig. 1) agree with neither those shapes nor for those calculated for large polarons. The only basis for concluding that the original bulk strontium titanate infrared data were "small" polarons was that the absolute absorbance measured by Baer was too small<sup>28</sup> by a factor of  $\times 5$  to fit the "large polaron" model of Gurevich *et al.*<sup>29</sup> even including the correction factors of Feynman *et al.*<sup>30</sup> However, even Reik,<sup>31</sup> while concluding that strontium titanate is described by a small polaron model, emphasizes that this material represents a "marginal case" between large and small. And both Schirmer<sup>32</sup> and Kudinov *et al.*<sup>33</sup> stress that the high-energy tail has "prevented complete interpretation of free small polaron.



FIG. 1. Infrared data at 293 K [fitted to a Eq. 1(a)] for strontium titanate crystal, showing the strong phonon peak (see Refs. 46 and 47) at 1280 cm<sup>-1</sup>; and for BST ceramic film, showing transmission interference.

laron absorptions." For the polaron coupling coefficient appropriate to BST, Emin calculated<sup>34</sup> the absorption position, width, and shape. The absorption peak lies near  $h\omega = 2W_p$ , where  $W_p$  is defined as the polaron energy; and its half width at half height is typically a few times  $h\omega_0$ , where  $h\omega_0$  is the energy of a characteristic phonon in the material (to be discussed later). Guettler *et al.*<sup>14</sup> and Reik and Heese<sup>35</sup> give the absorption as a function of frequency  $\omega$  by a slightly different approximation:

$$\sigma(\omega) = (\sigma_0/\omega) \exp\{-(h\omega - W_D - 4W_H)^2/(8W_H h\omega_0)\},$$
(1a)

where  $W_D$  is the difference in energy between empty and filled states,  $\omega_0$  is the phonon energy, and  $W_H$  is the polaron hopping energy, approximately equal to half the polaron binding energy  $W_p$ , and h is Planck's constant. (Note that this is a three-parameter fit, plus a scale factor.) In Eq. (1a), the term  $4W_H$  in the numerator is a function of assumed dimensionality and, hence, number of nearest neighbors. In a [3D] tetrahedrally coordinated system (four nearest neighbors) Schirmer has shown<sup>32</sup> it is 16/3 and in two-dimensional hexagonal arrays that it is six rather than four; it is eight for the Holstein two-well system. Dimensionality effects have also been considered by others.<sup>36,37</sup> Alexandrov *et al.*<sup>38</sup> have replaced the denominator by a term  $\eta^2$  which yields Eq. (1) only in the limit of extremely small polarons, but  $\eta$  is not separately and independently measurable. And Emin has argued<sup>39</sup> that the term  $h\omega_0$  in the denominator in Eq. (1) is actually the thermal average of the energy of the phonon with the strongest polaron coupling coefficient, which is  $\langle n(T) + 1/2 \rangle h \omega_0$  and is approximated at low temperatures by the zero-point energy  $h \omega_0/2$ . This introduces an important factor of approximately 2 in the fitting of data, and so for low- $T(kT \leq h \omega_0)$ , we rewrite Eq. (1a) as

$$[3D]: \sigma(\omega) = (\sigma_0/\omega) \exp\{-(h\omega - W_D - 4W_H)^2/$$

$$(8\langle n+1/2 \rangle W_H h \omega_0)\}$$

$$= (\sigma_0/\omega) \exp\{-(h\omega - W_D - 4W_H)^2/$$

$$(4W_H h \omega_0)\}; (1b)$$

and in the most general case, the denominator of the exponential in Eq. (1b) may be given by the Bose factor of phonon occupancy  $\langle n+1/2 \rangle$  as

$$8 W_{H}h\omega_{0}\langle n+1/2 \rangle = 8 W_{H}h\omega_{0}\{1/2 + [\exp(h\omega_{0}/kT) - 1]^{-1}\}; \qquad (1c)$$

We emphasize here that the experimental temperature dependence for linewidths in the feature in Fig. 1 do not satisfy either Eqs. (1a) or (1c); that is, the width is neither temperature independent, nor does it vary as rapidly as kT or as the Bose factor in Eq. (1c). This is the first indication that the spectra in Fig. 1, or Ref. 14, are not due to polarons.

For [2D] the formula equivalent to Eq. (1a) is

$$[2D]:\sigma(\omega) = (\sigma_0/\omega) \exp\{-(h\omega - W_D - 6W_H)^2/(8W_H h\omega_0)\},$$
(1d)

and for

$$[1D]:\sigma(\omega) = (\sigma_0/\omega) \exp\{-(h\omega - W_D - 8W_H)^2/(8W_H h\omega_0)\},$$
(1e)

for a two-well one-dimensional system. In general, assuming a dimensionality lower than [3D] does not improve or worsen the fit to experimental spectra; it merely yields a different value of polaron energy (half the peak energy, or a third, etc.).

The spectral shape for absorption from large polarons is quite different; it is asymmetric, non-Gaussian, and given above a threshold  $h\omega = 3W_p$  by

$$\sigma(\omega) = (\sigma_0/\omega)(kR)^3 [1 + (kR)^2]^{-4},$$
(1f)

where  $hk = [2m^*(h\omega - 3W_p)]^{1/2}$ . This curve [Fig. 1(b)] has a very steep slope on the low-frequency side and differs negligibly for [3D] and [2D] large polarons, unlike the smallpolaron case. Note that this formula does not contain any phonon energy.

Let us digress also to consider what the phonon frequency  $\omega_0$  is: The Froehlich interaction between electrons and phonons is Coulombic and involves only longitudinal optical (LO) phonons of the long wavelength. For a crystal with more than two atoms per primitive cell, such as strontium titanate or BST, there will be several LO phonon branches (three in the case of SrTiO<sub>3</sub>). However, in this family of materials, one branch (with transverse optical branch near 110 cm<sup>-1</sup> in SrTiO<sub>3</sub> or BST at ambient temperatures) has by far the strongest oscillator strength (polaron coupling coefficient  $\alpha = 4.5$ ). The frequency of the LO phonons in strontium titanate or BST associated with this TO

is  $815 \text{ cm}^{-1}$  (despite the fact that two weakly infrared-active LO/transverse optical (TO) pairs lie between the energies at 110 and 815 cm<sup>-1</sup>). Thus, the first question is whether  $\omega_0$  in Eq. (1) is 117 (TO) or  $815 \text{ cm}^{-1}$  (LO) or some weighted average of all branches and all wave vectors q. The conventional polaron theory of Landau or Feynman originally modeled carriers interacting only with long-wavelength LO phonons LO(q=0), but beginning with the Holstein model a short-range electron-lattice interaction was invoked similar to the deformation potential in covalent crystals. Eagles<sup>40</sup> for rutile and Salje<sup>41</sup> for  $WO_{3-x}$  have used rather highfrequency phonons. Reik<sup>31</sup> used  $\langle \omega \rangle = 692 \text{ cm}^{-1}$  for SrTiO<sub>3</sub>, corresponding in his notation to  $h\langle \omega \rangle \beta/2 = 1.7$  where  $\beta$ = 1/kT. This is the average of the three LO phonon energies weighted by the polaron coupling coefficient  $\alpha$  for each, from Barker: viz.,  $\alpha = 0.2$  for  $\omega_1(\text{LO}) = 170 \text{ cm}^{-1}$ ;  $\alpha = 1.2$  $\omega_2(\text{LO}) = 473 \text{ cm}^{-1}$ ; and  $\alpha = 4.5$  for  $\omega_3(\text{LO})$ for  $=773 \text{ cm}^{-1}$ . But others (e.g., Guettler *et al.* for PZT) have inserted very low TO or local-mode energies in these expressions and not LO frequencies. Perhaps the best (most selfconsistent) work is that of Calvani et al.42 who used the local-mode frequencies they measured independently, arising from oxygen vacancies in the same cuprate samples used to measure the polaron absorption. Almost all early theoretical publications on polarons ignore the LO/TO difference, along with wave vector dispersion, apparently erroneously thinking that both are small. Since  $\alpha = 4.5$  in SrTiO<sub>3</sub> is based on the LO frequency of  $815 \text{ cm}^{-1}$  and  $\alpha$  varies as  $\omega_0^{-5/2}$ , this is an important point. To use  $\alpha = 4.5$  but a value of  $\omega_0$  differing from  $815 \text{ cm}^{-1}$  is not self-consistent. In TiO<sub>2</sub>, the important  $\omega_0$  is evaluated as  $\omega_0 = \omega(\text{LO}) = 807 \text{ cm}^{-1}$  (Eagles),<sup>40</sup> and in  $\varepsilon$ -WO<sub>3</sub>, Salje finds<sup>41</sup>  $\omega_0 = 560 \text{ cm}^{-1}$  for polarons and  $\omega_0$  $=742 \text{ cm}^{-1}$  for bipolarons, both values approximating the known oxygen-stretching phonon energy range. We argue in the present article that in Eq. (1) the value of  $\omega_0$  that would be required to fit data for strontium titanate, BST or PZT does not correspond to any known optical phonon branch  $\omega(\text{TO}; q=0)$ , and that in particular the strongly Froehichcoupled LO phonon at 815 cm<sup>-1</sup> plays no particular role. Note that the system dimensionality affects the number of nearest neighbors, for the cubic BST structure, with six nearest neighbors for [3D] hopping; four for [2D]; two for [1D]; and only one for Holstein's original two-site model. In fact, Holstein in his early work<sup>43</sup> pointed out a difference of  $\times 2$ in the polaron bandwidth for the [3D] model of Yamashita and Kurosawa,<sup>44</sup> compared with his [1D] model, though it was by no means apparent that this arose from dimensionality arguments. In his original fit of polaron data on strontium titanate,<sup>45</sup> Barker avoided these problems by simply fitting data to a Gaussian whose peak position and linewidth were both free parameters, subject to no constraints at all. In our judgement, this is not sufficient to establish even that the spectra are due to polarons (as opposed to point defects or d-d absorption bands, or midgap states due to oxygen vacancy clusters).

None of our least-squares fits to the equations described herein yield a characteristic phonon energy corresponding to known q=0 phonons nor to the one-phonon density of states peak of approximately  $120 \text{ cm}^{-1}$  (from the two-phonon Raman spectra).<sup>46</sup>

The form of Eq. (1) is appropriate when the width of the rigid-ion (electron band calculated ignoring ion relaxation) polaron band is greater than  $W_H$ ; in this case, Firsov showed that the width of the absorption line is nearly temperature independent.<sup>47</sup> Generally, however, polaron absorption widths will depend upon temperature. In the opposite limit, in which the rigid-ion bandwidth is much less than  $W_p$ , the temperature dependence of the polaron absorption peak linewidth is given explicitly, in the present notation, by Bogomolov *et al.*<sup>48</sup> and also by Alexandrov *et al.*<sup>49</sup> as

$$\sigma(\omega) = (\sigma_0/\omega) \exp\{-(h\omega - 2W_p)^2/8W_pkT\},\qquad(2)$$

(here k is Boltzmann's constant) but Eq. (2) is valid according to Bogomolov only above 600 K (i.e., half the Debve temperature  $\Theta/2$ ) and, therefore, not useful in fitting our T-dependent data. This form derives from Eq. (1c). Note that in contrast to Eq. (1a) and (1b) this is only a one-parameter fit plus a scale factor; in general, it is impossible to fit experimental data for most materials to this equation, because  $W_{p}$  determines the peak position and also the linewidth of the polaron absorption, which in reality are independent, and the experimental polaron width increases much more slowly than linearly with T. [Unfortunately, this key Eq. (2) is misprinted and is dimensionally incorrect in the review by Austin and Mott.]<sup>50</sup> No equivalent *T*-dependent low-temperature expression is known to us. Bogomolov et al. also estimate bound polaron energies in TiO<sub>2</sub> (and related compounds with  $TiO_6$  octahedra such as BST) as

$$\sigma(\text{peak}) = 0.7 \text{ eV} = 5600 \text{ cm}^{-1}, \tag{3}$$

in reasonable agreement with the peak (which we will show to be an artifact) in present experiments, or those of Ref. 14. The theoretical estimate of the polaron absorption peak energy from  $Appel^{51}$  is (present notation):

$$W_D + 4W_H = 0.357 \,\alpha^2 h \omega_{\rm LO} = 5900 \,\rm cm^{-1}$$
 (4)

(where  $\alpha$  is the polaron coupling coefficient and *h* is Planck's constant; note especially that  $\omega_{LO}$  is not  $\omega_0$ ) and is also in fairly good agreement with the present experiment. (Fig. 1). [There is an algebraic error in Ref. 45, Eq. (4.11), p. 213; Appel gives our Eq. (4) incorrectly as, in his notation,  $J - E_0 = 0.1395 \alpha h \omega_0$  rather than  $J - 3E_0 = 0.357 \alpha h \omega_0$ , where 2*J* is the polaron bandwidth and  $E_0 < 0$ .]

[We emphasize the agreement between energy estimates in Eqs. (3) and (4) above and the spectral features in Fig. 1, or Ref. 14 because these were the important "red herrings" that produced erroneous interpretations of the data.]

Note that if we use  $\alpha = 4.5$ , we must use<sup>52,53</sup>  $\omega_{LO} = 815 \text{ cm}^{-1}$ , since the former was derived by Barker self-consistently from the latter for each LO phonon mode as

$$\alpha = (2\pi e^2 / h\omega_{\rm LO}^2) (2m_e \,\omega_{\rm LO})^{1/2} (Z/\varepsilon_\infty). \tag{5}$$

The high-frequency tail, emphasized in Fig. 1(b), should have been an early give away that these data are not due to polarons, but unfortunately another possibility has been discussed for  $SrTiO_3$  by Reik,<sup>31</sup> who suggested two explanations: (1) That the optical phonons in strontium titanate are

highly dispersive, and (2) that a nonadiabatic version of Eagles' theory<sup>54</sup> would explain the tail. We show that the real reason is that the spectra in Fig. 1 and Ref. 14 are artifacts due to interferences in the 300 nm films used, which unfortunately give an apparent peak in absorption (actually a dip in transmission) near energies predicted for polarons.

# 2. Linewidths and self-consistent values of $\gamma = W_p / \omega_{LO}$ : False clues

It has been of theoretical interest to examine the ratio of polaron energies  $W_p$  and phonon frequencies  $\omega_0$ . For PZT, Guettler et al.<sup>14</sup> fitted  $\omega_0 = 130 \text{ cm}^{-1}$ ,  $W_D = 0$ , and  $4W_H$ = 4080 cm<sup>-1</sup>, where  $W_p = 2W_H$ . However, in early theories, the phonon which dominates polaron interaction must be the long-wavelength q=0 LO phonon, and as just discussed, this lies<sup>52,53</sup> at  $815 \text{ cm}^{-1}$  in SrTiO<sub>3</sub> and in Sr-rich BST. (This is very nearly the same value of  $\omega_0$  as found in WO<sub>3</sub> and other perovskites by Salje and Hopman.)<sup>55</sup> And so, we have a similar question regarding the ratio  $\gamma$  as to whether it is  $\omega_0$ or  $\omega_{LO}$  which enters  $\gamma$ . We note that the ratio of parameters  $\gamma = W_p / \omega_0 = 15.7$  for PZT from Guettler *et al.* fails to satisfy (by  $\times$  3) all known theoretical models. That is, Ref. 14 is not self-consistent regarding peak energies and linewidths. For strontium titanate, if we examine the experimental ratio of  $\gamma = W_p / \omega_0$  for the value  $\alpha = 4.5$ , we must use the value  $\omega_{\Lambda\Omega} = 815 \,\mathrm{cm}^{-1}$  used by Barker to derive that value of  $\alpha$ . That is,  $\gamma$  has been calculated theoretically as a function of  $\alpha$ , and  $\alpha$  was calculated as a function of  $\omega_{\rm LO}$ ; hence, one must calculate  $\gamma$  self-consistently with this value of  $\omega_{LO}$ . The ratio (neglecting  $W_D$ ) of

$$\gamma = W_p / \omega_{\rm LO} = 2400 \,{\rm cm}^{-1} / 815 \,{\rm cm}^{-1} = 3,$$
 (6)

for the feature in Fig. 1 is plausible; this was a second "red herring" in assigning interference features to polarons in perovskites such as PZT and strontium titanate. Austin and Mott<sup>50</sup> have noted that this ratio is generally of order  $\gamma$  = 5.0 and for some models is 4.0, and Bogomolov *et al.* find  $\gamma = W_p / \omega_{\rm LO} = 4.0$  in TiO<sub>2</sub>; for values of  $\alpha = 4.5$ , eight different theoretical estimates<sup>56-63</sup> give  $W_p / \omega_{\rm LO} = 4.5$  to 4.9.

Finally, we can estimate the number density of trapped electrons in our BST films from the polaron peak position, using Barker's strontium titanate data;<sup>46</sup> for a peak near  $4200 \text{ cm}^{-1}$ , we estimate *n* as a few times  $10^{20} \text{ cm}^{-3}$ . This is in accord with other estimates of near-surface vacancy concentration for ABO<sub>3</sub> perovskites.<sup>64–67</sup> This is another plausibility argument that contributed to the misidentification of a spectral artifact in Ref. 14.

#### 3. Vacancy-concentration dependence

a. Of polaron absorption intensities: Another false clue. Our experimental data show very little change in absolute absorption intensity as the number of carriers n is varied via donor or acceptor doping. At first, this seems unreasonable for polarons, since the intensity should be linearly proportional to n, but as Barker<sup>46,53</sup> has pointed out, the imaginary part of the dielectric susceptibility is given by

$$C = cn/\omega_{\rm LO}^2,\tag{7}$$

 $\varepsilon''$ 



FIG. 2. Near-infrared transmission for 0.7% donor doping (La) and 0.7% acceptor doping (Mn) at 292 K.

where *c* is a constant, and due to coupling between plasmons and LO phonons,  $\omega_{LO}^2$  increases approximately linearly with *n*. For  $\omega > 2000 \text{ cm}^{-1}$  Barker finds experimental confirmation of his theoretical prediction that

$$\lim (n/\omega_{\rm LO}^2) = n/n = \text{constant as } n \to \infty.$$
(8)

b. Of absorption peak energies. The four expressions given in Eqs. (1)–(4) all generally agree: 4900 cm<sup>-1</sup>  $\pm$ 20%, theory and experiment, for polaron absorption peak energy. We note also that there is a simpler relationship which can be used to estimate the polaron absorption peak energy for polarons that are not too small: One-half the Froehlich polaron coupling coefficient  $\alpha$  is<sup>68</sup> the number of LO phonons dragged by each electron, and since the phonons involved have energy,<sup>52,53</sup> 815 cm<sup>-1</sup> and the polaron coupling coefficient in SrTiO<sub>3</sub> (and hence, BST) is known<sup>53</sup> to be  $\alpha$ =4.5 for the infrared mode of strongest oscillator strength, the product of these two numbers gives a rough estimate of the polaron energy  $W_p$  as

$$W_n = \alpha \omega_{\rm LO}/2 = 0.5 \times 4.5 \times 815 \,{\rm cm}^{-1} = 1834 \,{\rm cm}^{-1}$$
, (9a)

and peak absorption energy at

$$h\omega = 2W_p = 3668 \,\mathrm{cm}^{-1},$$
 (9b)

in reasonable agreement with experiment<sup>14</sup> (the slightly higher experimental value could conceivably involve some bipolaron contribution to the spectra, as discussed for perovskite oxides by Salje<sup>41</sup> and by Kostur and Allen).<sup>69</sup> Varying the oxygen-vacancy concentration of BST by donor doping with La (0.7%) or acceptor doping with Mn (0.7%) gave small but reproducible changes in the intensity, shape, and peak position in the absorption spectra (Fig. 2) near  $4000 \,\mathrm{cm}^{-1}$ ; we know now that these were simply due to changes in index of refraction and hence to the interference wavelength peak in the films studied. The conductivity at 1.0 V of the La-doped specimens was  $10^{-6}$  A/cm<sup>2</sup>; for the Mndoped specimens,  $2 \times 10^{-8}$  A/cm<sup>2</sup>; and for the undoped, 3  $\times 10^{-7}$  A/cm<sup>2</sup>. In our donor-doped specimen, a 2.5% shift in peak position from 4150 to  $4050 \,\mathrm{cm}^{-1}$  was observed. [A shift of the same sign and magnitude in polaron absorption peak frequency with donor or acceptor doping was also unfortunately observed for TiO<sub>2</sub> by Bogomolov and Mermin.<sup>70</sup> The profile (and width) of the BST peak and that in PZT are almost identical, which is expected in a simple oxygen-vacancy polaron model.]<sup>71-74</sup>

# 4. Polaron mass m<sup>\*\*</sup> in strontium titanate and barium strontium titanate

Despite the fact that much of the present article is devoted to explaining why prior data are *not* due to polarons, the theoretical considerations we provide about polaron mass, etc., may prove useful in other contexts.<sup>1,2</sup>

We note that the effective (band) mass<sup>75,76</sup>  $m^*$  in SrTiO<sub>3</sub> is ~5.1  $m_e$  and, hence, the polaron mass is<sup>56</sup>

$$m^{**} = m^{*} (1 - 0.0008 \alpha^{2}) / (1 - 0.167 \alpha + 0.0034 \alpha^{2})$$
  
= 3.1 m^{\*} = 16 m<sub>e</sub>, (10)

where  $m_e$  is the free electron mass. This value is in excellent accord with recent values from dielectric measurements and a model.<sup>2</sup> (This value assumes  $\alpha = 4.5$ , which, in turn, was based on an LO phonon energy of  $815 \text{ cm}^{-1}$ .) The polaron mass  $m^{**}$  in PZT was previously estimated<sup>14</sup> as  $3m^{*}$ , using the Froehlich approximation, in very close agreement with the value  $3.1 m^*$  for BST in Eq. (10). (The strong coupling limit of Landau and Pekar<sup>77</sup> gives an even larger estimate of  $m^{**} = m^* \alpha^4 / 48 = 9 m^*$ ; however, SrTiO<sub>3</sub> and BST are not in this very-small-polaron limit.) Austin and Mott have pointed out that  $m^{**} > 10 m_e$  is sufficient to prevent the formation of a cryogenic metallic state<sup>50</sup> in SrTiO<sub>3</sub>, and we note that reduced strontium titanate does not always become metallic; it can remain semiconducting down to mK temperatures (although it becomes superconducting).<sup>78-81</sup> This also supports the numerical value of  $16 m_e$  in Eq. (10). Note that some band structure models of strontium titanate have both light and heavy conduction electrons. Thus, it is also possible that the mass we calculate is for the heavy electrons, which could form polarons, whereas a metallic conduction arises from the light electrons; this is the point of view of Gong et al., to be discussed later. The polaron coupling coefficient  $\alpha = 4.5$  is relatively large in SrTiO<sub>3</sub>, producing a small or intermediate polaron (larger than the radius Kostur and Allen<sup>69</sup> calculate for the typical perovskite polaron of 50% of the lattice constant  $a_0$  in which the Rice-Sneddon model<sup>82</sup> is more accurate than the Landau-Pekar<sup>76</sup> treatment of the Froehlich Hamiltonian. We note that according to Devreese et al.,  $\alpha = 4.5$  is sufficient to form a bipolaron ground state in [2D] but not [3D]. Therefore, [2D] localization of oxygen vacancies may be of paramount importance in bipolaron stability in these materials.

Very recently, our polaron mass value of 16 has helped show that the bipolaron model of Levstik *et al.*<sup>83</sup> for dielectric anomalies at 37 K cannot be correct in strontium titanate; Ref. 83 is now known to be due to artifacts (series resistance in the dielectric bridge).

#### 5. Temperature dependence

The temperature dependence of our absorption spectra is shown in Figs. 3 and 4. Increasing T moves the absorption



FIG. 3. Apparent absorption spectra in BST at elevated temperatures (290 K<T<655 K). Traces are displaced along the ordinate axis by arbitrary amounts for clarity.

peak to lower frequencies in BST. The shift is rather small. This disagrees with the small polaron case considered by Reik (strongly T dependent).

Rather, more important than the temperature shift of the infrared peak position is the fact that the spectral linewidth widens with increasing temperature. A narrowing of width, unusual in solid-state physics, was predicted in the original polaron theory of Yamashita and Kurosawa,<sup>44</sup> who find spectral linewidth  $\Delta \omega$  given by

$$\Delta \omega = c_1 \exp(-A/kT), \tag{11}$$



FIG. 4. Apparent absorption spectra in BST at cryogenic temperatures (18 K<T<245 K); sample from J. Cuchiaro at Symetrix Corp. Ordinate is absorption in arbitrary units.

where  $c_1$  is a temperature independent constant and A is a characteristic energy; this dependence was also emphasized by Reik.<sup>31</sup> However, our data disagree qualitatively with Eq. (11) and quantitatively with Eq. (2).

According to standard defect chemistry theory, one would expect that substitution of  $La^{+3}$  for  $Sr^{+2}$  would result in oxygen wave function distortion and  $Ti^{+3}$  -like 3*d* states in the gap, which increase conductivity. This absence has also been observed by Higuchi *et al.*<sup>84,85</sup> for Mn and Nb substitutional for Ti in SrTiO<sub>3</sub> single crystals and suggests that much of the La did not substitute for Sr in our BST samples. It may have accumulated at grain boundaries in the form of  $La_2O_3$ . This shows the pitfalls of naively applying defect chemistry models to fine grained ceramic films. See Hofman *et al.*<sup>23</sup> for a discussion of this point. Finally, we note that our experiments on strontium bismuth tantalate (SBT) thin films revealed no polarons in the infrared spectra, as with pure SrTiO<sub>3</sub>

An additional complication to interpreting the data in Fig. 1 is that the broad peak lies very near in frequency to that of the characteristic O-H hydroxyl vibrations, which in the gas phase are always around  $3700 \text{ cm}^{-1}$ . It is known that hydrogen always goes into SrTiO<sub>3</sub> as hydroxyl ions, attaching to one of the Ti-O bonds to form Ti-OH [we note parenthetically that it is possible to get 100% hydroxyl occupation in a stable perovskite,<sup>86</sup> e.g., bernalite, Fe(OH)<sub>3</sub>]. We carried out measurements to high (650 K) and low (20 K) temperatures, with the results shown in Fig. 4. By going to low temperatures, we had hoped to see other features, such as the disappearance of any polaron peak (it disappears at 10 K in rutile)<sup>49</sup> or the infrared absorption of sharp-line OH spectra superimposed on the broad peak, but the lines at 3652 and 3756 cm<sup>-1</sup> are merely surface water. However, in hydroxl-structure perovskites such as Fe(OH)<sub>3</sub>, the O-H mode is shifted<sup>86</sup> substantially, from 3700 cm<sup>-1</sup> to lower energies near 3100 cm<sup>-1</sup>, and we tentatively interpret the broader absorption in Fig. 1 near  $3100 \text{ cm}^{-1}$  as due to OH clusters. Not shown in our spectra are the lines at lower frequencies; in addition to seeing the well-known infraredactive phonons of BST, we see the strong Si-O and Ti-O substrate lines at  $\sim 1100$  and  $600 \,\mathrm{cm}^{-1}$  respectively, identified by Craciun and Singh,<sup>87</sup> in our BST.

#### 6. Relationship to resistivities

It has been claimed, that in rutile, there is an empirical relationship<sup>88</sup> between the peak absorption coefficient  $I(\max)$  due to polarons and the electrical resistivity  $\rho$  (~3 ohm cm) of the samples. Near 300 K, it is given by

$$I(\max) \operatorname{cm}^{-1} \rho(\Omega \operatorname{cm}) = 5.3 \times 10^2 \,\Omega, \tag{12}$$

and is only 20% less at 700 K. We do not think that the relationship in Eq. (12) can be justified for any wide-bandgap oxide, such as  $SrTiO_3$ , BST, or rutile, since none of those materials exhibit ohmic conduction (they are Schottky or Frenkel–Poole conductors at voltages less than a few volts and Fowler–Nordheim above that, except at cryogenic temperatures). Therefore, one cannot *define* a resistivity in ohm cm for them in order to test Eq. (12). No relationship similar to Eq. (12) is expected even if the material were ohmic.

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FIG. 5. Infrared transmission peak energies vs T in BST film.

#### 7. Final disproof of the polaron interpretation

By varying the thickness of the thin-film samples studied, we find that the broad feature in Fig. 1 (and in PZT samples) varies exactly as predicted for thin-film transmission interference, and its shape corresponds closely to the predicted interference shape. In addition, if a wider range of wavelengths is measured (Fig. 5), additional interferences are observed. Hence, if one does wish to look for polarons in ferroelectric thin films, these interferences must be shifted out of the wavelength region of interest by carefully selecting film thicknesses. The aforementioned rather protracted account is designed to prevent other investigators from studying artifacts. Relatively, few publications in solid-state physics describe failures: We simply failed to measure polarons in BST or PZT films.

## **III. SECOND-HARMONIC GENERATION DATA**

### A. Experimental setup

The intensity of optical frequency-doubled light is usually several orders of magnitude less than that of the fundamental wave. For this reason, a high-intensity high-power laser light source is needed if optical SHG signals are to be detected from illuminated crystals. We used a *Q*-switched Nd–YAG laser with a high peak power and low jitter as the fundamental light source, with a 20 ns pulse width and 200 mJ energy pulse energy. This equates to a peak pulse power of around 10 MW, in a beam of 6 mm diameter, or around  $3.5 \times 10^7$  W cm<sup>-2</sup>. Measurements of SrTiO<sub>3</sub> were taken in transmission geometry, with the beam focused to a diameter of around 100  $\mu$ m. The beam was attenuated by passing it through beam splitters in order to avoid sample damage. The

laser was triggered using an external trigger from a control computer. The sample was held on an x-y stage, positioned vertically with the laser beam passing horizontally through it. The stepper motor controllers for the x-y stage were polled and set using the data acquisition and control computer, such that the beam could be rastered across the sample.

The light passing through the sample was filtered, to remove the fundamental wave, using a high-power interference beam splitter. A narrow band-pass (532 nm) filter was then used to exclude background light, and frequencydoubled light (532 nm) was measured using a lowbackground photomultiplier. In addition to the light measured at the sample, the fundamental beam was split before falling on the sample, and part passed through a second standard quartz sample, filtered in the same way as that at the sample, and passed to a photomultiplier, from which a measure of the incident intensity was made. Thus, the intensity at the sample was measured with respect to the intensity at a reference, for each shot of the laser. The signal from the photomultipliers was passed to an analogue-to-digital converter board on the computer via low-noise preamps, giving several decades of range to a high sensitivity. Further filters are placed along the optic axis of the instrument to exclude light from the laser flash lamp, the furnace, and interference of frequency-doubled light created at the sample with frequency-doubled light created at the quartz reference. The data acquisition and control software worked through a simply operated graphical interface, and incorporated pulse checking for each laser pulse measured. Checks were made to ensure that only pulses for which the reference and sample pulse peak maxima coincide and for which the onset of the reference and sample peaks coincident in the time domain were accepted.

A polished (100)-oriented single crystal of  $SrTiO_3$  was used to measure the spatial dependence of the frequencydoubled intensity of light, shown in Fig. 6. Further temperature-dependent measurements of a BST thin film were made in reflection geometry with an unfocused beam impinging upon a sample attached to the cold finger of a He-circulating cryostat. Data were collected between 20 and 270 K and the temperature-dependent SHG intensity is shown in Fig. 7.

#### B. Vacancy-concentration dependence

In Prosandeev's model,<sup>15,16</sup> the SHG intensity should be proportional to oxygen-vacancy concentration, with the *ansatz* that the vacancies form correlated extended defects; with each oxygen vacancy is associated a local dipole, and the correlation length describing the orientation of nearby dipoles is the parameter of interest. The SHG intensity is often described as proportional to "cluster size",  $\langle S(T) \rangle$ ; however, this term is misleading since  $\langle S(T) \rangle$  refers to the expectation value of the polarization of the vacancy dipoles (hence, correlation length), and is not closely related to the geometric size of the cluster. In particular,  $\langle S(T) \rangle$  and, hence, the SHG intensity both become vanishingly small as  $T \rightarrow \infty$ . The SHG intensity at 77 K is expected to be twice as



FIG. 6. SHG data (293 K) for a  $SrTiO_3$  crystal. Coordinates are real space (*x*, *y*), SHG intensity (*z*).

strong as at ambient and, at 4 K, is expected to be nearly one order of magnitude larger than at room temperature.

# C. Temperature dependence

Prosandeev *et al.*<sup>15,16</sup> also give an expression (Eq. 13) for SHG intensity I(T) as a function of temperature<sup>89,90</sup>

$$I(T) = I_0 [T_s \coth(T_s/T) - T_0]^{-1/2} + I_B, \qquad (13)$$

where  $T_s$  is a saturation temperature (known to be between 35 K and 38 K from the temperature at which the dielectric susceptibility flattens out upon cooling). The only adjustable parameter in Eq. (13) is  $T_0$ , which in isomorphic KTaO<sub>3</sub> is 0.48Ts; <sup>15</sup> so we take  $T_0 = 17$  K as a starting value in the least-squares fit of the present work. The constant  $I_B$  in Eq. (13) is not in Prosandeev's single-crystal theory but was added by us to represent the temperature-independent contribution of grain boundaries (and surfaces) in ceramic BST specimens.

Salje *et al.*<sup>91</sup> first introduced this saturation term involving  $[T_s \coth(T_s/T) - T_0]^{-1}$  in a different context. Kleemann *et al.*<sup>92,93</sup> later used this expression for SrTiO<sub>3</sub>:Ca. In the latter model, the saturation temperature was assumed to be somewhat smaller and given by  $T_s = T_E/2$ , where  $k_B T_E$  is the energy of an Einstein oscillator corresponding to the experimentally measured soft optical mode of long-wavelength q= 0 ( $T_E$ =34 K in SrTiO<sub>3</sub>; 23 K in Ca:SrTiO<sub>3</sub>).

Equation (13) is tested in Fig. 7 for both pure  $rac{SrTiO_3}$  from Kapphan *et al.*<sup>89</sup> and our BST data, and the single unknown parameter  $T_s$  is an adjustable parameter fitted to the data; the known value in  $rac{KTaO_3}{T_0} = 17$  K (the saturation temperature of the dipole pseudospins) agrees with values known independently for  $rac{SrTiO_3}{r_0}$  from both dielectric data and theoretical models.<sup>90</sup> Mueller<sup>94</sup> has used exactly the same value of  $T_s = 38$  K for  $rac{SrTiO_3}{r_0}$  as we have, and Dec and



FIG. 7. (a) SHG intensity vs temperature for strontium titanate reduced in hydrogen (diamond symbols) or vacuum (triangles). Solid curves are our fits [to Eq. (12)] with  $T_s = 38$  K and  $T_0 = 37$  K (H reduced) and  $T_0 = 30$  K (vacuum reduced) and  $I_B = 0$ . (b) SHG intensity in BST vs temperature (293 nm MOD film with no top electrode). Solid curve is [a fit to Eq. (12) with]  $T_s = 38$  K,  $T_0 = 25$  K, and  $I_B$  contributing 2.0 units of intensity. The anomalies at 77 K and 273 K are due to liquification of nitrogen and freezing of water on the sample surfaces and are intentionally shown as examples of artifacts that can occur.

Kleeman<sup>92,93</sup> have argued that although  $T_0$  might be much smaller than 38 K (nearly zero) in pure SrTiO<sub>3</sub>, it will be of the order of 20 K in SrTiO<sub>3</sub> mixed with CaTiO<sub>3</sub> (or perhaps BaTiO<sub>3</sub>). Thus, all independent sources support our value for this parameter for BST. The fit is very sensitive to the ratio  $T_s/T_0$ .

## **IV. PERCOLATION OF POLARIZATION**

Prosandeev's work<sup>15,16</sup> suggests that the ordering of oxygen vacancies in ABO<sub>3</sub> perovskites should give rise to a phase transition which is first order and of a percolation nature, rather than displacive (it is not clear that this is the 2  $\times 2 \times 1$  superlattice [actually 5<sup>1/2</sup> $\times$ 5<sup>1/2</sup> $\times$ 1] self-ordering actually observed in SrTiO<sub>3</sub>). To test this hypothesis, we have fitted the activation enthalpy data H(x) for oxygen–vacancy motion from Steinsvik *et al.*<sup>95,96</sup> The results are shown in Fig. 8. The exponent fitting the dependence of H upon va-



FIG. 8. Graph of activation enthalpy (see Ref. 98) for displacement of oxygen vacancies in strontium titanate vs vacancy concentration, showing percolation exponent (see Ref. 99) of  $\gamma = 7/4$  near a critical vacancy concentration of 7%.

cancy concentration *x* is  $\gamma = 1.78 \pm 0.10$ , which agrees within the small ( $\pm 5\%$ ) experimental uncertainty with the value 7/4 expected for a cubic lattice,<sup>97</sup> that is,

$$H = H_0 \left( x_c - x \right)^{\gamma},\tag{14}$$

with  $x_c = 7\%$  (i.e., SrTiO<sub>2.80</sub>) taken as the vacancy concentration at which  $2 \times 2 \times 1$  superlattices self-organize, as evidenced by bright planes in the high-resolution electron micrographs (HREM); this adds support to Prosandeev's general idea of *polarzation percolation*.

In a different context, it is clear from the Kelvin-probe work of Nowotny and Rekas<sup>98</sup> that there exists a great difference between the oxygen–vacancy concentration near the surface and in the bulk of barium titanate on Pt electrodes (and devices made from related compounds such as BST/Pt). This is manifested in the fact that the work function change versus oxygen partial pressure varies<sup>98</sup> with exponent 2.5  $\pm 0.3$  for surfaces (Kelvin-probe measurements) but 4.4  $\pm 0.4$  for bulk. Those authors interpret their results as evidence for a "segregation boundary layer" which they suggest may involve adsorbed species, primarily chemisorbed oxygen. They infer that there is a strong gradient in oxygen vacancy concentration in these ABO<sub>3</sub> perovskites, as in our PZT fatigue model.<sup>1–3</sup>

An important addition to Prosandeev's model is the insight from Becerro *et al.*<sup>99</sup> (and earlier work by Grenier *et al.*)<sup>100–102</sup> that the oxygen–vacancy clusters in perovskites are not isotropic but, in fact, develop along [101] directions and, at higher vacancy concentrations, along planes. However, this may be true only in Fe-doped SrTiO<sub>3</sub> or CaTiO<sub>3</sub> and not in reduced SrTiO<sub>3</sub>, because Gong *et al.*<sup>103</sup> find only very short-range ordering in the latter (and a slight preference for vacancies at one site in the tetragonal phase of reduced SrTiO<sub>3</sub>; note that the room-temperature tetragonal phase of reduced SrTiO<sub>3</sub> is *not* the same phase as unreduced SrTiO<sub>3</sub> exhibits below 105 K, but one without a doubled-unit cell). Most recently Marion *et al.*<sup>99</sup> have shown that large (×100) electrical conductivity increases occur at 1300 K in 7% vacancy-concentration CaTiO<sub>3</sub>. The known phase diagram shows that this is not due to a displacive structural phase transition; and they conclude that it is a percolative transition from a low-conductivity ordered-vacancy state below 1300 K to a disordered ionic conductor. Janovec (private communication) has pointed out that the low-energy (uncharged) domain walls in PZT are along [110] directions, parallel to the chains of oxygen vacancies inferred by Becerro *et al.*; this supports our model of domain wall pinning by ordered vacancies.<sup>3,5</sup>

#### V. RUTHERFORD BACKSCATTERING DATA

Rutherford backscattering spectroscopy data for BST have been shown elsewhere<sup>104</sup> which yield a peak hydrogen concentration of 150 ppm (0.15 at.%); the concentration is not uniform but is maximum in a layer 147 nm from the ferroelectric surface, i.e., midway through the 300 nm thick film. Concentrations in PZT and SBT are lower and peak closer to the surface. Hydrogen is known not to substitute interstitially in perovskite oxides but to form hydroxl ions at oxygen sites. The strongly detrimental effects of even small amounts (<4%) of H<sub>2</sub> on PZT and SBT were detailed very recently<sup>104</sup> and include the fact that in the presence of H, Pt-electroded SBT partially decomposes into elemental Bi (as reported by Hartmann *et al.*)<sup>104</sup> and PZT partially decomposes at 823 K to yield 0.3% Pb.

# VI. CONCLUSIONS: RELATIONSHIP BETWEEN SECOND-HARMONIC GENERATION AND INFRARED DATA

The present spectroscopic study does not confirm the presence of strong polaron coupling in BST or strontium titanate films. The assignment and quantitative analysis are ambiguous even in the early "classic" infrared studies of Barker or Reik on bulk material (Klinger<sup>105</sup> has remarked that  $d \leftrightarrow d \operatorname{Ti}^{+3}$  transitions also occur in this same 0.6–0.8 eV energy region, but Bogomolov et al.<sup>106</sup> and Austin and Mott<sup>50</sup> have pointed out that the absorption in  $TiO_2$  (or BST) is  $50 \times$  too large for that interpretation, on the basis of comparisons between  $TiO_2$  and  $Ti_2O_3$ ). It had originally been thought<sup>106</sup> that small polarons were much more likely in TiO<sub>2</sub> than in SrTiO<sub>3</sub>, based upon the anisotropic manyvalley band structure model of the latter material by Kahn and Leyendecker;<sup>107</sup> however, that model is no longer viewed as even qualitatively correct.<sup>108,109</sup> The conclusion of Austin and Mott that  $TiO_2$  is qualitatively different from SrTiO<sub>3</sub> in this respect is disproved by the uv reflectivity spectra of both as obtained by Cardona<sup>110</sup> and by Kurtz.<sup>111</sup> (The argument of Austin and Mott was based on the assumption that there are no d electrons in  $TiO_2$ , but that there are in stoichiometric SrTiO<sub>3</sub>. We emphasize that pure SrTiO<sub>3</sub> has a  $d^0$  configuration and is an insulator by virtue of its band structure, not a correlated Mott-type insulator.) We see (Fig 1) no polaron absorption whatsoever in pure (unreduced) strontium titanate.

Polarons could, in principle, dominate the electrical transport properties of BST under many conditions of practical interest. We note however that<sup>51</sup> "the mean free path for electrons in a polar crystal is determined from the band mass

 $m^*$  and not the polaron mass  $m^{**}$ , since the electron– phonon interaction is short range and unscreened." The SHG data and the activation enthalpy data of Steinsvik show that oxygen vacancy clustering is important and that Prosandeev's model of polarization percolation is appropriate for these ferroelectric oxides; we not only confirm Prosandeev's model in quantitative detail for SHG intensity, but we show that Steinsvik's activation enthalpies fit the expected 7/4 percolation exponent. We note that evidence for oxygenvacancy self-ordering into planar structures has very recently also been obtained in Bi<sub>2</sub>Ti<sub>4</sub>O<sub>11</sub> (which consists of natural layers of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> and TiO<sub>2</sub>); <sup>112</sup> in this system, the oxygen vacancies order within the TiO<sub>2</sub> planes.

The relationship between the SHG data on oxygen clustering and the infrared data, interpreted in terms of polarons, is manifested by the recent studies of Crandles et al.<sup>113</sup> on highly reduced strontium titanate. They carried out infrared studies of SrTiO<sub>3</sub> for carrier concentrations from 10<sup>18</sup> to  $10^{21} \text{ cm}^{-3}$  and observed that the midinfrared reflectance near  $4000\,\mathrm{cm}^{-1}$  is temperature independent, as we observe here for BST. Based upon that, they conclude that, contrary to earlier interpretations by Barker,<sup>46</sup> by Lee et al.,<sup>114</sup> and by Reik and Heese,<sup>115</sup> these are not polaron spectra. They also reject the interpretation by Calvani et al.<sup>116</sup> of intervalley carrier scattering. They conclude that the midinfrared spectra are probably due to oxygen clustering, which Shanthi and Sarma<sup>117</sup> have shown to produce midgap states, although they also conclude that the plasmon is weakly *localized*. Thus, even in bulk, the interpretation of polaron spectra remains moot.

We end this article with mention of a puzzling coincidence: As Shanthi and Sarma discuss, based upon the Hall measurements of Gong et al.,<sup>103</sup> for SrTiO<sub>3-x</sub> each oxygen vacancy contributes only 1.0 conduction electron contrary to the 2*e* expected from defect chemistry models, for x < 9 $\pm 2\%$ ; and for x > 9% contributes only 0.5 e. (By comparison, substituting La for Sr contributes exactly 1.0 e, as expected from defect chemistry.)<sup>118</sup> This unexplained threshold at which the defect chemistry changes qualitatively has a value remarkably similar to the level  $x = 7 \pm 2\%$  at which Steinsvik's data show self-ordering of oxygen vacancies. This unexpected coincidence has not been noted previously in literature and has a suggested explanation.<sup>119</sup> Perhaps oxygen vacancies above  $\sim 8\%$  each contribute 0.5 electron to the conduction band plus 1.5 that remain trapped as a polaron at the vacancy site. The hypothesis of Gong et al. is that this "filling factor" of  $\sim 0.5 e$  per oxygen vacancy arises from the light and heavy electron conduction bands in strontium titanate, and that only  $\sim 25\%$  of the electrons liberated by oxygen vacancies wind up in the light electron band; hence, the other 75% contribute negligibly to conduction because of their very heavy mass. A relevant model with delocalized states that become localized by impurities has been discussed for oxides by Alexandrov et al.<sup>120</sup>

We emphasize that oxygen vacancy clustering in these materials is a surface or near-surface phenomenon, not a bulk property.<sup>121</sup> The kinetics of oxygen vacancies and stoichiometry changes at surfaces in  $SrTiO_3$  have been analyzed very recently by Maier *et al.*<sup>121</sup> Thus, despite a number of careful

studies of oxygen–vacancy behavior in strontium titanate, <sup>103,121–123</sup> further work will be required on thickness dependence. Work by Maglione<sup>124</sup> uses polarons to explain the low-temperature dielectric and ultrasonic loss anomalies<sup>125</sup> in strontium titanate. Based upon earlier studies of relaxation,<sup>126</sup> he provides a "quantum polaron" theory connecting polarons and oxygen–vacancy clustering. Although no explicit connection to Prosandeev's model is provided, this may be made through the earlier work of Vugmeister and Glinchuk.<sup>127</sup>

Notable is the fact that Maglione invokes polaron coupling with the lowest frequency *transverse* optical phonon (TO)—not the LO. This is the "soft mode."<sup>128</sup> But Maglione's model of dielectric loss at cryogenic temperatures differs from that of Scott<sup>129</sup> or of Kityk *et al.*<sup>130</sup> Other very recent studies of self-trapped electrons in perovskites include the theoretical models of Kotomin *et al.*<sup>131,132</sup> which explain the green luminescence in KTaO<sub>3</sub>.

Recent results from a theoretical investigation by Donnerberg and Birkholz<sup>133</sup> show unambiguously that the electronic ground state of oxygen vacancies  $V_0^+$  in BaTiO<sub>3</sub> is of  $e_g$  symmetry, as predicted by Eglitis *et al.*,<sup>134</sup> whereas the electron paramagnetic resonance spectra of Ti<sup>+3</sup>, <sup>135,136</sup> as well, show that it is  $t_{2g}$ . This implies that the EPR of Ti<sup>+3</sup> polarons trapped near oxygen vacancies do not recombine with the oxygen-vacancy ground state—an unexpected and unexplained wrinkle which merits additional study. Perhaps of even greater importance, Schirmer *et al.* (in press) have shown that BaTiO<sub>3</sub> exhibits a mixture of small Anderson-localized polarons and intermediate polarons is detected.

We emphasize in closing that, in addition to artifacts that can arise from optical studies of thin films, intrinsic differences should also be present between polarons in thin films and in bulk. As emphasized by Xi *et al.*<sup>137</sup> and Petzelt *et al.*,<sup>138</sup> the defect density and strain in films of pure strontium titanate reveal very different soft-mode behavior in films and different roles for oxygen vacancies. These differences should be studied further via film spectroscopy, now that the pitfalls are understood.

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