Optical properties of the compounds $BaTiO_3$ and $SrTiO_3$

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$BaTiO_3$ and $SrTiO_3$ are ceramic materials having immense technological applications. We present state-of-the-art calculations of the frequency-dependent dielectric function using the full potential linear augmented plane wave method. We find that compared to the previous calculations, our calculations show better agreement with the experimental data. We studied $BaTiO_3$ in both the room-temperature tetragonal and high-temperature cubic phase. The calculated optical properties for the tetragonal phase are found to be in better agreement with experiment as compared to those for the cubic phase. The effect of tetragonality on band structure and density of states is found to be very small, while it is significant for the optical properties. The calculated results for the room-temperature cubic phase of $SrTiO_3$ also are in much better agreement with experiment than previous calculations.

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$BaTiO_3$ and $SrTiO_3$ are ceramic materials useful for capacitor applications and infrared detectors. $BaTiO_3$ is ferroelectric with a Curie temperature of 120 °C. Above 120 °C, it is paraelectric with a cubic perovskite-type structure, while from 120 to 5 °C it has a tetragonal phase. It has acquired importance, as adjusting the preparation conditions can change many of its properties. On the other hand, the low-temperature behavior of $SrTiO_3$ is quite interesting and has been the subject of many experimental and theoretical studies. It has a simple cubic perovskite structure at room temperature with a very large static dielectric constant. Being very close to a ferroelectric state, it can be induced to become ferroelectric by application of an electric field or uniaxial stress or by substituting some Sr ions by Ca ions. Its failure to transform into a ferroelectric phase with lowering of temperature has been interpreted as a quantum paraelectric state in which the quantum fluctuations of the atomic positions lead to a stabilized paraelectric state suppressing the ferroelectric transition.[1] This is supported by a recent experiment[2] showing that isotopically exchanged $SrTiO_3$ appears to become ferroelectric at 23 K, suggesting that the usual $SrTiO_3$ must indeed be very close to a ferroelectric transition.

The experimental studies on these two compounds include infrared spectra,[3] x-ray photoemission spectroscopy (XPS) measurements,[4,5] optical properties,[6,7] and investigation of structural, elastic, and thermal properties.[8] On theoretical side, the electronic structure of $BaTiO_3$ and $SrTiO_3$ has been calculated by many authors.[9] More recently, electronic structure and optical properties of $BaTiO_3$ have been calculated by Bagayoko *et al.*[10] and Saha *et al.*,[11] and those of $SrTiO_3$ by Saha *et al.*[12] Bagayoko *et al.* have studied $BaTiO_3$ in the tetragonal phase using a self-consistent linear combination of atomic orbitals method with a Ceperley-Alder form of exchange-correlation (xc) potential within the local density approximation (LDA). Even though they obtained good agreement for the energy gap, the structures in their frequency-dependent dielectric function, $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$, are much more closely spaced than in the experimental data. Saha *et al.*[11,12] have studied both the compounds in the cubic phase using the tight binding linear muffin tin orbital method with Barth-Hedin xc potential. Besides $\varepsilon(\omega)$, they also calculated related optical constants. However, the agreement for their band gap as well as optical properties with the experimental data is not encouraging. Also there is a significant difference between the calculated results for the tetragonal phase[10] and cubic phase[11] of $BaTiO_3$ even though the c/a ratio in the tetragonal phase is very close to unity. These works have taken the transition matrix elements into account while calculating the optical properties. However, these are not full-potential calculations. Hence there is a need to perform accurate calculations for the optical properties of $BaTiO_3$ and $SrTiO_3$. To rule out the possibility of differences in the calculated results for the tetragonal and cubic phases being an artifact of the method used, we have performed calculations using full potential linear augmented plane wave (FPLAPW) method where no shape approximation has been used for the potential.

The FPLAPW method, as implemented in the WIEN97 code,[13] was used. This includes local orbitals for the high-lying ''semicore'' states. xc potentials are treated in the LDA using the parametrization of Perdew and Wang.[14] Core states are treated fully relativistically and the valence states scalar-relativistically. We used the experimental lattice constants[15] $a=7.55$ a.u. and $c=7.62$ a.u. in the tetragonal phase, and $a=7.57$ a.u. in the cubic phase for $BaTiO_3$, and $a=7.38$ a.u. for $SrTiO_3$. The atomic positions using the experimentally measured data for the tetragonal phase are Ba (0,0,0), Ti (1/2,1/2,0.514), O1 (1/2,1/2,0.975), and O2 (0,1/2,0.488) and (1/2,0,0.488). The shifts of the atoms in the tetragonal phase of $BaTiO_3$ destroy the inversion symmetry of the lattice, leading to a displacement polarization. The Brillouin zone (BZ) integrations were performed using the modified tetrahedron method of Blöchl *et al.*[16] with 105 (84) **k** points in the irreducible BZ of tetragonal (cubic) unit cell. The frequency-dependent optical properties were obtained using the joint density of states weighted by the dipole matrix elements of the direct interband transitions using a lifetime broadening of 0.2 eV. In the tetragonal phase, $\varepsilon(\omega)$ is anisotropic and has two different components, $\varepsilon_{xx}(\omega)$ and $\varepsilon_{zz}(\omega)$, corresponding to the electric field perpendicular and parallel to the c axis, respectively. Since the experimental data for these compounds have been measured on polycrystalline

samples, we present an average over the two components as $[2\varepsilon_{xx}(\omega)+\varepsilon_{zz}(\omega)]/3$ for the tetragonal phase. Using the $\varepsilon(\omega)$, as output of WIEN97 code, we calculated various optical constants[11] such as spectral reflectivity $R(\omega)$, absorption coefficient $I(\omega)$, electron energy loss function $L(\omega)$, real part $n(\omega)$, and imaginary part $k(\omega)$ of the refractive index with a simple independent program.

We have calculated the total density of states (DOS) and the site- and angular-momentum-resolved DOS and found a good qualitative agreement with previous calculations.[10,11] Hence we decide not to show these. The valence band (VB) width is 4.5 eV for both tetragonal and cubic phases compared to 4.8 eV from Ref. 10 (for the tetragonal phase) and Ref. 11 (for the cubic phase). All are less than the experimental value[4] $\sim$6 eV. We find that the DOS for the tetragonal and cubic phases differs only slightly with respect to peak positions as well as magnitudes indicating that the DOS is not sensitive to the crystal structure, in agreement with Ref. 17. The main peaks in the calculated VB are shifted to lower binding energies with respect to the XPS peaks.[4] The Ba p states are located at about -10 eV from the Fermi energy (E_f), whereas the O p states are the chief contributors to the VB, spread in the range 0 to 4.5 eV below E_f, and are hybridized strongly with Ti d states. In agreement with earlier calculations,[10,11] the chief contributor to the conduction band (CB) are the Ti d states hybridized with the O p states. The calculated band gap of 1.85 (1.78) eV for the tetragonal (cubic) phase is lower than the experimental value of 3.2 eV. Bagayoko *et al.*[10] and Saha *et al.*[11] obtained it as 2.6 and 1.2 eV, respectively. These observations, as also for $SrTiO_3$ (discussed later), are consistent with the well-known fact that LDA underestimates band gaps by as much as 50%.

The total DOS reveals that the CB and the VB are spread over an energy range of about 13.5 eV. Since the Ba p states and the O s states are quite far from E_f, the VB (predominantly O p states) to CB (predominantly Ti d states) transitions dominate the optical spectra from the onset up to about 13.5 eV. We present the optical properties only in this energy range for both $BaTiO_3$ and $SrTiO_3$. Experimentally, the complete optical spectra from the 0 to 32 eV range has been presented for these compounds by Bauerle *et al.*[7] with the low-energy data from Cardona.[6] The calculated $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ versus the photon energy are displayed in the left panel of Fig. 1 along with the experimental data.[7] Also presented are the results from other calculations.[10,11] We obtain a good qualitative agreement with the experimental data; however, the calculated peaks and other structures are shifted towards lower energies by about 1 eV for the tetragonal phase, and by a slightly larger amount for the cubic phase. The shift is $\sim$2 eV for Saha *et al.*,[11] and $\sim$0.5 eV for Bagayoko *et al.*[10] Interestingly, there is a noticeable difference between the optical properties of the tetragonal and cubic phases of $BaTiO_3$ even though the DOS curves are similar. This shows that the optical properties are more sensitive to the c/a value. We observe that the $\varepsilon_2(\omega)$ from our calculations (for both tetragonal and cubic phases) is able to reproduce all the structures of the experimental curve except for the low-energy ($\sim$4 eV) shoulder present in the experimental data. Magnitudewise, our calculations for the tetragonal phase are in overall better agreement with experiment while those for the cubic phase give much higher values. The experimental curve shows structures at 4.8, 6, 7.3, 8.2, 10.5, and 11.7 eV, displayed in our work for the tetragonal phase at 4, 6, 8.5, 10, 11, and 11.5 eV. The structures for the cubic phase are shifted to lower energies by about 0.5 eV on an average with respect to the tetragonal phase. The work of Bagayoko *et al.* shows a very sharp main double peak, in contrast to the experiment and this work, around 4.6 eV. Beyond this it shows a shoulder and some sharper and closely spaced peaks, which suggest that the structures spread in the 0 to 13 eV range in the experimental curve are confined within 0 to 9 eV in their work. The $\varepsilon_2(\omega)$ from Saha *et al.*, on the other hand, shows much less features and much lower magnitudes as compared to the experiment.

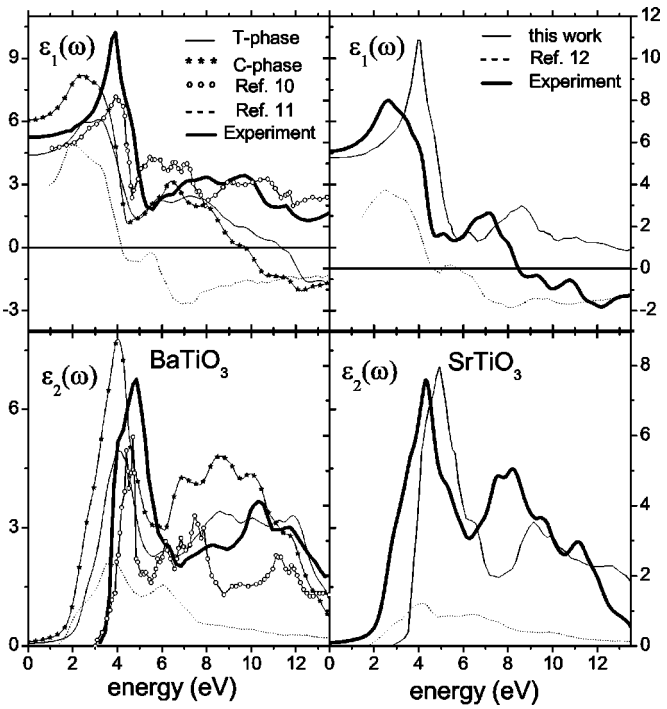

FIG. 1. Real and imaginary part of $\varepsilon(\omega)$ for $BaTiO_3$ (left panel) and $SrTiO_3$ (right panel) from various works.

The $\varepsilon_1(\omega)$ was obtained from $\varepsilon_2(\omega)$ using the Kramers-Kronig analysis. The $\varepsilon_1(0)$ value in the tetragonal (cubic) phase from our calculations is 4.3 (6.2), while the experimental value for the tetragonal phase is 5.2. This is to be compared with an extrapolated value of $\sim$3 from the work of Saha *et al.* (for the cubic phase) and of $\sim$4.5 from Bagayoko *et al.* (for the tetragonal phase). As in $\varepsilon_2(\omega)$, the structures in the experimental curve are present in our $\varepsilon_1(\omega)$ with the characteristic shifting towards lower energies. The $\varepsilon_1(\omega)$ curve from Saha *et al.* has, on the whole, a much smaller magnitude as compared to the experimental data and shows much less structure with a larger shifting towards lower energies as compared to our work, Ref. 10, and experiment. The work of Bagayoko *et al.*[10] shows fair agreement with experiment with the main peak at 4 eV; however, again the structures spread over the 13 eV range in experimental data appear to have condensed to within 0 to 8 eV in their work. The $\varepsilon_1(\omega)$ from Bagayoko *et al.* is relatively flat beyond 8 eV, while ours dips to negative values beyond $\sim$11.5

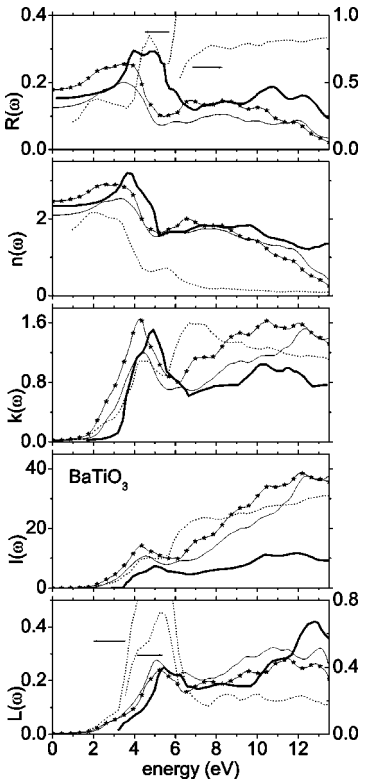

FIG. 2. Frequency-dependent optical properties of $BaTiO_3$ with legends as displayed in the left panel of Fig. 1.

($\sim$10) eV for the tetragonal (cubic) phase. We find that this drop to negative values is sensitive to the lifetime broadening, and for a larger broadening our $\varepsilon_1(\omega)$ remains positive in the given energy range.

The optical constants, calculated with our $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ as input, are presented in Fig. 2 along with those from experiment[7] and Saha *et al.*[11] Our calculations are in good agreement with the experiment for the shape as well as position of structures for all the optical constants. We are able to obtain almost all the structures, though the positions, as expected, are shifted to lower energies by $\sim$1 eV, a manifestation of smaller bandwidth. The structures in the reflectance spectrum and the corresponding energy from experiment[7] and theory are listed in Table I. Of all the calculations, our results for the tetragonal phase give the best agreement with the experiment for the magnitude and position of the structures. The $R(\omega)$ from Saha *et al.* has highly elevated values beyond 5.5 eV, and the shape is much different from the experimental curve. Hence it is difficult to identify many structures. Nevertheless, we have listed these in the Table I. We obtain $n(0)$ as 2.1 (2.5) for the tetragonal (cubic) phase, in fair agreement with the experimental value of 2.3. The work of Saha *et al.* predicts a much smaller value for $n(\omega)$ in the entire energy range, showing a sharp drop after the broad main peak with the $n(0)$ value, on extrapolation, close to 1.7.

For $SrTiO_3$ the calculated VB width of 5 eV is the same as from Ref. 12, both being smaller than the experimental value[5] of 6.5 eV. We obtain a band gap of 1.78 eV, in slightly better agreement with experiment (3.3 eV) in comparison to 1.4 eV from Saha *et al.*[12] The contributions to the VB and CB come predominantly from O *p* states and Ti *d* states, respectively. The Sr *p* states are around -14.5 eV from E_f. $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, in the right panel of Fig. 1, have structures dominated by the transitions from the O *p* states to the Ti *d* states. Our calculations for $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ faithfully reproduce all the features of the experimental curve albeit with a shifting (also present in other calculations[10–12]) by 0.5 to 1.5 eV towards lower energies. We obtain $\varepsilon_1(0)$ for $SrTiO_3$ as 5.6 in good agreement with the experimental value of 5.2. The extrapolated value from Saha *et al.* is $\sim$2.5. Their work shows much less structure and also drastically underestimates the magnitude of the peak heights in $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.

The calculated optical constants are presented in Fig. 3. We discuss briefly the reflectivity spectrum $R(\omega)$ shown in Fig. 3. The energy values for the structures in $R(\omega)$ are listed

TABLE I. Energy (in eV) of structures in the reflection spectra of $BaTiO_3$ and $SrTiO_3$ with the labels (not applicable to values from Refs. 11 and 12) according to the experiment (Ref. 7). The fundamental absorption edge, E_0, has been taken from the $\varepsilon_2(\omega)$.

$BaTiO_3$					$SrTiO_3$			
Label	Expt.	This tetragonal phase	This cubic phase	Ref. 11	Label	Expt.	This work	Ref. 12
E_0	3.2	2.2	2.2	2.21	E_0	3.4	2.2	2.24
B1	3.91	2.68	2.63	3.00	A1	4.0	2.84	3.29
B2	4.45	-	-	4.49	A2	4.86	3.50	4.71
B3	4.85	3.55	3.58	4.72	A3	5.5	4.25	6.00
B4	5.25	4.39	4.94	7.41	A4	6.52	5.24	7.65
B5	6.10	6.14	5.95	7.71	A5	7.4	-	8.12
B6	7.25	7.52	6.82	9.59	A6	9.2	7.58	11.29
B7	8.1	8.31	8.42	11.34	A7	10.2	8.34	
B8	10.3	10.05	10.08		-	10.7	9.72	
B9	11.8	11.31	11.90		A8	12.0	11.40	
B10	12.7	12.01			A9	13.0	12.15	

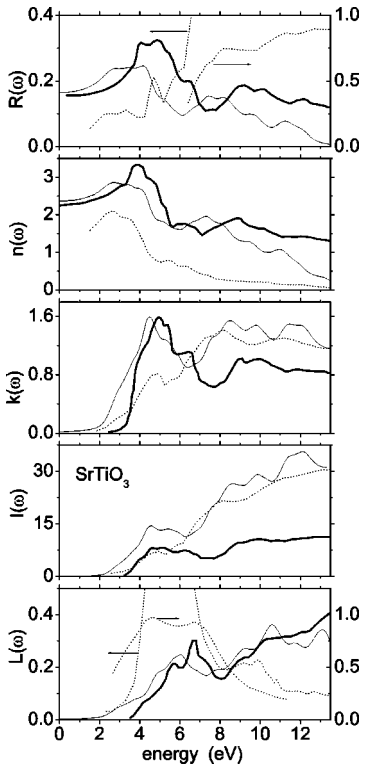

FIG. 3. Frequency-dependent optical properties of $SrTiO_3$ with legends as displayed in the right panel of Fig. 1.

in Table I. We obtain all the features except for the small peak A5 of the experimental curve. Hence A5 is not listed in the table, while the structure at 10.7 eV in the experimental data (not labeled in Ref. 7) is present in ours at 9.72 eV (Table I). The overall shape and magnitude of our curve is very similar to the experimental curve, and it is very encouraging that our calculations reproduce almost all the experimentally observed structures. Saha *et al.* obtain a much larger range of variation in $R(\omega)$ with a steep rise after 6 eV. Again, it was difficult to identify the experimentally observed structures in their calculations, yet we have listed the energies for these structures in Table I. Our calculations for other optical constants (Fig. 3) also give a good qualitative as well as quantitative agreement with the experimental data. The calculations of Saha *et al.*[12] show much less structure with the magnitude highly underestimated or overestimated in certain energy ranges.

We have reported a state of the art calculation for the optical properties of $BaTiO_3$ in tetragonal and cubic phases and $SrTiO_3$ in the cubic phase. The DOS for tetragonal and cubic phases of $BaTiO_3$ are quite similar, showing that the effect of tetragonality on band structure is very small, in agreement with Michael-Calendini and Meslard.[17] However, the optical constants for the two phases have noticeable differences, suggesting that tetragonality leads to a significant change in the wave functions affecting the height and position of the peaks in the optical spectra. The results for the tetragonal phase are in overall better agreement with experimental data in comparison to those for cubic phase. Nonetheless, our results for the cubic phase are also in fair agreement with the experiment, as should be the case with $c/a \sim 1$, whereas a comparison of the previous calculations[10,11] suggested otherwise. For the cubic phase, our results are in much better agreement with the experiment as compared to those from Saha *et al.*[11] Hence the cubic phase, if treated as the first approximation to the tetragonal phase, yields good enough results, e.g. with full-potential calculations. Though Bagayoko *et al.*[10] obtain a much better band gap, our calculations reproduce the spread of the structures in $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ in a better manner. The shifting of the structures towards the lower energies, present in our as well as other[10–12] calculations for $BaTiO_3$ and $SrTiO_3$, is a manifestation of the shortfall in the calculated VB width in comparison with the XPS data. Our calculations for $SrTiO_3$ yield a very encouraging agreement with the experiment for the optical properties as compared to previous results.[12] Thus, we conclude that our *ab initio* FPLAPW calculations give consistently good overall agreement with the experimental $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ and related optical constants establishing the accuracy and consistency of the full-potential calculations.

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