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Bismuth disproportionation in $BaBiO_3$ studied by infrared and visible reflectance spectra

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$BaBiO_3$, the end member of the system $(Ba,K)(Pb,Bi)O_3$, raises a number of problems that are interesting to study as a step towards the understanding of superconductivity in certain compounds of the series. Using infrared and visible reflectivity spectroscopy, the thermal evolution of the reflectance of a $BaBiO_3$ single crystal is reported, analyzed, and compared to an oxygen-deficient sample. Oxygen effective charges are also evaluated. The results are discussed within the framework of possible bismuth disproportionation and its consequences in terms of bismuth-oxygen distances, crystal symmetry, oxygen breathing mode, charge density wave, opening of a gap at the Fermi energy, or polaron formation.

INTRODUCTION

With the discovery of high-T_c superconductivity in copper oxides by Bednorz and Müller,[1] the interest in conducting and superconducting oxides has been renewed. Among these materials, $BaBiO_3$ and its related compounds with doping of K in Ba sites and Pb in Bi sites is the object of a long-standing controversy. One of the most attracting features of this family is the existence of the highest T_c for noncopper (and more generally nonmagnetic ion) based superconductors [$T_c = 30$ K in $Ba_{0.6}K_{0.4}BiO_3$ (Refs. 2 and 3)]. This is also—with certain alkali-doped fullerenes—the highest T_c in nonlayered structures. It seems that a fundamental point to help the comprehension of superconductivity in these compounds passes through the understanding of the semiconducting origins of the end member $BaBiO_3$. In this material, bismuth atoms are sitting at a +4 site. The electronic configuration of Bi^{4+} would be $5d^{10}6s^1$. With its unpaired s electron, such an ion would be expected to be magnetic and the compound to be metallic due to the half-filled conduction band. But, experimentally, the compound is not magnetic. On the other hand, whereas band structure calculations did predict a metallic behavior for $BaBiO_3$,[4–6] (except Ref. 7), experimental works[8,9] show that the material is a semiconductor. One possibility would be to consider the chemical composition $BaBi^{III}O_{2.5}$, but the oxygen stoichiometry has been studied by several authors and the actual oxygen composition has been checked to be O_3. To solve this problem, a charge disproportionation

$$2\ Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$$

is generally considered, based on the aversion of bismuth for the +4 valence. Indeed, while Bi_2O_3 and Bi_2O_5 compounds do exist, BiO_2 does not exist. If this situation prevails, several properties are expected to derive from the disproportionation. (i) Since Bi^{3+} and Bi^{5+} have different ionic radii (1.03 and 0.76 Å, respectively, in octahedral configuration),[10] two different Bi-O distances are expected. (ii) The opening of a gap at the Fermi energy is also expected. (iii) Photoelectron spectroscopy should provide a signature of both bismuth ionization states. (iv) Structural distortions with respect to the simple perovskite structure are expected to occur due to both Bi-O distances. (v) The actual crystalline structure should have several consequences in terms of lowering of symmetry and lifting of degeneracies of certain excitations, phonons, for example.

In the literature of the last decade, the bismuth disproportionation has been discussed in terms of a charge-density-wave (CDW) instability by many authors.[9,11] The CDW may open a gap at the Fermi surface, consistent with the semiconducting character of $BaBiO_3$. But other experimental data seem to be contradictory. X-ray diffraction indicates a monoclinic distortion with respect to the simple cubic perovskite. Neutron diffraction experiments[12] reported different Bi-O distances, viz., 2.28 and 2.12 Å, results conformed by Thornton and Jacobson.[13] Later, a more detailed study performed by Chaillout and Santoro[14] showed that, depending on previous thermal treatments undergone by the sample, the Bi(1)-O distance ranges from 2.20 to 2.26 Å with a Bi(1) "effective valence" which varies from +3.9 down to +3.5, while the Bi(2)-O distance ranges from 2.19 to 2.13 Å [with Bi(2) effective valence varying from +4 to +4.4, respectively]. More recent extended x-ray-absorption fine structure (EXAFS) measurements give Bi(1)-O=2.11 Å and Bi(2)-O =2.29 Å.[15] The differences of bond lengths are thus found to be smaller than what would be expected from the sum of ionic radii. For example, in the cubic double perovskite compound $Ba_2(Ba_{2/3}Bi^{III}_{1/3})Bi^{V}O_6$, where the complete disproportionation is effective (the compound is an insulator), the Bi^{V}-O distance is only 1.89 Å.[16] The Bi^{III}-O reaches 2.5 Å. However, the latter value should be regarded as an upper limit because in this compound the Bi^{III} ion shares the site with barium which has a larger ionic radius (1.35 Å in octahedral coordination). In $BaBiO_3$, one may of course consider (i) possible incomplete disproportionation as suggested by the effective valences which fit powder neutron diffraction data, and (ii) possible partial Bi-O hybridization which would also minimize the charge transfer. Note, however, that photoemission measurements hardly found a Bi^{5+} signature.[17–19] Only a broadening of the $4f$ peak has been reported. Another question to be raised is whether the charge disproportionation is static or dynamic, or part of each. By "dynamic," we consider the vibrational motion within an oxygen breathing mode pattern which would significantly renormalize the local chemical bonding, at the time scale of

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atomic vibrations. This renormalization can happen even at a lower frequency if the motion is highly anharmonic because instantaneous Bi^{3+} and Bi^{5+} configurations are more stable than the ion ionized four times.[20,21]

Infrared reflectivity spectroscopy has been used by several authors to try to conclude about the points summarized above. For example, de Hair and Blasse[22] claimed there is no bismuth disproportionation. Conversely, Tajima and co-workers[9,11] concluded to two signatures of bismuth disproportionation in the reflection spectrum, one as a "forbidden" mode in the infrared, and another near 2 eV. In addition to giving information about the symmetry of the structure, infrared reflectivity spectroscopy also allows one to deduce the ionic effective charges, a key point in the discussion above. The temperature dependence (4 K up to room temperature) of the infrared and visible reflection spectra of $BaBiO_3$ is reported here and analyzed within the framework of the controversy raised by this compound. We also present the effect of reducing the sample ($BaBiO_{2.91}$) in the spectra and analyze its consequences.

EXPERIMENTAL

A $BaBiO_3$ single crystal has been obtained by progressive crystallization of molten BaO and Bi_2O_3. Samples obtained in this way present a monoclinic distortion of the simple cubic perovskite structure. Reduction to $BaBiO_{2.91}$ is obtained by treating the sample for 3 h at 750 K under an atmosphere of Ar with 5% hydrogen. Loss of oxygen was verified by thermogravimetric analysis (TGA) measurements. Reflection spectra have been recorded by means of a Bruker IFS 307 spectrometer which consists of two Michelson interferometers working in tandem and covering the spectral ranges 10–15 000 and 3000–42 000 cm^{-1}. The liquid helium cryostat has been equipped with polyethylene, KRS5, and Suprasil 300 windows covering energy intervals up to 500, 400–8500 cm^{-1}, and above 8000 cm^{-1}, respectively. Temperature control accuracy of 0.5 K has been obtained. With this apparatus, we have obtained reflectance spectra ranging from 20 to 22 000 cm^{-1} between 4 K and room temperature.

MODELING INFRARED AND VISIBLE SPECTRA

In order to fit the data, we have used the factorized form of the dielectric response.[23] This model is based on the fact that, from Maxwell equations, transverse (TO) and longitudinal (LO) optical modes are complex poles and zeros of the dielectric function, respectively. Writing this factorized form of the dielectric function in terms of TO and LO frequencies (Ω) and dampings (γ), one obtains

$$\frac{\varepsilon}{\varepsilon_\infty}=\prod_j \frac{\Omega_{\mathrm{LO}j}^2-\omega^2+i\gamma_{\mathrm{LO}j}\omega}{\Omega_{\mathrm{TO}j}^2-\omega^2+i\gamma_{\mathrm{TO}j}\omega}. \tag{1}$$

Reflectivity near normal incidence is related to the dielectric response via

$$R=\left|\frac{\sqrt{\varepsilon}-1}{\sqrt{\varepsilon}+1}\right|^2. \tag{2}$$

An advantage of Eq. (1) when compared to the more commonly used Lorentz oscillator formula is that Eq. (1) is phenomenological and thus can be used to fit any excitation which contributes to the dielectric response. As an example, we can set $\Omega_{\mathrm{TO}}=0$ and $\Omega_{\mathrm{LO}}=\Omega_{\mathrm{plasma}}$ and arrive at an extended Drude model which has shown to be very useful in conducting and superconducting oxides.[23–25] One can also relate dampings to the interactions of elementary excitations.[23] The most simple version of the anharmonic model states that the relaxation time of an excitation can be understood, at first order, by means of interaction of this excitation with other excitations, with energy and momentum conservation:

$$\omega_0=\omega_1\pm\omega_2, \tag{3a}$$

$$\mathbf{k}_0=\mathbf{k}_1\pm\mathbf{k}_2. \tag{3b}$$

Equation (3a) represents the energy conservation where ω_0 is the excitation frequency and ω_1 and ω_2 are the excitations with which ω_0 interacts in a third-order anharmonic process. Equation (3b) represents the conservation of momentum. Positive signs stand for additive processes, and negative for subtractive. For acoustic phonons, by lack of lower energy excitations, subtractive processes are dominant but for higher energy excitations additive processes contribute more, statistically. Evaluation of the thermal behavior of the damping function with bosonlike excitations yields

$$\gamma=|V^{(3)}|^2(n_1+n_2+1), \tag{4}$$

where $V^{(3)}$ is an interaction potential and n_1 and n_2 are Bose-Einstein population factors. In Eq. (4) only additive processes are considered. It can be rewritten as

$$\gamma=|V^{(3)}|^2\left(\frac{1}{e^{\hbar\omega_1/kT}-1}+\frac{1}{e^{\hbar(\omega_0-\omega_1)/kT}-1}+1\right). \tag{5}$$

In Eq. (5), ω_0 and ω_1 are those of Eq. (3a).

ANALYSIS OF REFLECTIVITY SPECTRA

Figures 1 and 2 show infrared and visible reflectivity spectra obtained for $BaBiO_3$ between 4 and 300 K. The spectra consist of two parts: (i) phonons at low frequencies and (ii) a reflection band near 15 800 cm^{-1} (~1.96 eV).

A. Low frequencies

The far-infrared response ($\omega<1000$ cm^{-1}) of $BaBiO_3$ is presented in Fig. 1. As already reported in the literature, at room temperature, it is typical of insulator (or semiconducting with low charge carrier concentration) spectra at any temperature from 4 up to 300 K. The expected three main bands corresponding to the F_{1u}-type modes of the simple perovskite structure are complemented by several additional modes, consistent with the noncubic actual structure: a fourth strong mode at low frequency plus a number of very weak additional modes that are most clearly resolved at 4 K. Pei *et al.*[26] refined the structure of $BaBiO_3$ and obtained the space group $I2/m$ between 150 K and room temperature and a slightly modified group $P2/m$ below 150 K. Both space groups have most symmetry elements in common, since their

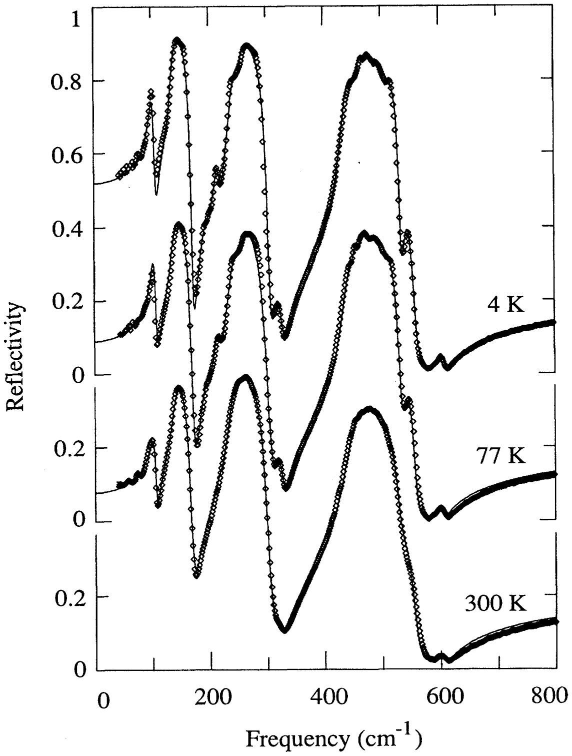

FIG. 1. Far-infrared spectra of $BaBiO_3$ between 4 and 300 K. Symbols are experimental data and solid line best fits obtained via Eqs. (1) and (2).

point group is $2/m$ in both cases (C_{2h} in Schoenflies notation). For this point symmetry, Sugai *et al.*[27] calculated by group theory the number of vibrational modes and obtained

$$7A_g \oplus 5A_u \oplus 7B_g \oplus 11B_u .$$

Excluding the acoustic (translational) modes—$1A_u \oplus 2B_u$—one is left with 15 possible infrared active modes ($6A_u \oplus 9B_u$). As a result, all the peaks present in the low-frequency region could be attributed to normal mode vibrations. One remaining open question, however, is why the oscillator strength of the main additional low-frequency mode is of the same order of magnitude as that of the strongest modes deriving from the F_{1u}-type modes.

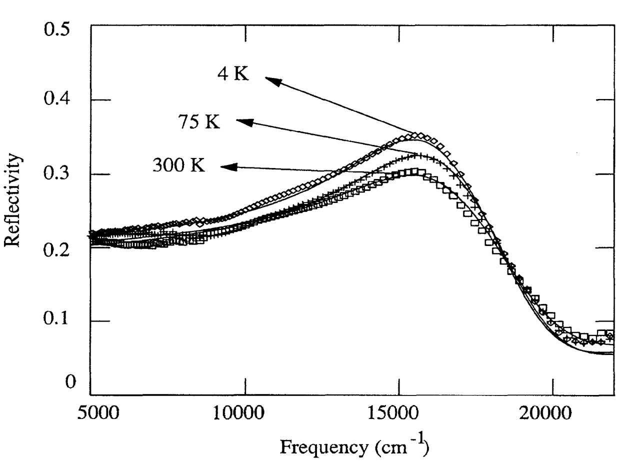

FIG. 2. Temperature dependence of 2 eV excitation in $BaBiO_3$. Solid lines are best fits to experimental data (symbols).

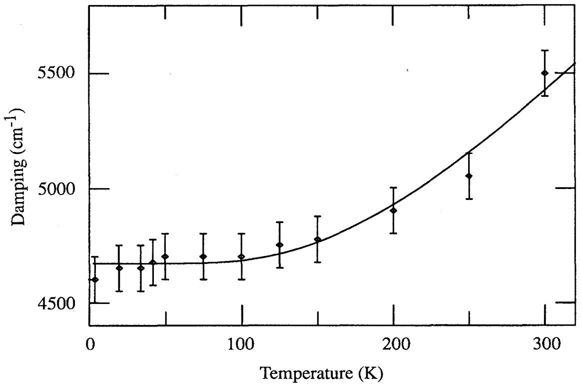

FIG. 3. Thermal evolution of relaxation time of 2 eV excitation in $BaBiO_3$. Symbols are dampings obtained from fitted spectra. The solid line is the behavior expected from an anharmonic coupling of this 2 eV excitation with a phonon-type mode (possibly oxygen breathing mode).

B. Visible spectra

Figure 2 shows the visible part of the spectra with a reflection band observed near 2 eV (symbols are experimental data and the full curve is the best fit to them). This band has been attributed to a gap opened by the CDW instability.[9,11] However, the origin of this CDW is controversial. On one hand, if it is very tempting to assign the origin of the CDW to a charge disproportionation of $Ba_2(Bi^{3+}Bi^{5+})O_6$, on the other hand, many attempts in measuring both Bi valence states failed.[17–19,22] The thermal evolution of damping for this band (linewidths of the TO and LO components were found to be equal at each temperature) is shown in Fig. 3. It is found that the temperature dependence can be fitted by means of Eq. (5). Taking $\omega_0 = 16\,000$ cm^{-1} and $\omega_1 = 410$ cm^{-1}, one obtains the solid curve of Fig. 3 (the fitted value for the interaction potential is $|V^{(3)}|^2 = 4670$ cm^{-1}). This result means that the 2 eV (ω_0) excitation is relaxed via an anharmonic process involving phonons with an average frequency centered at about 410 cm^{-1}, not very far from the oxygen breathing mode near the Brillouin zone boundary.[28] In other words, we interpret the origin of the linewidth via an anharmonic coupling between two bosonic excitations, ω_0-ω_1 presumably belonging to the same dispersion branch as ω_0, and a lattice vibrational mode ω_1.

C. Oxygen effective charge

Effective charges can be evaluated from the splitting of polar vibrational optical modes into TO and LO components via

$$\sum_j (\Omega_{j\mathrm{LO}}^2 - \Omega_{j\mathrm{TO}}^2) = \frac{1}{\varepsilon_v V} \sum_k \frac{(Ze)_k^2}{m_k}, \tag{6}$$

where the sum in the left-hand side of the equation is over all atoms k of mass m_k contained in the elementary volume V.[20] ε_v is the dielectric constant of vacuum. Equation (6) together with charge neutrality $\Sigma_k(Ze)_k=0$ can be used to determine effective charges in a diatomic system. For compounds with three different atoms, we need an estimate of the effective charge of one of them. Note that each term in the right-hand side of Eq. (6) is proportional to the inverse of the mass of the atoms. Thus, the determination of the effective charge of lighter atoms is more accurate.

Using this procedure we have calculated the average oxygen effective charge. The result $(Ze)_o=-1.11e$ is found to be practically independent of the values attributed to the effective charge of the barium ion allowed to vary between $+1$ and $+2$. This confirms the earlier evaluation $(Ze)_o=-1.18e$ by Uchida *et al.*[29] This result means that the Bi-O bond is partly hybridized and that charge disproportionation should be considered with a factor which should not exceed 0.55 times an electron charge. This result parenthetically is consistent with the "effective valence" reported by Chaillout and Santoro[14] from their Rietveld refinements of neutron diffraction data.

INFRARED REFLECTIVITY OF REDUCED $BaBiO_3$ AND DISCUSSION

Another way to interpret the peaks in excess of the three expected F_{1u}-type modes derived from the cubic perovskite structure is based upon the interpretation proposed by Calvani *et al.*[30] of infrared spectra in the Nd_2CuO_{4-y} family. The intensities of extra peaks appearing in the far infrared are both temperature and doping dependent, whereas peaks attributed to phonons are less dependent on these external parameters. Based on an electron-phonon interaction, they have interpreted these extra peaks as the signature of trapped electrons (polarons, and more precisely small polarons). Sugai[31] also argued for a small polaron scenario in $Ba(Pb, Bi)O_3$ compounds, based on an analysis of Raman measurements. He also claimed that the absence of isolated spins was a signature of bipolarons rather than single polarons. Polarons are electrons or holes trapped by the ionic lattice, and interact strongly with the lattice. Rüscher, Heinrich, and Urland[32] also proposed a bipolaron absorption in this system, but in their work, the polaronic signature is attributed to the 2 eV band.

Oxygen nonstoichiometry is expected to create holes and, therefore, to increase the number of polarons. In Fig. 4 we compare the phonon spectra of reduced $BaBiO_{2.91}$ obtained at 77 K to that of stoichiometric $BaBiO_3$ measured at 75 K. The comparison is made on the same sample before and after the thermal treatment. The sum of oscillator strengths of extra peaks (all but four main modes) from the stoichiometric to the nonstoichiometric sample decreases slightly, by 10% at most. The signature of polarons as additional peaks observed in the same region as phonons, according to the scenario of Calvani *et al.*, is therefore not substantiated here. We rather suggest that the polaronic signature is expected at higher frequency (0.3–0.5 eV) together with the appearance of a phenomenological plasmon which corresponds to the motion of polarons above the mobility edge. This latter scenario applies well to rare-earth nickelates,[33] and presumably cuprates too, but is not observed in $BaBiO_3$.

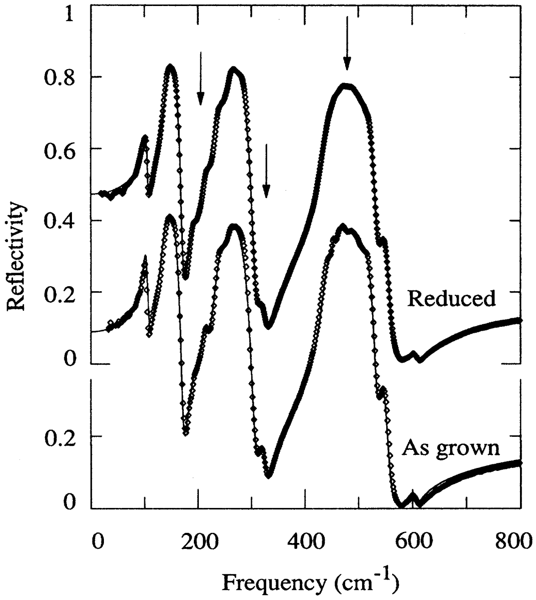

FIG. 4. Far-infrared spectra of $BaBiO_3$ (as grown) and reduced $BaBiO_{2.91}$ samples at 75 and 77 K, respectively. The slight change observed in some modes (indicated by arrows) can be attributed to a variation in the rate Bi^{3+}/Bi^{5+}.

If this decreasing of the intensities of the small peaks cannot be attributed to small polarons, it can be well described by the effect on phonons of a diminution of the disproportionated bismuth. Reducing the sample yields an increase of the rate Bi^{3+}/Bi^{5+}. For $BaBiO_{2.91}$ the expected number of disproportionated bismuth is about 9% lower than in $BaBiO_3$. Thus, this less disproportionated sample is expected to have a slightly smaller monoclinic distortion, which decreases the intensities of the weaker peaks. Another effect that corroborates this idea of diminishing the disproportionation of the sample is observed in the 2 eV band. Figure 5 shows the near-infrared and visible spectra at room temperature for stoichiometric and reduced samples. We observe a clear diminution of the reflectivity level in the reduced sample. The oscillator strength of this excitation is 10% smaller in $BaBiO_{2.91}$ when compared to $BaBiO_3$. On the other hand, its energy is practically unchanged. Then we can say that we still have a CDW gap originated by the bismuth disproportionation, and the lower intensity of this band in the reduced sample would be explained by the smaller population of disproportionated bismuth.

To finish with the information that may be extracted from infrared and visible spectra, we are left with the problem of the fourth main infrared mode. The question is why the oscillator of this extra mode is the only one to be so strong. Uchida *et al.*[29] proposed a realistic explanation for this situation. They showed how the bismuth disproportionation is able to activate the zone boundary acoustic mode of the cubic perovskite structure. In this mode, first-neighbor bismuth ions move in antiphase, and one of both against all oxygen atoms. Schematically, the motion may be viewed as that of bismuth against neighbor octahedral. The effective mass is near that of bismuth and the frequency is expected, therefore,

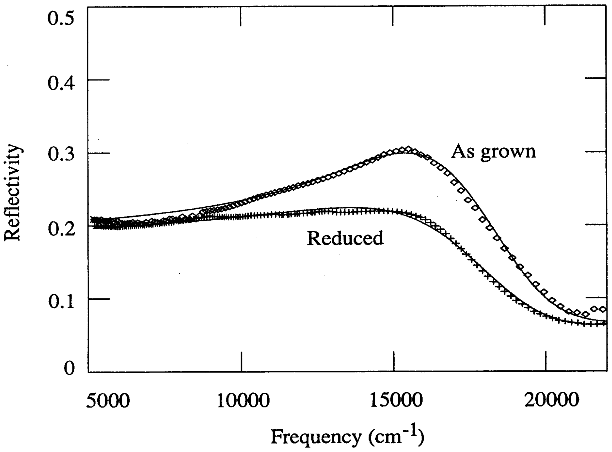

FIG. 5. Oxygen stoichiometry dependence of the 2 eV excitation at room temperature. The CDW gap energy remains unchanged but its intensity decreases with the increase of Bi^{3+} with respect to Bi^{5+}.

to be low. This description is substantiated by the progressive increase of the oscillator strength of the mode at 141 cm^{-1}, the second lowest-frequency one, with bismuth concentration in the system $BaPb_{1-x}Bi_xO_3$. Note that the oscillator strength of this mode decreases slightly (about 3%) in the nonstoichiometric sample compared to the stoichiometric one. In $BaBiO_{2.91}$, the expected number of disproportionated bismuth is only 9% lower than in $BaBiO_3$, consistent with the present observation.

Finally, we want to suggest that a part of the bismuth disproportionation is definitely static in view of the set of the experiments which could not be understood within any other framework: Bi-O double distance as seen by both neutron diffraction and EXAFS, the fourth strong infrared mode, the 2 eV gap, the absence of magnetic properties. At least one point remains quantitatively unclear: is there an additional dynamic bismuth disproportionation related to the oxygen breathing mode? This would explain why the difference between both Bi-O distances is minimized with respect to (i) the difference of ionic radii of Bi^{3+} and Bi^{5+} in octahedral configuration and (ii) the larger distance difference observed in $Ba_2(Ba_{2/3}Bi^{III}_{1/3})Bi^{V}O_6$.

CONCLUSIONS

By comparison with previous infrared reflection studies of barium bismuth oxide, the present study shows that the small extra modes related to the lattice distortion are present at all temperatures, even if the evaluation of their oscillator strength is more accurate at the lowest temperatures, and that their oscillator strengths do not vary significantly with temperature. The small change in the infrared and visible spectra due to the reduction of the sample is consistent with a slight decrease of bismuth disproportionation. The evaluation of the average oxygen effective charge confirms that Bi-O bonds remain slightly more ionic than covalent, contrary to the general belief reported in the literature, mainly based upon band structure calculations. The 2 eV CDW gap can be attributed to the Bi^{3+}-Bi^{5+} disproportionation and its optical response intensity is related to the amount of disproportionated bismuth. Finally, we suggest that the difference of both Bi-O bonds found to be smaller than what is expected either from the difference of Bi^{III} and Bi^{V} ionic radii or from the larger distance difference observed in $Ba_2(Ba_{2/3}Bi^{III}_{1/3})Bi^{V}O_6$ may result from a partial dynamic disproportionation.

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