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X-ray photoelectron spectroscopy of amorphous and quasiamorphous phases of $BaTiO_3$ and $SrTiO_3$

David Ehre,[1] Hagai Cohen,[2] Vera Lyahovitskaya,[1] and Igor Lubomirsky[1,*]
[1]*Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel*
[2]*Chemical Research Support Unit, Weizmann Institute of Science, Rehovot 76100, Israel*

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Nonpolar amorphous and polar quasiamorphous phases of substrate-supported $BaTiO_3$ and $SrTiO_3$ were studied with x-ray photoelectron spectroscopy (XPS) to characterize the structural and chemical changes accompanying the transformation of the former into the latter. It was found that there are two spectral features distinguishing the amorphous from the quasiamorphous films: (1) an extra peak in the valence band spectra of amorphous films and (2) a satellite line in the XPS O 1*s* spectra of the amorphous films. On the basis of literature data, we suggest that both these features may be interpreted as originating from an oxygen-oxygen chemical bond. During the thermally driven transformation of an amorphous into a polar quasiamorphous phase, the oxygen-oxygen chemical bond breaks, leading to volume expansion and the development of inhomogeneous in-plane mechanical stress.

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I. MOTIVATION

As crystals, $BaTiO_3$, $SrTiO_3$, and $BaZrO_3$ have very different dielectric properties. $BaTiO_3$ is a ferroelectric, $SrTiO_3$ is an incipient ferroelectric, and $BaZrO_3$ is a dielectric. Nevertheless, all three compounds can form a noncrystalline yet pyroelectric and piezoelectric phase.[1,2] This phase, called quasiamorphous, is obtained by pulling amorphous films deposited by rf sputtering on Si through a temperature gradient.[1,3] It was found that the formation of the quasiamorphous phase is linked to anomalous behavior observed for amorphous as-deposited phases of $BaTiO_3$ and $SrTiO_3$. The most unusual feature is that upon heating in the absence of mechanical constraints, amorphous as-deposited films undergo a large ($>10\%$) prenucleation expansion.[4] Furthermore, the crystallization enthalpy of amorphous as-deposited $BaTiO_3$ is abnormally low (<10 kJ/mol).[3,5] X-ray absorption fine structure (XAFS) and x-ray photoelectron spectroscopy (XPS) studies[6,7] of the amorphous and quasiamorphous phases of $BaTiO_3$ and $SrTiO_3$ revealed that both phases contain a similar random network (RN) of local bonding units (LBUs), TiO_6 octahedra. The TiO_6 octahedra are connected in up to three ways: apex to apex, edge to edge, and/or face to face.[7,8] The RN-LBU theory, which was based on these findings for $BaTiO_3$, was successful in predicting the conditions required to transform an amorphous as-deposited film into a quasiamorphous phase.[3,7] The synthesis of polar noncrystalline $BaZrO_3$ and $SrTiO_3$ (Ref. 2) is the result. The model suggested by RN-LBU markedly differs from the random network described for regular (covalent) glasses:[9] (1) TiO_6 octahedra in amorphous and quasiamorphous phases of $BaTiO_3$ and $SrTiO_3$ have six apices instead of the maximal value of four allowed in classical glasses. (2) LBUs of TiO_6 can connect to each other in three different ways, whereas in covalent glasses they are connected only apex to apex. The question that we address below is what are the differences in structure and chemical bonding between amorphous and quasiamorphous phases. To answer this question, we performed a detailed XPS study of the oxidation states of the constituent elements of amorphous, quasiamorphous, and crystalline films of $SrTiO_3$ and $BaTiO_3$.

II. EXPERIMENT

Preparation of the 50–200 nm thick amorphous, quasiamorphous, and crystalline films of $BaTiO_3$ and $SrTiO_3$ followed the protocol described earlier.[1,3,6] X-ray diffraction (XRD, Rigaku D-max/B) measured in the θ-2θ mode was used to analyze film structure. Scanning electron microscopy images (Leo Supra55) of film surfaces and cross sections were analyzed with the SCION IMAGE software. XPS measurements (Kratos, AXIS-HS) were acquired from the films of $BaTiO_3$ and $SrTiO_3$.[7] To eliminate differential charging effects, an electron flood gun was used while the samples were electrically isolated from the grounded chamber. This procedure ensures the reproducibility of ±25 meV for peak positions within a given spectrum. To define a common energy scale for the different samples, we have taken the carbon 1*s* line at 284.6 eV as a reference. Although in many cases this procedure is very effective, in the case under consideration, a catalytic activity of crystalline $BaTiO_3$ and $SrTiO_3$ toward carbon-oxygen interaction[10–12] may cause some uncertainty in the position of the carbon 1*s* line, which we experimentally found to be below ±0.2 eV.[13] Therefore, we base most of our conclusions on the peak positions relative to each other within a given spectrum. Energy dispersive x-ray fluorescence spectroscopy and XPS confirmed (data not shown) that the stoichiometry of the amorphous, quasiamorphous, and crystallized phases is identical to that of the $BaTiO_3$ and $SrTiO_3$ sputtering targets (Semiconductor Materials, 99.98% metal base).

III. RESULTS

Neither amorphous nor quasiamorphous films of $SrTiO_3$ and $BaTiO_3$ produced any detectable x-ray diffraction peaks, whereas the presence of the perovskite phase in crystalline films was easily detectable.[7,3,6] The scanning electron microscopy observations agreed with XRD data, revealing crystallites only in the crystalline films.[7,3,6]

The positions of the Ti $2p_{3/2}$ peak and its satellite in the XPS spectra of all samples are indistinguishable within the experimental accuracy (peak at 457.7 eV, satellite [O $2p \rightarrow$ Ti $3d$ (Ref. 14)] at +13.9 eV for $SrTiO_3$ and at +13.0 eV for $BaTiO_3$, Figs. 1(a) and 1(b), Table I). The binding energy and the satellite position [marked (5) in Figs. 1(a) and 1(b), Table I] are consistent with those of a Ti ion in the perovskite titanates of Sr, as well as of Ba, Pb, and Ca.[15–17] We expect that if the local environment of Ti is different in the three phases, it would likely be detectable, because for different coordination numbers, the chemical shifts of Ti ions extend over more than 4 eV.[18] Thus, we conclude that the TiO_6 local bonding unit is preserved in all three phases, which agrees with the earlier XPS and extended x-ray absorption fine structure (EXAFS) data.[6,8] In addition, one has to point out that the core-level Ti $2p_{3/2}$ peaks of the amorphous and quasiamorphous phase are slightly but consistently broader than those in the crystalline phase (Table I), which correlates with the EXAFS finding that the TiO_6 octahedra are distorted.[6,8]

The O $1s$ lines [marked (1) in Figs. 2(a) and 2(b), Table I] of the amorphous and quasiamorphous $BaTiO_3$ and $SrTiO_3$ samples are practically identical (529.2 eV) and slightly shifted with respect to the corresponding line of the crystalline samples (528.8 $SrTiO_3$ and 528.9 $BaTiO_3$). This shift is on the order of the uncertainty in energy calibration; therefore, rather than using the absolute peak positions, the O $1s$ lines are characterized by their shifts relative to the Ti and/or Ba/Sr peaks. The O $1s$ peak position of ≈529 eV is a typical value for oxygen in perovskites.[17,18] This indicates that the oxygen ions remain coordinated in TiO_6 octahedra, which also agrees with the fact that the width of the O $1s$ line is the same in all three phases. The O $1s$ spectra also contain components previously identified as belonging to hydroxyl groups typical for absorbed water [530.6 eV, marked (2) in Figs. 2(a) and 2(b), Table I] and a component that can be assigned to C-O groups [531.6 eV, marked (3) in Figs. 2(a) and 2(b), Table I].[16,18,19] Both these components originate in the sample surface as proven by angle dependent measurements (data not shown).

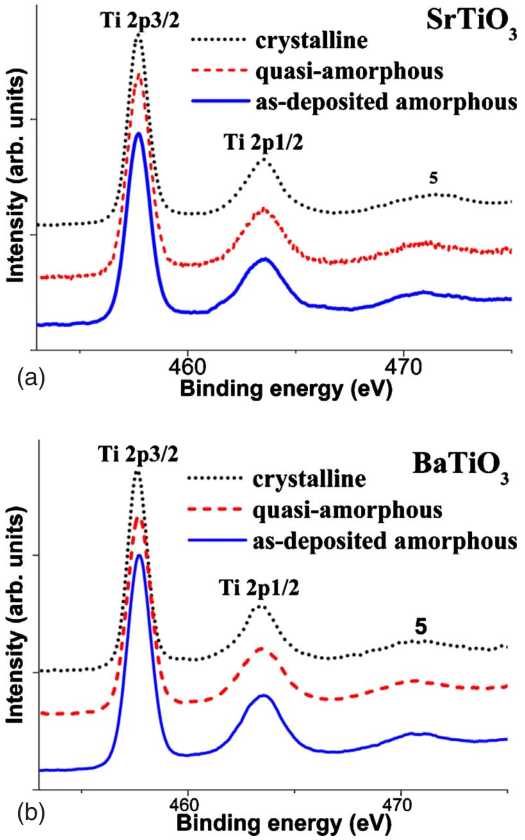

FIG. 1. (Color online) XPS spectra of Ti $2p_{3/2}$: (a) $SrTiO_3$; (b) $BaTiO_3$.

In contrast to the similarity in the O $1s$ electron binding energy of all samples, there is a satellite feature [marked (4) in Figs. 2(a) and 2(b), Table I] that appears only in the amor-

TABLE I. Binding energy values (in eV) in $BaTiO_3$ and $SrTiO_3$. The satellite values represent energy differences with respect to the corresponding main line. The full width at half maximum is given in parentheses.

Sample	Sr, Ba[I], Ba[II]	O $1s$	Satellite	O-H	O-C	Ti $2p_{3/2}$	Satellite
Marked in figures		(1) in Fig. 2	(4) in Fig. 2	(2) in Fig. 2	(3) in Fig. 2		(5) Fig. 1
$SrTiO_3$	Sr $3d_{5/2}$						
As-deposited amorphous	132.55 (1.5)	529.2 (1.1)	(1)+8.0	530.6		457.7 (1.1)	457.7+13.9
Quasi amorphous	132.50 (1.5)	529.2 (1.1)		530.6		457.7 (1.1)	457.7+13.9
Crystalline	132.10 (1.0)	528.75 (1.1)		530.6	531.5	457.7 (1.0)	457.7+13.9
$BaTiO_3$	Ba $3d_{5/2}$						
As-deposited amorphous	779.15 (1.3) [II]	529.2 (1.1)	(1)+7.8	530.6	531.5	457.7 (1.1)	457.7+13
Quasi amorphous	779.05 (1.3) [II]	529.2 (1.1)		530.6	531.5	457.7 (1.1)	457.7+13
Crystalline	779.25 (1.3)[II], 777.95 (1.0)[I] (intensity 1:2.12)	528.9 (1.1)		530.6		457.7 (1.0)	457.7+13

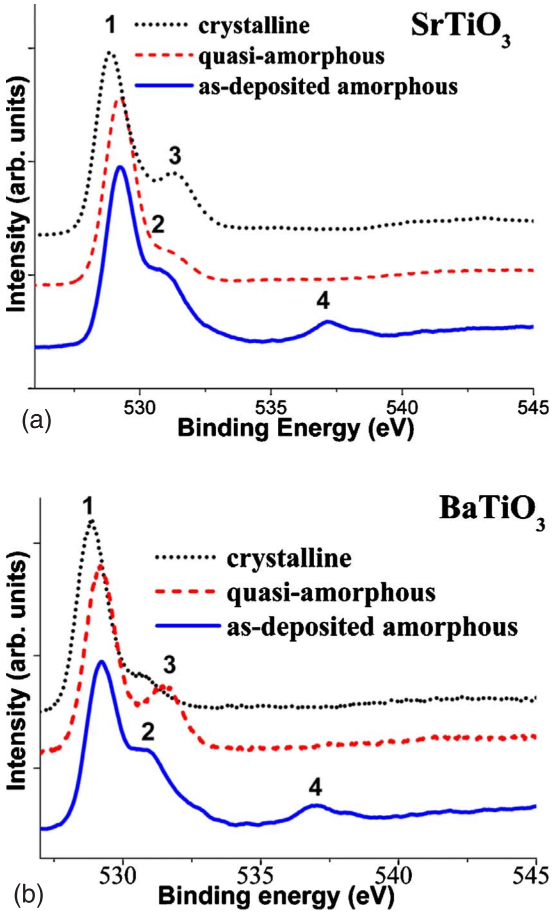

FIG. 2. (Color online) XPS spectra of O $1s$: (a) $SrTiO_3$; (b) $BaTiO_3$.

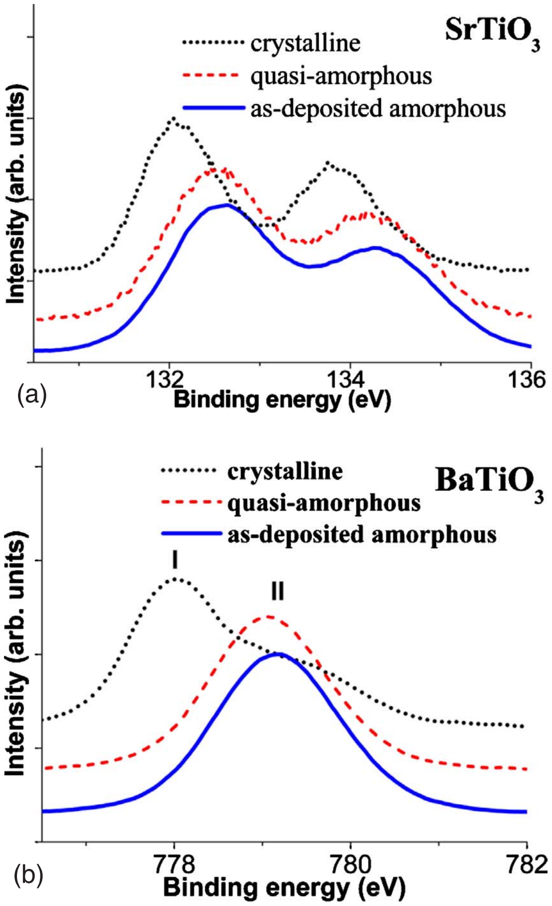

FIG. 3. (Color online) XPS spectra of (a) Sr $3d$ doublet and (b) Ba $3d_{5/2}$ (see Table I and Ref. 7).

phous $BaTiO_3$ and $SrTiO_3$, separated from the main core-level peak by 7.8 and 8.0 eV, respectively. These energies do not correspond to any known XPS peaks of crystalline titanates.[14] This satellite peak is not related to contamination and/or surface states, as verified by angle dependent measurements (data not shown). One possibility, to be discussed further below, is that it is due to an electron shake-up transition usually caused by fast screening (relaxation) mechanisms, involving neighboring atoms.

The position of the Ba $3d_{5/2}$ and the Sr $3d$-doublet lines shows a similar tendency for decreasing binding energy, from amorphous to quasiamorphous and further to crystalline phases (Fig. 3, Table I). The difference between peak positions of the amorphous and quasiamorphous samples is 0.05 eV (Sr $3d_{5/2}$) and 0.1 eV [Ba $3d_{5/2}$ (Ba II)].[7] Due to the uncertainty of the absolute energy scale calibration, these shifts must be viewed relative to the Ti or oxygen peaks. The difference between the peak positions of Sr $3d_{5/2}$ in quasiamorphous and crystalline samples is 0.4 eV. In $BaTiO_3$, due the to the presence of a thin amorphous layer at the surface of the crystalline phase,[7,20] the Ba (II) peak does not completely disappear, thus coexisting with the crystalline Ba (I) component (see Table I). The shift of the Sr peak and the split between the amorphous Ba (II) and the crystalline Ba (I) peaks (Table I) are significantly larger than the energy scale uncertainty. Therefore, the combined information from peak shifts and line broadening indicate that the chemical environment of Ba and Sr is different in the noncrystalline phases as compared to the crystalline phase.

The spectrum of the first valence band consists of two peaks [P1 and P2 in Figs. 4(a) and 4(b); 4.8 and 6.9 eV for $BaTiO_3$; 4.9 and 7.25 eV for $SrTiO_3$]. These peaks are attributed to O 2π and σ bonding orbitals.[21,22] They are well resolved in the crystalline phase but smeared in both noncrystalline phases. This smearing is consistent with the disordered structure of the noncrystalline films. A broad peak at 10.2–11.8 eV (marked A in Fig. 4) appears in the valence band spectra of amorphous $BaTiO_3$ and $SrTiO_3$, whereas it is absent in the spectra of quasiamorphous and crystalline films. This extra peak was previously identified[23] in both compounds, $BaTiO_3$ and $SrTiO_3$, as belonging to O $2p$ electrons in oxygen ions with less positively charged neighbors than in the perovskite lattice of $SrTiO_3$ (Ref. 21) and $BaTiO_3$.[24] For instance, this peak may appear as a result of oxygen deficiency and concomitant partial reduction of Ti ions.[25]

IV. DISCUSSION

By comparing (1) crystalline versus noncrystalline films and (2) amorphous versus quasiamorphous films, we construct below a model for the chemical bonds and the function

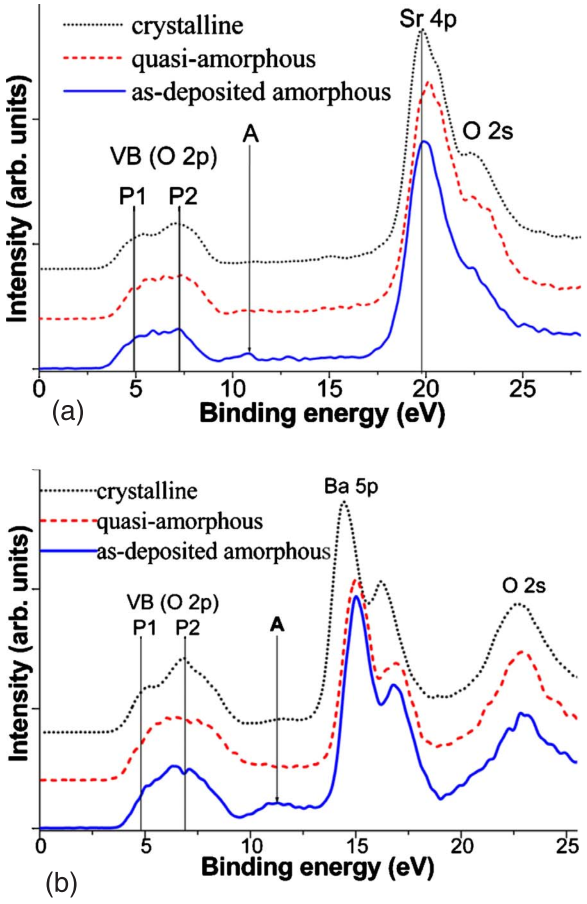

FIG. 4. (Color online) Valence band spectra of (a) $SrTiO_3$; (b) $BaTiO_3$.

of the cations in the random network of the local bonding units. This model is based on the data presented above and on the previous XPS, EXAFS, structural, and optical studies.[3,4,6–8]

A. Oxygen, Ba, and Sr coordination environment

The crystalline perovskite phases of $BaTiO_3$ and $SrTiO_3$ contain TiO_6 octahedral local bonding units connected to each other apex to apex. In this apex-sharing arrangement, each oxygen ion is coordinated with two Ti ions and four Ba or Sr ions [Fig. 5(a)]. Each of the latter has 12 oxygen neighbors in a cuboctahedron-shaped space formed by TiO_6 octahedra. EXAFS data[6,8] conclusively prove that amorphous and quasiamorphous films also contain TiO_6 LBUs. Therefore, the octahedral coordination of Ti ions with oxygen is similar to that in the crystalline phase. However, in contrast to the crystalline phases where all TiO_6 LBUs share apices, in the noncrystalline amorphous and quasiamorphous phases, there are also edge-sharing[8] and, possibly, face-sharing TiO_6 octahedra. Therefore, depending on whether an oxygen ion participates in edge sharing, apex sharing, or is not shared by different TiO_6 octahedra, it may have three, two, or one Ti neighbors, respectively [Fig. 5(b)]. Since the coordination of Ti ions with oxygen is invariant, preservation of local electroneutrality requires that the change in the coordination of oxygen ions must be accompanied by a change in the coordination of Ba and Sr [Fig. 5(b)].

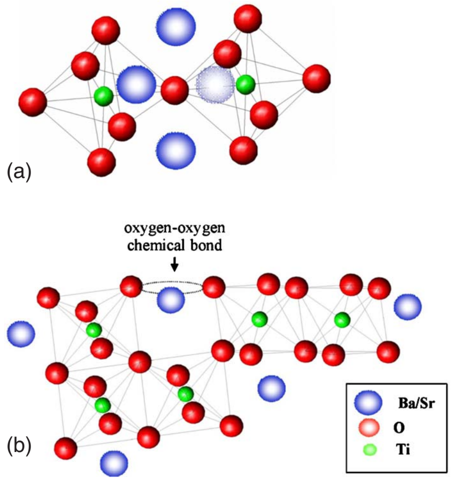

FIG. 5. (Color online) (a) Two apex-sharing TiO_6 octahedra coordinated with Sr (Ba) in a perovskite structure; (b) fragment of a random network of edge- and apex-sharing TiO_6 octahedra with proposed coordination of Sr/Ba ions. The oxygen-oxygen bond shown in the figure is a cartoon.

The density of the amorphous phase is only 82–85% of that of the crystalline phase.[2,3] Since the volume of the TiO_6 octahedra as measured by EXAFS does not appreciably change,[6,8] the space available for Sr and Ba ions in the noncrystalline phases must be much larger than that in the crystal. This implies that the Sr and Ba atoms may move within the increased available space, leading to variation in the local environment from ion to ion. Indeed, the EXAFS data clearly show that the local environment of Sr ions in the noncrystalline phases is irregular.[8] At the same time, despite the change in the local environment of the oxygen ions, neither splitting nor broadening of the XPS O 1*s* peak (Fig. 2) is observed. This indicates that there must be a mechanism that equilibrates the binding energy for all O 1*s* electrons in order to render them indistinguishable by XPS. In addition, although Sr and Ba ions do not have a regular environment in the noncrystalline phases, their XPS peaks, while slightly broadened, are not split. This implies that the same mechanism that equilibrates the binding energy of oxygen electrons must also minimize the differences in the binding energy of Ba and Sr electrons. The equilibration of the electron binding energy can only be achieved by redistribution of the effective charges of all cations. In support of this suggestion, we note that in the noncrystalline phases, the binding energies of the oxygen, and Ba and Sr electrons increase with respect to the binding energy of Ti 2*p* electrons.[18] This is a clear indication that oxygen becomes less negative with respect to titanium, whereas Ba and Sr become more positive. Alternatively, one may look at this charge redistribution as a slight reduction of the Ti ions at the expense of the oxygen and Sr (Ba).[18]

B. Amorphous film to quasiamorphous film

The XPS data presented above and the EXAFS data in Ref. 8 show that the transformation of a film from the amorphous to the quasiamorphous state is characterized by the following spectral features: (a) the O 1*s* satellite peak and peak A in the valence band spectra disappear; (b) the local environment of the Sr ions[8] undergoes a marked change (a corresponding effect in $BaTiO_3$ is unobservable in EXAFS due to Ti-Ba signal overlap[6]), and (c) the binding energies of the Ba/Sr electrons decrease (Fig. 3, Table I). On the other hand, these data also clearly show that the local environment of Ti, its off-center displacement within the TiO_6 octahedra, and the relative position of the Ti $2p_{3/2}$ XPS peak with respect to the O 1*s* peak do not change. Fourier transform of the Ti *K*-edge EXAFS spectrum of the quasiamorphous phase is slightly different from that of the amorphous one only in the region characterizing the second-neighbor shell.[6,8] This fact implies that the transformation from the amorphous to quasiamorphous phase does not cause significant changes to the TiO_6 octahedra but involves changes in the second-neighbor shell. From the above, one can learn the following. The appearance or disappearance of an O 1*s* satellite peak is a marker for a change in the electronic configuration of the oxygen ion and/or its neighbors.[18] The disappearance of peak A in the valence band spectra is another indication of a change in the electronic configuration of oxygen, as this peak is attributed to O 2*p* electrons. Since there are no indications that the electronic configuration of the TiO_6 octahedra is different in the quasiamorphous as compared to the amorphous phase (XAFS data,[6,8] Fig. 1, and Table I: no change in the Ti 2*p* spectra; Fig. 2 and Table I: no change in the O 1*s* core-level peak) and since all oxygen ions participate in at least one octahedron, the disappearance of the O 1*s* satellite peak must be related to changes in either the mutual disposition of the TiO_6 octahedra and/or to changes in the interaction of oxygen with Sr (Ba). However, the fact that the satellite peak has almost the same energy in both $BaTiO_3$ and $SrTiO_3$ (Table I) strongly suggests that this satellite does not correspond to a direct oxygen—Ba/Sr electron transition. We therefore propose that the electronic shake-up transition which is responsible for the O 1*s* satellite peak probably involves oxygen ions of at least two different octahedra. Changes in the oxygen-oxygen interaction would therefore promote the destabilization of the amorphous film and its transition to the quasiamorphous state. The transformation of the amorphous into the quasiamorphous phase is also characterized by a significant increase in volume ($>3\%$) (Ref. 26) and development of a very large in-plane compressive stress (>2 GPa).[26] In the absence of mechanical constraints (self-supported films), the amorphous phase undergoes an anomalous volume expansion of more than 10%.[4] This expansion is a clear indication of breaking of chemical bonds, which, we suggest, would be accompanied by rearrangement of the TiO_6 octahedra.

C. Ba/Sr mediates the oxygen-oxygen interaction

Ba and Sr are known to form extremely stable peroxides; they may serve as mediators which stabilize oxygen-oxygen bonds.[19,27–30] Density functional theory calculations show that the stabilization of the peroxide ions in BaO_2 and SrO_2 is due to an effective pressure generated by the short range exchange correlation of the surrounding metal ions in the lattice.[27] This possibility is especially appealing in the present case. Although, as pointed out above, the difference in the position of the O 1*s* satellite peak in the XPS spectra of amorphous $BaTiO_3$ and $SrTiO_3$ is small, it nevertheless does suggest that some mediation by Ba and Sr is present. In addition, Fourier transform of the Sr *K*-edge EXAFS spectrum shows that transformation from the amorphous to quasiamorphous phase involves the rearrangement of the Sr ions in both the first and second Sr-O coordination shells.[8] We also note that when there is a Ba deficiency in the amorphous films, the formation of the quasiamorphous phase of $BaTiO_3$ is suppressed.[26] These facts, although suggestive, are however insufficient to describe the electronic structure of the putative oxygen-oxygen bond and the possible mediation by Ba or Sr. Furthermore, although there are reports in the literature which discuss the difference in the electronic configuration of oxygen in edge-sharing versus apex-sharing TiO_6 octahedra,[31,32] these works deal with crystalline $SrTiO_3$, rutile or anatase, which makes them inapplicable for amorphous materials. It is possible that Raman or EPR spectroscopy could prove useful for further characterizing the noncrystalline phases of $BaTiO_3$ and $SrTiO_3$ amorphous thin films, although the specimen thickness (<100 nm) may pose experimental difficulties.

V. SUMMARY

In summary, we have presented XPS data of nonpolar amorphous and polar quasiamorphous phases of substrate-supported $BaTiO_3$ and $SrTiO_3$. These data were used to characterize the structural and chemical changes accompanying the transformation of the former to the latter. There are two spectral features which suggest that an oxygen-oxygen bond, with the possible mediation of strontium or barium, contributes to the formation of the random network of TiO_6 local bonding units in the amorphous phase of $BaTiO_3$ and $SrTiO_3$. Dissociation of the oxygen-oxygen bonds accompanies the transition from the amorphous to the quasiamorphous phase. Our findings provide support for the previously proposed RN-LBU model[2–4,6–8] and may contribute to the understanding necessary for the preparation of novel noncrystalline pyroelectric and piezoelectric quasiamorphous materials.

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*igor.lubomirsky@weizmann.ac.il

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