

## Photoelectrochemical studies on the mixed oxides, $A_6Nb_8Ti_2O_{30}$ (A = Ba, Sr)

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**Abstract.** The photoelectrochemical behaviour of oxide bronzes of the type  $A_6Nb_8Ti_2O_{30}$  (A = Ba, Sr) has been studied. They show good photoactivity with photopotentials of the order of 700–800 mV. The flat band potential has been estimated to be  $-0.9$  V vs SCE. The band gap estimated from the spectral response is 3.1 eV.

**Keywords.** Photoelectrochemical cells; titanates; niobates; oxide bronzes.

### 1. Introduction

Of the various oxides that have been studied as semiconductor photoelectrodes for the photoassisted electrolysis (PAE) of water, the mixed oxide titanates and niobates have proved to be excellent candidates (Wrighton *et al* 1976; Kung *et al* 1977; Hormadaly *et al* 1980; Subba Rao *et al* 1984; Matsumoto *et al* 1986; Paranthaman *et al* 1986). The main features of all titanates and niobates are the large negative flat band potential and their remarkable stability in strong acidic/alkaline solutions. The large negative flat band potentials ( $V_{fb}$ ) result from the low electronegativity of Ti and Nb (1.5 for Ti and 1.6 for Nb, according to Pauling's scale). Because of the large  $V_{fb}$ , electrolysis of water is possible with a little applied bias. It has been demonstrated that with  $n$ -SrTiO<sub>3</sub> (Wrighton *et al* 1976) and  $n$ -Zn<sub>2</sub>TiO<sub>4</sub> (Matsumoto *et al* 1986), it is possible to electrolyse water without any applied bias. The stability of these oxides in aqueous solutions is due to the fact that the photoanodic decomposition potentials of these oxides are more positive compared to  $E(O_2/H_2O)$ , especially at higher pH values. In most of these oxides, electronic conductivity can be induced easily (and hence the material can be made  $n$ -type) either by H<sub>2</sub> reduction or by suitable substitution (e.g. La substitution in SrTiO<sub>3</sub>). The  $n$ -type conductivity arises from the Ti<sup>3+</sup>  $3d^1(t_{2g})$  or Nb<sup>4+</sup>  $4d^1(t_{2g})$  electronic levels which act as shallow donor centres. The only disadvantage of these oxides is their large and indirect band gap (usually > 3 eV). Because of the large band gap, these materials can absorb only the UV light, which constitutes only 3% of the solar spectrum. The indirect nature of the fundamental absorption leads to low absorption coefficient. Attempts to induce absorption in the visible region by substitution at Ti site with Cr, Ni etc were only partially successful. However, these ions lead to localized sub band gap levels, which act as recombination centres and thus give lower quantum efficiencies of light conversion.

Studies on various titanates and niobates have shown that the photoactivity of these compounds can be uniquely attributed to the presence of TiO<sub>6</sub> and NbO<sub>6</sub> octahedra. Since the photoelectrochemical (PEC) properties are influenced mainly by the band gap and the flat band potential and since these parameters depend on

the structure, search for new mixed oxide titanates and niobates with various structures is essential. Toward this end, we have chosen a series of oxide bronzes and have carried out PEC studies on them. Our earlier studies (Ramakrishnan *et al* 1993) on the hexagonal oxide bronzes,  $\text{Ba}_3\text{Nb}_4\text{Ti}_4\text{O}_{21}$  have shown that they could be potential candidates for use as semiconducting electrodes in PEC cells. Presently we report our studies on the oxide bronzes of the type,  $\text{A}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$  ( $\text{A} = \text{Sr}, \text{Ba}$ ). These compounds crystallize with a tetragonal bronze structure with space group  $P4bm$ . The lattice constants of these compounds are  $a \sim 12.5 \text{ \AA}$  and  $c \sim 4 \text{ \AA}$ . Single crystal structural analysis on  $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$  was reported by Stephenson (1965). The lattice is constructed of  $\text{MO}_6$  octahedra joined by corners, every oxygen atom thus being common to two M atoms. The  $\text{TiO}_6$  and  $\text{NbO}_6$  octahedra are statistically distributed. The dielectric properties have been extensively studied in the literature (Jamieson *et al* 1969; Itoh *et al* 1970; Ikeda *et al* 1971; Itoh and Iwasaki 1973; Varaprasad 1985; Neurgaonkar *et al* 1988, 1990; Choudhary *et al* 1993). The compounds are reported to be ferroelectric with  $T_c = 518 \text{ K}$  for  $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$  and  $403 \text{ K}$  for  $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ . However the PEC behaviour of these compounds has not been explored. In the present study, we have carried out PEC studies on these phases, since these phases contain photoactive  $\text{NbO}_6/\text{TiO}_6$  octahedra. Present results show that the photoelectrochemical behaviour of these compounds is comparable to that of the well known  $\text{SrTiO}_3$  and  $\text{TiO}_2$ .

## 2. Experimental

Polycrystalline  $\text{A}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$  ( $\text{A} = \text{Sr}, \text{Ba}$ ) were synthesized from high purity  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{TiO}_2$  (all of Cerac, UK) and  $\text{Nb}_2\text{O}_5$  (99.9%) (SMP, Hyderabad). Stoichiometric

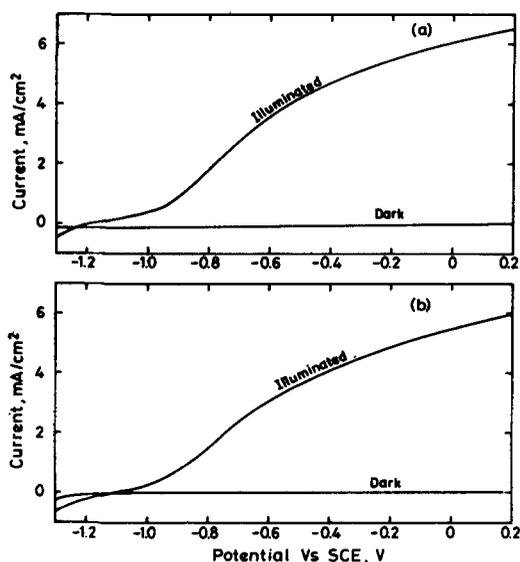


Figure 1. Potentiostatic current-voltage curves of the cell, (a)  $n\text{-Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}/1 \text{ M NaOH/Pt}$  and (b)  $n\text{-Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}/1 \text{ M NaOH/Pt}$  (1000 W Xe lamp; full intensity  $> 1.5 \text{ W/cm}^2$ ).

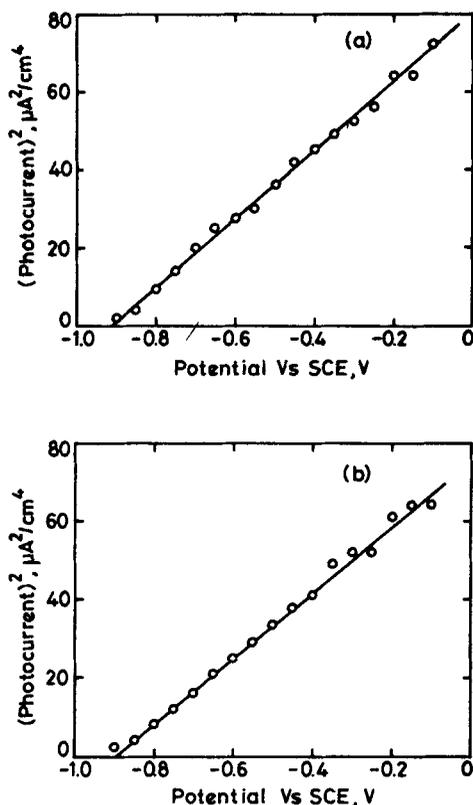


Figure 2. Flat band potential,  $V_{fb}$ , determination from  $i_{photo}^2$  vs  $V$  plot for (a)  $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$  and (b)  $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ . Data taken at 370 nm using monochromator. The data points are LSQ fitted to extrapolate to  $V_{fb}$ .

amounts of the oxides/carbonates were thoroughly mixed in an agate mortar and heated in air at 1473 K for 72 h with two intermittent grindings. The reacted powders were pressed into pellets (8 mm dia, 1–2 mm thick; WC lined SS die; hydraulic press: 3 tonnes) and sintered at 1473 K for 24 h and at 1623 K for 6 h. Phase formation was checked by using a computerized powder X-ray diffraction (XRD) unit (Rich Seifert, Germany; XRD 3000P, 35 kV; 30 mA;  $\text{CuK}\alpha$  radiation). The compounds were reduced in  $\text{H}_2$  atmosphere or by Ti gettering to induce electronic conductivity. PEC studies were carried out in aq. 1 M NaOH electrolyte. The preparation of the electrodes and electrolyte and the details of PEC experimental set-up are as described elsewhere (Ramakrishnan *et al* 1993). The working electrode (semiconductor electrode) was etched with 5% aqueous HF solution for 1–2 min before measurements.

### 3. Results and discussion

All compounds were single phasic in nature. The XRD patterns could be indexed on the basis of a tetragonal unit cell and the lattice parameters calculated by the

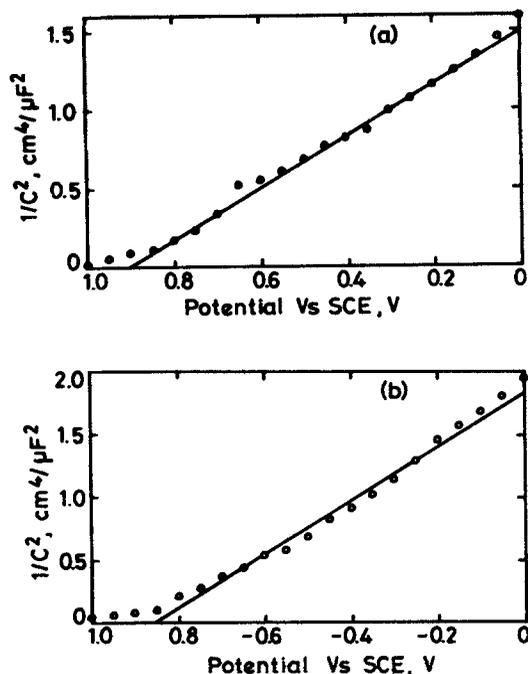


Figure 3. Mott-Schottky plots for (a)  $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$  and (b)  $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$  in 1 M NaOH solution.

LSQ fit of the high angle lines viz.  $a = 12.353 \text{ \AA}$ ,  $c = 3.99 \text{ \AA}$  for  $\text{Ba}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$  and  $a = 12.447 \text{ \AA}$ ,  $c = 3.86 \text{ \AA}$  for  $\text{Sr}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$ , agree well with those reported in the literature. Phases were stable upon reduction as confirmed by X-ray diffraction. The as-sintered pellets were white in colour and upon reduction they turned black indicating the creation of  $\text{Ti}^{3+} 3d^1(t_{2g})$  and/or  $\text{Nb}^{4+} 4d^1(t_{2g})$  levels. The room temperature resistivities of the reduced pellets were  $\sim 10^2 \text{ ohm cm}$ , while the unreduced pellets were insulators having resistivities  $> 10^7 \text{ ohm cm}$ .

Photopotentials were observed immediately upon irradiation of the electrode/electrolyte interface with negligible dark potentials. The shift in the potential upon irradiation was towards the negative direction indicating the  $n$ -type nature of the electrode. A maximum  $V_{oc}$  of the order of 700–800 mV was observed. Photocurrent ( $i_{photo}$ ) stability plot at a potential of +0.2 V vs SCE shows  $I_{photo}$  of the order of  $6 \text{ mA/cm}^2$ . Sharp rise and cut off in  $V_{oc}$  as well as  $I_{photo}$  before and after irradiation and the stability during illumination indicates good quality of the electrode and the absence of recombination centres in the space charge region.

The  $I$ - $V$  characteristics for  $\text{A}_6\text{Nb}_8\text{Ti}_2\text{O}_{30}$  ( $A = \text{Sr}, \text{Ba}$ )/1 M NaOH/Pt, are shown in figure 1. The plots show negligible anodic dark current indicating the rectifying nature of the semiconductor-electrolyte interface. The photocurrent almost saturates above a potential of 0 V vs SCE, indicating fairly good absorption of light by the phases. The onset of the photocurrent was observed in the potential range  $-1.2$  to  $-1.1 \text{ V vs SCE}$ .

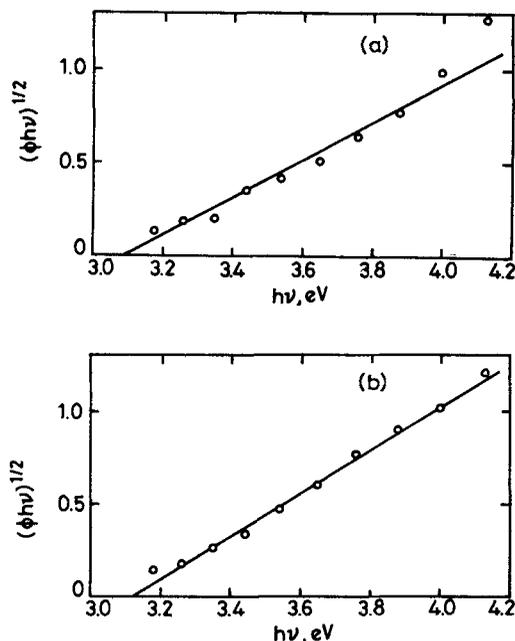


Figure 4. Determination of indirect band gap of (a)  $Ba_6Nb_8Ti_2O_{30}$  and (b)  $Sr_6Nb_8Ti_2O_{30}$  from the plot of  $(\Phi hv)^{1/2}$  vs  $h\nu$ .

The flat band potentials were determined from the  $I$ - $V$  characteristics using monochromatic radiation (350 nm) using the relation,

$$I_{\text{photo}}^2 \propto (V - V_{\text{fb}}). \quad (1)$$

Figures 2a and b show the  $I_{\text{photo}}^2$  vs  $V$  (vs SCE) plot for  $A_6Nb_8Ti_2O_{30}$  ( $A = \text{Ba}$  and  $\text{Sr}$  respectively). The linear plot obtained by the LSQ fit of the data points extrapolate to an identical  $V_{\text{fb}}$  of  $-0.9$  V vs SCE for both the compounds. The flat band potentials were also estimated from the Mott-Schottky plots using the Mott-Schottky equation, viz.

$$1/C^2 = (2/\epsilon\epsilon_0 qN_D) [(V - V_{\text{fb}}) - (kT/q)], \quad (2)$$

where,  $k$  is the Boltzmann constant and  $T$  the absolute temperature. Hence,  $1/C^2$  is directly proportional to the applied potential at a given temperature and the extrapolation of the linear plot of  $1/C^2$  vs  $V$  gives the flat band potential. The values of the flat band potential obtained from Mott-Schottky plot are  $-0.9$  V vs SCE for  $Ba_6Nb_8Ti_2O_{30}$  and  $-0.855$  V vs SCE for  $Sr_6Nb_8Ti_2O_{30}$  (figure 3). This slight shift towards positive value for the Sr analogue is not observed in the values obtained from  $I^2$  vs  $V$  (vs SCE) plot which gave identical value of  $-0.9$  V vs SCE. These values of flat band potentials are more positive than that of  $\text{SrTiO}_3$  ( $-1.3$  V vs SCE) and  $\text{TiO}_2$  ( $-1.0$  V vs SCE).

Photocurrents were measured as a function of wavelength at an applied bias of +0.2 V vs SCE, using Jobin–Yvon monochromator. The measured  $I_{\text{photo}}$  values were normalized to the input light flux as measured by a thermopile and the quantum efficiency ( $\Phi$ ) values were calculated. Quantum efficiencies of about 50% were observed for lower wavelengths which are comparable to that observed for SrTiO<sub>3</sub> and the quantum efficiency decreased to low values at wavelengths > 380 nm. According to Gartner's model, the quantum efficiency,  $\Phi$ , is related to the energy of photons ( $h\nu$ ) by the equation

$$(\Phi h\nu) \propto (h\nu - E_g)^{n/2}, \quad (3)$$

where  $n = 1$  for direct band gap and  $n = 4$  for indirect band gap. Thus, the band gap and its nature can be found by extrapolation of the linear portions of  $(\Phi h\nu)^{2/n}$  vs  $h\nu$ . Indirect band gap ( $E_g$ ) values of 3.10 and 3.12 eV were estimated from  $(\Phi h\nu)^{1/2}$  vs  $h\nu$  plot for the Ba- and Sr-analogues respectively (figure 4). The observation of near identical band gap for both the compounds is due to the fact that the bottom of the conduction band is constituted of Ti/Nb orbitals and the A-ion has negligible influence in spite of the structural similarity. However, the ferroelectric Curie temperature ( $T_C$ ) values differ indicating the covalency effects of the A–O bond w.r.t. Ti–O and Nb–O bonds. Sr–O bond is more covalent making Ti–O/Nb–O bonds more ionic in Sr<sub>6</sub>Nb<sub>8</sub>Ti<sub>2</sub>O<sub>30</sub> and thereby reduced  $T_C$ .

#### 4. Summary

The oxides A<sub>6</sub>Nb<sub>8</sub>Ti<sub>2</sub>O<sub>30</sub> (A = Sr, Ba) have been studied for the first time as photoanodes. They show good photoactivity and stability in strong alkaline solution. They have a fairly large negative flat band potential of –0.9 V vs SCE and hence it is possible to electrolyse water with a little applied bias. They have a wide band gap of 3.1 eV. However, the structure provides ample scope for manipulation of band gap by chemical substitutions and these studies are underway.

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