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Difference in electronic structure between tetragonal and cubic SrNbO$_2$N

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We report here a comparative study of the electronic structure of earlier known cubic phase and the recently, reported correct tetragonal phase of SrNbO$_2$N. We performed the calculations within the framework of density-functional theory (DFT) by using the WIEN97 code. The valence band consists of N 2p while the conduction band consists of Nb 4d in cubic system; on the contrary, these Nb 4d states show a strong interaction with anion p states in tetragonal system and indicate theoretically, a metallic behavior. The direct forbidden gap of tetragonal system was 0 eV, whereas for cubic system was 0.2 eV; the relative difference in the band gap of two systems is possibly attributed to the high covalency and is possibly acquired due to the presence of the shorter bond length of Nb–N than that of Nb–O in the tetragonal system. The results of electronic structures have been discussed in the light of optical applications of this oxynitride in solar energy conversion. The calculated optical-absorption coefficient $I(w)$ from real and imaginary parts of dielectric function, further clarifies the suitability of the application. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2032612]

I. INTRODUCTION

In recent years, oxynitrides have become a rapidly growing field of interests[1–3] due to their potential uses as industrial nontoxic inorganic pigments, photocatalysts, and solar energy conversion materials. These materials show altered physicochemical properties induced due to the partial introduction of nitrogen atom into the anionic oxygen site. Specially, such a N-anion introduction in the metal oxide lattice has been shown[4] to redshift the band gap of the original lattice in the visible region thereby making them active candidates for visible-light photocatalysis and several other optoelectronic applications. Especially, the perovskite layered and unlayered structures[5–7] have been found to display a dramatic effect on enhancing the photocatalytic activities. Thus a combined approach of the N-anion incorporation in perovskite lattices is likely to yield on high activity, visible-light active photocatalyst and hence, is of particular interest to the photocatalyst community for solar energy conversion applications. This motivated us to study the electronic structure of the oxynitride of strontium niobate with a specific attention on their optical properties. Its oxide form has been found to be a highly active photocatalyst for water splitting under ultraviolet (UV) light.[5,8]

It has been known in an earlier study that SrNbO$_2$N exists in a cubic perovskite structure.[9] However, recent findings showed that the oxynitride actually exists in a tetragonal phase of the *I*4/*mcm* space group.[10,11] The ambiguity was attributed to the analogous x-ray atomic form factors of O and N. The dissimilar neutron-scattering lengths of O and N were thus utilized to understand the correct space group of SrNbO$_2$N.[11] The neutron-diffraction study established that SrNbO$_2$N crystallizes in tetragonal crystal structure, space group *I*4/*mcm* with a=5.7056 Å and c=8.1002 Å at room temperature. The electronic structure of a compound mainly relies on its crystal structure. Thus, in order to understand the electronic and optical properties of a compound with a correct space group, the theoretical investigation is as important as the experimental study. Until now, there has been no report on the electronic and optical properties of SrNbO$_2$N. The present study focuses on the electronic structure of the recently reported tetragonal phase, and investigates the difference from that of the earlier reported cubic phase. We believe that the knowledge of an electronic (optical) structure is desired and very useful for understanding the optical candidacy of these phases for relevant applications, such as visible-light photocatalysis.

II. METHODS AND COMPUTATIONAL DETAILS

Theoretical calculations were performed with the full potential linearized augmented plane-wave (FP-LAPW) method as implemented in the WIEN97 code with density-functional theory (DFT) in a generalized gradient approximation (GGA).[12] In the LAPW method the unit cell is divided in two types of regions, the atomic spheres centred upon nuclear sites and the interstitial region between nonoverlapping spheres. Inside the atomic spheres, the wave functions are replaced by atomlike wave functions, while in the interspheres region the wave functions are replaced by atomiclike wave functions. The muffin-tin radii for Sr, Nb, O, and N were chosen to be 2.0, 1.8, 1.6, and 1.6 a.u., respectively in these calculations. The convergence parameter RK$_{max}$ was set to 6.0. The calculation was iterated with the charge convergence criteria of 0.0001. Self-consistency was carried out on an 18 k-point mesh in the irreducible Brillouin zone of SrNbO$_2$N. Further a fine mesh of 102 (100) k points in the irreducible Brillouin Zone (BZ) of the tetragonal (cubic) unit cell was used to calculate the frequency dependent

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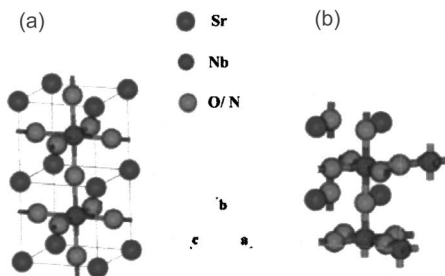
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FIG. 1. Crystal structures of the (a) cubic, double unit cell, and (b) tetragonal $SrNbO_2N$, showing the random distribution of O/N.

absorption coefficient $I(\omega)$ from real and imaginary parts of the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. A procedure similar to Gupta et al.[13] was followed for this calculation of $I(w)$ which is given as $I(\omega) = \sqrt{2}(\omega)[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)]^{1/2}$. The atomic coordinates were adopted from literature.[9–11] For the band-structure calculation of the cubic structure, a supercell with two $SrNbO_2N$ units was constructed from the available crystallographic data.[8]

III. RESULTS AND DISCUSSION

A. Crystal structure of $SrNbO_2N$

$SrNbO_2N$ was reported to exist in the form of a cubic perovskite structure with a space group of $Pm\bar{3}m$, no. 221, and a lattice constant of $\mathbf{a} = 4.044$ Å.[7] Figure 1(a) shows the cubic structure wherein Nb is octahedrally coordinated to O/N atoms. The recent finding shows that the stable structure is tetragonal.[10] We have studied both these crystal structures in the present work. Figure 1(b) shows the schematics of a unit cell of the tetragonal crystal structure of $SrNbO_2N$ with space group $I4/mcm$, no. 140, and $a = b = 5.710\,68$ Å and $c = 8.104\,00$ Å. We used the respective crystallographic data for the band-structure calculations. We believe that the reported structures obtained from neutron-diffraction refinements are the thermodynamically stable structures that prefer the random distribution of O/N atoms in the crystal. It has also been shown by Fang et al.[14] that the O/N random structure of oxynitride is a stable structure.

B. Electronic structure of $SrNbO_2N$

Figures 2(a) and 2(b) display the total and partial computed density of states (DOS) for the tetragonal and cubic $SrNbO_2N$, respectively. It clearly demonstrates that the calculated band gap of tetragonal structure is 0 eV and that of the cubic structure is 0.2 eV. In the case of tetragonal structure, the low-energy DOS between −20.0 and −12.0 eV is due to the contribution of Sr $4p$, O $2s$, and N $2s$ states. The high-energy DOS at the top of the valence band has a dominant contribution from N $2p$ states. These states mostly hybridize with the Nb $4d$ states and to a lesser extent with an admixture of s and p states over the whole region of the valence band, indicating a strong covalent interaction between Nb and anion atoms. In the case of high-energy bands above Fermi energy, the Nb $4d$ states are dominantly contributing to the conduction band with a partial share from the N $2p$ and O $2p$ states. The absence of a forbidden gap (band
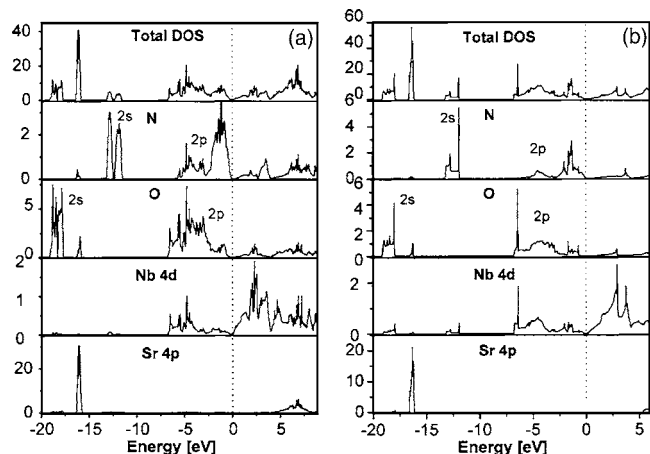

FIG. 2. Total and partial DOS for the (a) tetragonal and (b) cubic $SrNbO_2N$. The unit of the Y axis is states/(eV unit cell). The Fermi level is set at 0 eV in each case.

gap 0.0 eV) obtained from the DOS, indicates the possible metallic nature of the tetragonal structure. The cubic phase also shows similar contributions of various states as described above for the tetragonal structure. The key difference is found to be the forbidden gap of 0.2 eV, revealing the semiconducting nature of cubic structure.

Figures 3(a) and 3(b) for the dispersion of the electron bands for tetragonal and cubic systems, respectively, further clarify the above picture. The band structure reveals that the tetragonal structure shows a 0-eV gap at the Γ and R points, thereby indicating theoretically a metallic nature. However, the cubic phase has a direct forbidden gap (i.e., dipole forbidden) of band gap 0.2 eV at Γ. This can be attributed to the asymmetrical geometry of the tetragonal structure. The Nb–(O/N) bond length possibly plays a decisive role in yielding a smaller band gap to cubic phase. The close observation of bond lengths in tetragonal (Nb–N=2.026 a.u. and Nb–O=2.0287 a.u.) and cubic (Nb–O/N=2.026 a.u.) systems throws some light on the issue. The former structure possessing a shorter bond length for Nb–N than Nb–O, ought
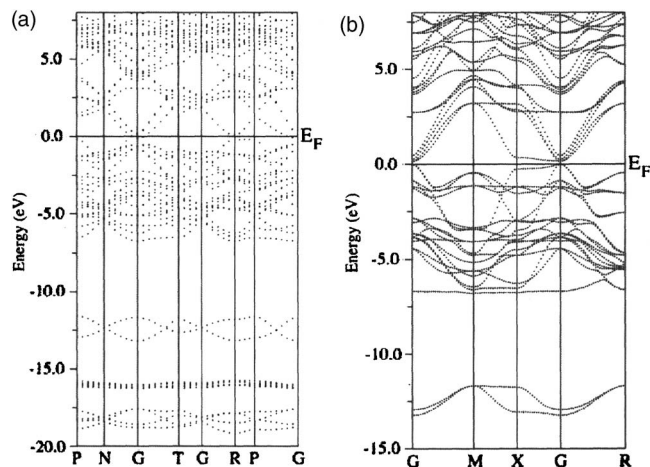

FIG. 3. Band structure of the (a) tetragonal and (b) cubic $SrNbO_2N$ along high-symmetry directions of the irreducible Brillouin zone. The top of the valence band is taken as zero energy.
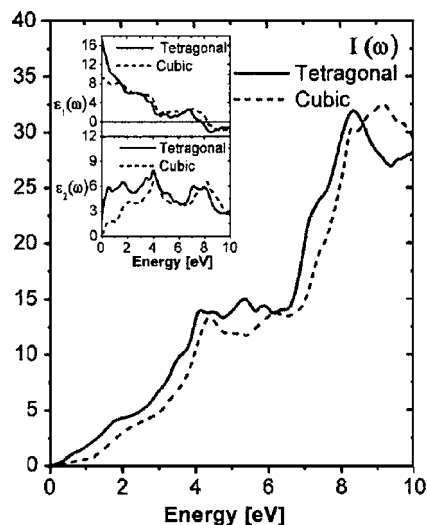
FIG. 4. Calculated absorption coefficient $I(\omega)$ of the tetragonal and cubic $SrNbO_2N$ as a function of the photon energy. Inset shows the calculated real and imaginary parts of the dielectric function for the two structures.

to be held responsible for larger hybridization between Nb $4d$ and O $2p$ or N $2p$ states, as seen in Fig. 2(a).

Figure 4 shows the results of comparison of calculated energy-dependent absorption coefficients $I(\omega)$ for tetragonal and cubic $SrNbO_2N$. The tetragonal structure shows a larger $I(\omega)$ at lower energies than the cubic structure, indicating its ability to respond to low-energy photons. The inset of Fig. 4 shows calculated real and imaginary parts of the dielectric function $\varepsilon(\omega)$, that are used for the calculation of $I(\omega)$ of two structures. These are presented to provide the results of an important intermediate step that was used during the calculation of $I(\omega)$. As the main interest in the present context is $I(\omega)$, hence we do not discuss the results of the inset of Fig. 4, in any further detail. The $I(\omega)$ curves for both structures show similar trends with main difference that the optical response of tetragonal structure is redshifted. In addition, tetragonal $SrNbO_2N$ shows higher absorption coefficients than the cubic structure in low-energy range of $0-1$ eV. These results of optical property calculation clearly show that the tetragonal structure responds to lower-energy electromagnetic radiation in a rather more efficient manner than the cubic structure.

In order to validate the observed facts, we discuss the present theoretical results along with the reported experimental observations.[9,10] In Table I we show the optical band gaps of two crystal assignments. The calculated band gap for tetragonal structure was smaller than that of the cubic structure. However, the absolute values of calculated band gaps

are drastically underestimated, a fact that is well-known shortcoming of the single-particle Kohn-Sham approach.[15] With this restriction in mind if we analyze the band gaps, it reveals that Nb atoms interact strongly with N and O atoms in tetragonal system. This is also supported by the fact that there are shorter Nb−O/N bond lengths in tetragonal system.

C. Possible better candidate as visible light absorber

It has been known that the optical properties of oxynitrides are well suited for light absorption applications in solar energy conversion. Our study validates the fact for $SrNbO_2N$. The theoretical and experimental results displayed in Table I show that the tetragonal structure $SrNbO_2N$ has a small band gap, suggesting that it is surely a well-suited candidate for visible-light absorption, as desired for solar energy conversion and the photosplitting of water under visible light. The higher absorption coefficients at low energies observed for the tetragonal structure (as compared to cubic) also reveals this fact. Such oxynitrides have also been sought as an environmentally harmless substitute for the toxic metal containing inorganic pigments especially CdS.[16]

IV. CONCLUSION

The paper reports on the theoretical investigations of electronic structure of the tetragonal and cubic $SrNbO_2N$. In short, we have shown that the Nb $4d$ states in tetragonal structure interacts, on a relative scale, more strongly with anion p states than the Nb $4d$ states of the cubic structure. The theoretical calculations along with the results of frequency-dependent optical-absorption calculations of the recently reported tetragonal system of $SrNbO_2N$ indicate that it is a better suited material for potential application as a light absorber in a solar energy conversion device.

TABLE I. Comparison of calculated direct gaps and experimental band-edge absorption values for the tetragonal and cubic assignments of $SrNbO_2N$ (NA—not applicable; NR—not reported).

$SrNbO_2N$ system/assignments	Theoretical work (band-gap eV)	Experimental work (band-gap eV)	
		Ref. 2	Ref. 9
Tetragonal	0.0	NA	1.9
Cubic	0.2	NR	NA

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