

## Photophysical Properties and Electronic Structure of Highly Donor Doped (110) Layered Perovskite Material

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$\text{Sr}_2\text{Nb}_2\text{O}_7$ , a donor doped (110) layered perovskite material was synthesized by solid state reaction method and studied for its photo physical properties. The morphology, crystal structure and optical properties were characterized respectively by SEM, XRD and UV-DRS spectroscopies. We performed the electronic band structure calculations on orthorhombic crystal structure of  $\text{Sr}_2\text{Nb}_2\text{O}_7$ , within the framework of density functional theory (DFT) by using Wien97 code. The photo physical and electronic properties indicate  $\text{Sr}_2\text{Nb}_2\text{O}_7$  to be a better photocatalyst than conventional or other known candidates *viz.*  $\text{TiO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ .

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### I. INTRODUCTION

Among various methods of solar energy conversion, much attention has been paid to the photocatalytic water splitting for its potential significance in obtaining directly clean and high energy containing  $\text{H}_2$  from abundant  $\text{H}_2\text{O}$ . If successfully developed with an economic viability, this could be the ultimate technology that could solve both the energy and the environmental problems altogether in the future. The perovskite materials such as  $\text{SrTiO}_3$  and  $\text{CaTiO}_3$  have photocatalytic activities for water splitting under UV light irradiation [1-3]. However, the quantum yields (% of absorbed photons that have been actually used to generate a photoreaction product) of these materials are very low (ca. < 1 %). Thus there is need to explore the photo physical properties of newer materials.

The layered perovskite-type materials [4-6] are of wide interest, because these materials, including (100) and (110) group layered perovskite, exhibit large ferroelectric constants, large nonlinear optical coefficients, large dielectric constants and high quantum yields for overall photocatalytic water splitting [7-11]. Indeed,

(100) layered perovskite materials such as  $\text{K}_4\text{Nb}_6\text{O}_{17}$  and  $\text{A}_4\text{Ta}_x\text{Nb}_{6-x}\text{O}_{17}$  (A=K, Rb) were found by Domen and coworkers [12] to be much more efficient (quantum yields of ca. 5 %) photocatalysts for overall water splitting. The greatly improved quantum yield of these layered perovskites has been attributed to the role played by the existing interlayer spaces as reaction sites. Owing to the important role of the interlayer spaces, most of the recent reports have focused on the layered structures [13, 14]. At such reaction sites the electron-hole recombination process could be retarded by the physical separation of electron and hole pairs generated by photo-absorption, which mainly contributes in yielding higher quantum yields. Recently, we also found that highly donor-doped (110) layered perovskite materials exhibited higher water splitting activities than the previously-known (100) layered perovskite materials under UV light irradiation [15-18]. These novel materials are a series of homologous structures with a generic composition of  $\text{A}_m\text{B}_m\text{O}_{3m+2}$  ( $m = 4, 5$ ; A = Ca, Sr, La; b = Nb, Ti). The water splitting photocatalytic activities of these layered perovskites were strongly dependent on their electronic band structure [19]. Though (110) layered perovskite materials have a high potential as novel photocatalysts for hydrogen production from water, information on their structure or electronic properties is limited [19].

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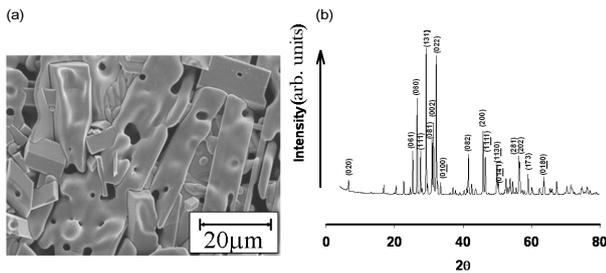


Fig. 1. The SEM image (a) and typical XRD (b) spectrum of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  sintered in air.

In this paper, we report the photo physical properties of highly donor-doped (110) layered perovskite material,  $\text{Sr}_2\text{Nb}_2\text{O}_7$ , along with its electronic band structure calculations. We further discuss the experimental and theoretical results in light of the photocatalysis.

## II. EXPERIMENTAL

$\text{Sr}_2\text{Nb}_2\text{O}_7$  was prepared by the conventional solid state reaction method. The stoichiometric mixtures of appropriate salts viz.  $\text{SrCO}_3$  (99.99 %, Aldrich) and  $\text{Nb}_2\text{O}_5$  (99.9 %, Aldrich) were mixed and ground in ethanol. The pelletized powders were calcined at 1273 – 1573 K for 48 h in static air. The finally obtained layered perovskite-type materials were characterized. The morphology of the samples was observed by SEM on a Hitachi S-2460N electron microscope. The sample was mounted on a steel holder and a thin layer of gold was coated on it for analysis. In case of the calcined samples, SEM images were obtained without fracturing its raw pellet. The structural phases were determined by X-ray diffractometry (Mac Science Co., M18XHF). The diffuse reflectance spectra of the synthesized compounds were recorded on UV-vis diffuse reflectance spectrophotometer (Shimadzu UV 2401). These electronic band-structure calculations were based on the FLAPW (full potential linearized augmented plane wave) method. This uses the generalized gradient approximation (GGA) within the density functional theory and is known for yielding high accuracy results for much electron system. The Wien97 package was used for this study for the calculations [20]. The crystallographic parameters for calculation were adopted from the literature [21].

## III. RESULTS AND DISCUSSION

Figure 1(a) shows the SEM image of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  synthesized by sintering the ground mixture of  $\text{SrCO}_3$  and  $\text{Nb}_2\text{O}_5$  at 1573 K for 5 h in air. The average particle size after grinding the sintered materials was estimated to be 20  $\mu\text{m}$  from SEM photograph. Figure

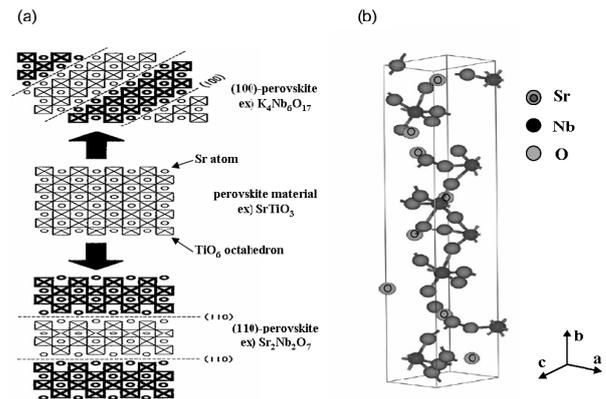
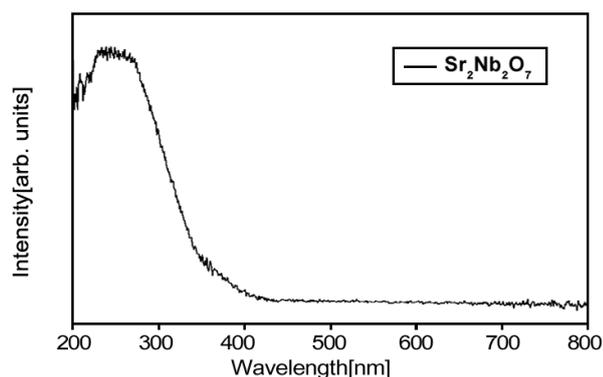
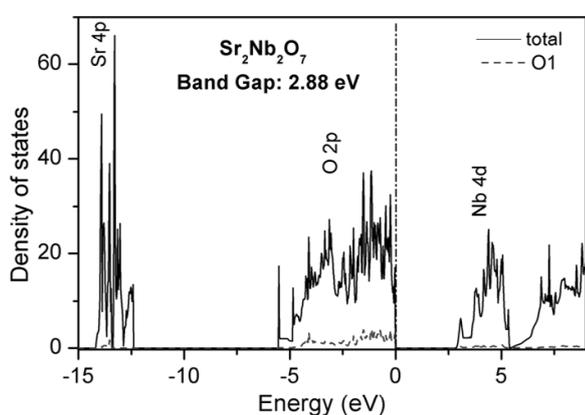


Fig. 2. (a) Schematic of various perovskite-types, (b) Typical crystal model of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and (b) the crystals models for  $\text{Sr}_2\text{Nb}_2\text{O}_7$  (orthorhombic).

1(b) shows the room temperature XRD spectrum of  $\text{Sr}_2\text{Nb}_2\text{O}_7$ . The peaks are attributable to (110) layered perovskite  $\text{Sr}_2\text{Nb}_2\text{O}_7$  with an orthorhombic structure, which is a room temperature stable phase of  $\text{Sr}_2\text{Nb}_2\text{O}_7$ . Thus, the typical samples prepared at 1573 K were found to possess an orthorhombic structure without any impurity phase.

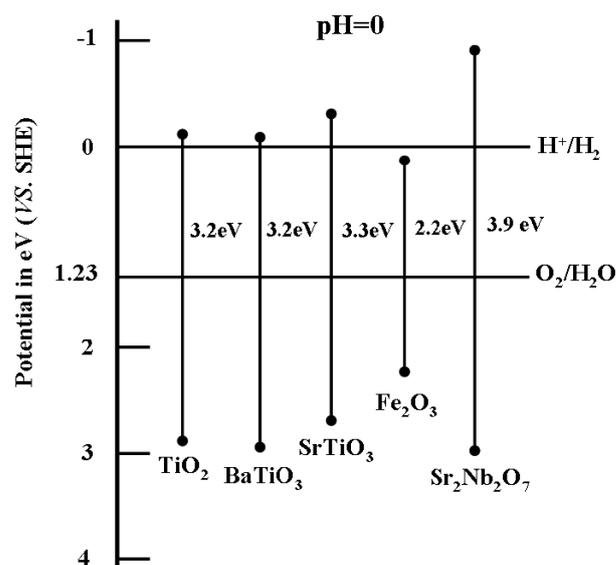
Layered perovskite-type could be classified as (100) and (110) group by the crystalline alignment. The schematic structures of the layered and ideal perovskite-type materials are illustrated in Figure 2(a). As typical example of the (100) group, Sr-Ti-O system was first time studied by Ruddlesden and Popper [22]. They studied  $\text{Sr}_3\text{Ti}_2\text{O}_7$  structure in this category. It consisted of 2  $\text{TiO}_6$  contained perovskite slab and one  $\text{SrO}$ , as rock salt type, fixed in interlayer space. On the other hand,  $\text{Sr}_2\text{Nb}_2\text{O}_7$  a typical example of the (110) group as illustrated in Figure 2(b), is a Carpy and Galy type structure with a space group of  $Cmc2_1$ , and has an orthorhombic unit cell with lattice parameters of  $a = 3.95 \text{ \AA}$ ,  $b = 13.99 \text{ \AA}$ ,  $c = 5.7 \text{ \AA}$ . If the  $\text{TiO}_2$  component of  $\text{SrTiO}_3$  is completely replaced by  $\text{Nb}_2\text{O}_5$ , i.e. if the composition is  $2 \text{ SrO} + \text{Nb}_2\text{O}_5$ , the product is  $\text{Sr}_2\text{Nb}_2\text{O}_7$ . This structural substitution gives highly donor-doped (110) layered perovskite materials. Thus, this material is in the donor rich state which results in distorted, cation-deficient, and oxygen-rich interlayer. The excess oxygen in these structurally modified (110) perovskites comes from a very high concentration of donor impurities. In this structure, every slabs along (110) axis are shifted to  $c/2$  distance based on the  $\text{ABO}_3$  unit cell. It consisted with 4  $\text{NbO}_6$  contained perovskite slab and no interlayer component, different from (100) group materials. Such highly donor doped perovskites have been shown by us to possess high photocatalytic efficiencies compared to the other binary simple metal oxides [19].

Figure 3 shows UV-vis diffuse reflectance spectra (DRS) of  $\text{Sr}_2\text{Nb}_2\text{O}_7$ . The band gap energy estimated

Fig. 3. UV-Vis diffuse reflectance spectrum of  $\text{Sr}_2\text{Nb}_2\text{O}_7$ Fig. 4. Calculated total and partial (for O1) density of state (DOS) of orthorhombic  $\text{Sr}_2\text{Nb}_2\text{O}_7$ .

from UV-vis DRS was 3.97 eV, which was larger than the energy ( $>1.23$  eV) required to decomposed water. This makes it absorb UV radiation thereby resulting in an UV active photocatalyst.

In order to obtain a detail insight of the electronic structure and band gap, we performed the electronic band structure calculation on  $\text{Sr}_2\text{Nb}_2\text{O}_7$ . Figure 4 shows the total and projected partial densities of states (DOS) for  $\text{Sr}_2\text{Nb}_2\text{O}_7$ , where the top of the valence band was set to 0 eV. Figure 2(b) shows a structure model that was used in calculation. The muffin-tin radii for Sr, Nb and O were chosen to be 2.0, 1.8 and 1.6 respectively, in these calculations. The convergence parameter of  $\text{RK}_{max}$  was set to 6.0. The calculation was iterated with the charge convergence criteria of 0.0001. The low-energy DOS between  $-15$  and  $-10.0$  eV is due to the contribution of Sr  $4p$  states. In the intermediate energy DOS, O  $2p$  states mainly contribute to form the valence band. 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 oxygen atoms. In the case of high-energy bands above Fermi energy, the Nb  $4d$  state is dominantly contributing to the conduction band

Fig. 5. Schematic representing the experimental positions of valence and conduction bands for materials in contact with aqueous electrolyte at  $\text{pH} = 0$  [24].

with a partial share from the O  $2p$  state. The computed band gap of the highly donor-doped (110) layered perovskite material,  $\text{Sr}_2\text{Nb}_2\text{O}_7$ , was ca.  $\sim 2.9$  eV, which is underestimated to that of the value estimated from UV-vis DRS. However the theoretical results are acceptable within the limits of theoretical errors as suggested by single particle Kohm-Sham approach [23].

We made a correlation of experimental and theoretical observations. Figure 5 shows the position of valence and conduction band edges for several oxides materials in contact with aqueous electrolyte at  $\text{pH} 0$  along with the known [24] band edge positions for  $\text{Sr}_2\text{Nb}_2\text{O}_7$ . The energy positions of the conduction band and the valence band edges are well known to be very important for photocatalytic reactions. Thus, the complete photocatalytic decomposition of water is possible if the conduction band energy is at least as negative (*i.e.*, higher in the energy position) as that required to reduce water to hydrogen gas (0.0 eV in acid solution), and the valence band is at the least as positive (*i.e.*, lower in the energy position) as that required to oxidize water to oxygen gas (+1.23 eV). In present case observed and calculated band edge positions satisfy these conditions. The band gap energies of  $\text{TiO}_2$ ,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{Sr}_2\text{Nb}_2\text{O}_7$  as shown in Figure 5 were 3.2, 3.18, 3.3 and 3.9 eV [25], respectively. Although  $\text{TiO}_2$ ,  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  have good band position for  $\text{H}_2$  production from water, quantum yields of these materials are very low because their conduction band edge positions are similar to the reduction potential of water. However, in the case of  $\text{Sr}_2\text{Nb}_2\text{O}_7$ , the conduction band edge position is more negative than those of  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$ . The difference in the conduction band levels and corresponding difference in the band gaps leads to different quantum yield for the water

splitting. Thus the correlation clearly reveals the better efficiency of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  than other conventional unlayered oxides.

#### IV. CONCLUSIONS

Highly donor doped  $\text{Sr}_2\text{Nb}_2\text{O}_7$  was synthesized by solid state reactions. The photo physical properties were studied and their correlation with electronic structure as calculated here is discussed. The known valence and conduction band positions are mainly responsible for the reported high photocatalytic activity in UV region.

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