Behaviour of acceptor states in semiconducting BaTiO_3 and SrTiO_3

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Abstract. The semiconductivity in MTiO_3 ($M = \text{Ba}, \text{Sr}$) in the temperature range of practical applications is greatly influenced by the electronic charge redistribution among the acceptor states, arising from the frozen cation vacancies as well as the transition metal ion impurities. The conductivity measurements and defect chemistry investigations above 800 K indicate that the predominant lattice defects are M - and oxygen vacancies. There is dominant p -type conduction at higher p_{O_2} values in acceptor doped materials at high temperatures. However, they are insulating solids around room temperature due to the redistribution of electrons between the neutral, singly- or doubly-ionised acceptor states. Results from EPR and resistivity measurements show that the above charge redistribution is dependent on crystal structure changes. Hence the electron or hole loss by the acceptor states is influenced by the soft modes which also accounts for the differences in electrical properties of BaTiO_3 and SrTiO_3 . The results are also useful in explaining the positive temperature coefficient in resistance and some photo-electrochemical properties of these solids.

Keywords. BaTiO_3 ; SrTiO_3 ; semiconductivity in perovskites; acceptor states.

1. Introduction

Semiconducting MTiO_3 ($M = \text{Ba}, \text{Sr}$) perovskites find applications in positive temperature coefficient resistors (PTCR), grain-boundary and intergranular layer capacitors, electrodes for photoelectrochemical reactions and photochromic devices. The electrical conductivity of these solids in the temperature range of practical applications has peculiar variations. For example, around the Curie point (T_c), the electrical resistivity of n -type BaTiO_3 ceramics increases with temperature by several orders of magnitude. Another case is of SrTiO_3 annealed in a H_2 -atmosphere, whose resistivity increases with temperature (metallic behaviour) whereas the donor-doped SrTiO_3 exhibits decreasing resistivity with temperature (semiconductor behaviour). These diverse features arise from the behaviour of acceptor states in MTiO_3 , which are caused by cation vacancies in the M -sublattice or the impurities, particularly the $3d$ metal ions. It is possible that either (i) the concentrations of the atomic defects formed at high temperatures (of crystal growth or sintering) remain frozen and the electronic (charge) equilibrium is readjusted or (ii) the defects remain in equilibrium with the surroundings all through the cooling history. Our observations indicate that possibility (i) is to be preferred. The present investigations confirm the redistribution of charges between neutral, singly- or doubly-ionised defects, being controlled by crystal structure changes and hence, influenced by the soft modes.

2. The conduction mechanism

The conduction and valence bands in MTiO_3 arise from the $3d^0$ orbitals of Ti^{4+} and the $2p^6$ orbitals of O^{2-} respectively. They are separated by an energy gap of 3.0–3.3 eV.

Thus the conduction electron corresponds to Ti^{3+} and the positive hole to $\text{O}^- \cdot M\text{TiO}_3$ can be made an n -type conductor either by doping with donors or by annealing in an atmosphere of lower oxygen partial pressure (p_{O_2}) above 800 K. *Donor* denotes any impurity with the nominal ionic charge more than that of the lattice sites it substitutes (La^{3+} at M^{2+} or Nb^{5+} at Ti^{4+} sites). The charge compensation of the donor in $M\text{TiO}_3$ can be by electron (e') in the conduction band (electron compensation), cation vacancy (vacancy compensation) or acceptor impurity (impurity compensation). *Acceptor* denotes the dopant having a lower valence than the replacing ion (Na^+ at M^{2+} or Fe^{3+} at Ti^{4+} sites). The acceptor is charge compensated by a positive hole (h'), oxygen vacancy or donor impurity. More than one type of compensation is possible simultaneously. At higher p_{O_2} , electron or hole compensation alone leads to change in electrical conductivity. At lower p_{O_2} , the oxygen vacancies formed can ionise, leading to electrons in the conduction band. Although a given metal ion impurity can occupy both the M^{2+} and Ti^{4+} sites and hence can act as donor and acceptor simultaneously, the substitution is mostly guided by ionic radii as well as the crystal field energy.

The nature of the charge carriers in n -type $M\text{TiO}_3$ continues to be debated, whether they are small polarons or band electrons. The electrical and optical properties can be interpreted either way (Ihrig and Hennings 1978). The presence of a conductivity-dependent optical absorption maximum around 0.6 eV (Berglund and Braun 1967) favours the small polaron concept. However, the drift mobility of 0.1–0.5 $\text{cm}^2/\text{V sec}$ in BaTiO_3 (Seuter 1974) and 3.3–8.0 $\text{cm}^2/\text{V sec}$ in SrTiO_3 is too high for thermally activated small polaron hopping. This together with the fact that the drift and the Hall mobilities are the same, support the band conduction. From the extensive discussions available in literature, it seems that the electrical properties of $M\text{TiO}_3$ cannot be explained by electrical experiments alone, and that the nature of the charge carriers has to be interpreted in the context of optical and electrical measurements, defect chemistry investigations and chemical analyses. All these data support the small polaron model with negligibly small or even negative kinetic transport terms and low donor dissociation energy of ≈ 0.1 eV. The enhanced mobility is due to the correlation of successive polaron hops. It can be considered that conduction in $M\text{TiO}_3$ comes close to the so-called 'transition region' between the validity of the adiabatic and nonadiabatic theories.

3. Defect chemistry

Since the acceptor states arise from the lattice defects, it is necessary to present some facts regarding conductivity behaviour and defect chemistry of $M\text{TiO}_3$ above 800 K and try to extrapolate them to lower temperatures.

Figure 1 shows the high temperature conductivity of undoped, donor- as well as acceptor-doped BaTiO_3 as functions of equilibrium p_{O_2} values. It is evident from the figure that undoped BaTiO_3 is a p -type conductor at $p_{\text{O}_2} > 10^{-5}$ atm whereas it is an n -type at lower p_{O_2} . Away from the conductance minimum, a linear relation,

$$\log \sigma = (1/m) \log p_{\text{O}_2}, \quad (1)$$

with slope $1/m = -\frac{1}{6}$ is followed. As temperature decreases, the conductance minimum shifts to lower p_{O_2} values and the slope of (1) changes to $-\frac{1}{4}$. Donor-doped BaTiO_3 shows n -type behaviour all through the p_{O_2} range. Three regions can be

Figure 1. Electrical conductivity of BaTiO_3 as a function of equilibrium p_{O_2} at different temperatures (a) undoped, (b) doped with 0.3 at % donor (c) doped with 0.3 at % acceptor. The individual points are the experimental values. The full lines are calculated from the model explained in the text.

distinguished on the curves in figure 1b: increase in conductivity with falling p_{O_2} (region 1), followed by the p_{O_2} -independent conductivity (region 2) and further increase at very low p_{O_2} (region 3). This behaviour is indicative of three independent mechanisms operating in different p_{O_2} regions. The shape of the conductivity curve is different for donor-doped specimens equilibrated below 1400 K (figure 1b). Incorporation of acceptors shifts the conductivity minimum to lower p_{O_2} and enhances the p -type conductivity at $p_{\text{O}_2} > 10^{-6}$ atm. Thus the conductance behaviour at higher temperatures (figure 1c) clearly indicates that the acceptor impurities are dissolved in the bulk of the specimen. Around room temperature, the acceptor-doped specimens are very insulating and p -type conductivity has never been observed in these samples. This led to the hypothesis that the acceptor dopants do not dissolve in the bulk of the grains but segregate preferentially at the grain boundaries (Heywang 1971; Brauer 1974).

The above results can be explained on the basis of the defect chemistry of BaTiO_3 , with the following simplifications. The defects due to interstitial atoms can be excluded on account of the close-packed structure of the lattice. Because the Ti^{4+} ion is placed in a deep potential minimum and a high valence is associated with it, the existence of vacancies in the Ti^{4+} -sublattice is neglected. Further, defect clusters and the effects of defect associations are ignored (Seuter 1974). Thus, the predominant lattice defects in MTiO_3 will be neutral, singly- and doubly-ionised oxygen (V_{O} , $V_{\text{O}}^{\cdot}$, $V_{\text{O}}^{\cdot\cdot}$) and Ba- (V_{Ba} ,

$V'_{\text{Ba}}, V''_{\text{Ba}}$) vacancies. The electroneutrality can be represented as

$$n + [V'_M] + 2[V''_M] + [A'] + 2[A''] = p + [V'_O] + 2[V''_O] + [D'] + 2[D''], \quad (2)$$

where $[A']$, $[A'']$, $[D']$ and $[D'']$ are the concentrations of the singly- or doubly-ionised acceptor or donor impurities, n and p are the concentrations of electrons and holes respectively.

Above 800 K, the concentration of oxygen vacancies varies with p_{O_2} and temperature, in accordance with the reaction,

where $\text{O}_{\text{O}^{2-}}$ = oxygen in the regular lattice sites, and O_2 = oxygen molecule in the gas phase. From the law of mass action, it follows that,

$$[V''_{\text{O}}]n^2 = K_0 e^{-E_0/kT} p_{\text{O}_2}^{-1/2}, \quad (4)$$

with E_0 = the energy of formation of V''_{O} , k = Boltzmann constant and K_0 = the preexponential factor. Due to their extremely low diffusion coefficient, the Ba-vacancies are in equilibrium with the surroundings only above 1400 K, involving the modified Schottky relation:

$$[V''_{\text{Ba}}][V'_{\text{O}}] = K_s e^{-E_s/kT}, \quad (5)$$

where K_s is the preexponential factor and E_s , the activation energy for the reaction occurring at the grainboundary layer, leading to the generation of most of the Ba-vacancies (Wernicke 1976):

where $\text{Ba}_{\text{lattice}}$ and $\text{O}_{\text{lattice}}$ are from the regular lattice positions of BaTiO_3 .

Besides the 3d metal ion impurities, one encounters Ba-vacancies as acceptors being frozen-in below 1400 K due to the low diffusion coefficient. The acceptors are characterised by their ionisation energy. It follows from the band theory that the acceptors occupy suitable positions in the forbidden gap and obey the Fermi statistics so that,

$$[A^0] = [A]/\{1 + \frac{1}{2} e^{(E_f - E)/kT} + e^{(2E_f - E' - E'')/kT}\}, \quad (7)$$

$$[A'] = \frac{1}{2} [A^0] e^{(E_f - E)/kT}, \quad (8)$$

$$[A''] = [A^0] e^{(2E_f - E' - E'')/kT}, \quad (9)$$

where $[A]$ = total concentrations of the acceptors (Ba-vacancies and impurities);

$[A^0]$ = the concentration of neutral acceptors;

E' , E'' = the energy levels of singly- and doubly-ionised acceptors;

E_f = Fermi energy.

Besides ionic defects, one has to also consider the concentrations of electrons and holes:

$$n = N_c e^{-(E_c - E_f)/kT}, \quad (10)$$

$$p = N_v e^{-(E_f - E_v)/kT}, \quad (11)$$

where N_c and N_v are the density of states in the conduction and valence band respectively; E_v and E_c are the upper limit of valence band and lower limit of conduction band respectively.

Figure 2. Calculated defect concentration as a function of p_{O_2} for (a) undoped BaTiO₃ equilibrated at 1400 K (b) doped with 0.3 % donor equilibrated at 1100 K (c) doped with 0.3 at % donor equilibrated at 1400 K and (d) doped with 0.3 atom % acceptor equilibrated at 1400 K.

The unknown concentrations of the neutral and ionised defects can be calculated if a proper choice of the material parameters (E' , E'' , K_0 , E_0 etc.) are made in the light of reliable experimental points and with the assumption that electroneutrality of the solid, as per equation (2), is preserved. Setting up simultaneous equations from (2), (4) and (7)–(11), one can numerically solve for the concentrations of various defects at selected temperature and p_{O_2} and relate them to conductivity:

$$\sigma = e(n\mu_n + p\mu_p), \quad (12)$$

where μ_n and μ_p are the mobilities of electrons and holes available from Seuter (1974). The full lines in figure 1a–c are obtained by this procedure. The deviations of the calculated values from the experimental points are more on the p -type side, particularly for the acceptor-doped BaTiO₃.

Figure 2 shows the p_{O_2} -dependence of defect concentrations for BaTiO₃ at higher temperatures. Accordingly, the electroneutrality for the undoped BaTiO₃ can be simplified as:

$$[V'_A] = p, \text{ at } p_{O_2} > 10^{-5} \text{ atm}$$

and $n = [V'_O] + 2[V''_O]$ at lower p_{O_2} , which accounts for the p -type behaviour changing over to n -type as p_{O_2} is lowered. For donor-doped BaTiO₃, the electro-neutrality relation can be simplified as:

$n = [D^{\cdot}] - [A'] - 2[A'']$ in region 1, $n = [D^{\cdot}]$ in region 2, and $n = [V_O^{\cdot}] + 2[V_O^{\cdot\cdot}]$ in region 3, so that n -type conductance prevails throughout the p_{O_2} range.

For the acceptor doped $BaTiO_3$,

$$p = [V_O^{\cdot}] + 2[V_O^{\cdot\cdot}] - [A'] \text{ at } p_{O_2} > 10^{-9} \text{ atm}$$

and $n = [V_O^{\cdot}] + 2[V_O^{\cdot\cdot}] - [A'] + [A'']$ at lower p_{O_2} values. However, the significant point in figure 2c is the existence of larger concentrations of neutral acceptors at higher p_{O_2} .

Very similar results, as above, are obtained for the defect chemistry of $SrTiO_3$ as well.

The prediction of conductivity behaviour at lower temperatures, using the materials parameters from high temperatures has to involve a number of assumptions. Below 1400 K, the Ba-vacancies and below 800 K the oxygen vacancies are no more in equilibrium with the surroundings. Therefore, at lower temperatures, the concentration of the atomic defects are frozen whereas the electronic equilibria will readjust so that,

$$[V_O] = [V_O^{\cdot}] + [V_O^{\cdot\cdot}] = \text{a constant}, \quad (13)$$

$$[V_{Ba}] = [V_{Ba}^0] + [V_{Ba}^{\cdot}] + [V_{Ba}^{\cdot\cdot}] = \text{a constant}, \quad (14)$$

where $[V_O]$ and $[V_{Ba}]$ are the total concentrations of the corresponding vacancies.

No details of these charge readjustments are known except that the empty levels in the band gap are successively filled with electrons from bottom upwards. Using (7)–(11) and assuming the constancy of total atomic defects as in (13) and (14), one can calculate the temperature dependence of conductivity, provided one assumes that the donor is

Figure 3. Calculated electrical conductance of $BaTiO_3$ at 300 K, using high temperature parameters; (—) undoped; ($\times \times \times$) donor doped, equilibrated at 1400 K; (...) donor doped and equilibrated at 1100 K; (---) acceptor doped and equilibrated at 1400 K.

fully ionised, whereby

$$[D^{\cdot}] = [D] / \{1 + 2e^{(E_f - E_D)/kT}\}, \quad (15)$$

where $[D^{\cdot}]$ = concentration of singly-ionised donor and E_D = energy of the donor levels.

Figure 3 shows the conductivity of BaTiO₃ at 300 K as a function of p_{O_2} . The *n*- and *p*-type regions are noticeable in undoped and acceptor-doped BaTiO₃ with extremely low conductivity values. Donor-doped BaTiO₃ equilibrated at 1400 K has lower conductivity than the sample equilibrated at 1100 K. The experimental observations show that the room temperature conductivity is dependent on the rate of cooling from the sintering temperature (~ 1600 K). When cooled at moderate rates (50–150 K/hr), the samples are conducting ($\sigma \approx 0.1 \text{ ohm}^{-1} \text{ cm}^{-1}$) whereas at a 2–10 K/hr cooling rate the samples are insulating ($\sigma \leq 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$). This is not in accordance with the prediction from defect chemistry, which also indicates similar behaviour for SrTiO₃. Experimentally one observes that donor-doped SrTiO₃ when sintered in air is insulating, irrespective of the cooling rates. It is, therefore, obvious that the nature of charge redistribution between the various acceptor states is not identical and hence, the low temperature electroneutrality relations have to be modified.

4. EPR and resistivity results

The electronic redistribution between the acceptor type defect states can be followed by electron paramagnetic resonance (EPR). BaTiO₃ as such showed no EPR spectrum at any temperature of measurement (80–500 K) indicating very low concentrations of paramagnetic impurities. Donor-doped BaTiO₃, sintered in air at 1650 K, showed an asymmetric signal of $g = 1.963$ and a very weak signal of $g = 1.997$ at 300 K (figure 4). The weak $g = 1.997$ signal is absent when no extra TiO₂ is added (usually ~ 0.5 mole %) as the sintering additive. Above the Curie point ($T_c \approx 398$ K), the $g = 1.997$ signal acquires pronounced gain in intensity, whereas the $g = 1.963$ signal becomes more symmetric with no difference in intensity. In the case of BaTiO₃ annealed at $p_{O_2} \approx 10^{-20}$ atm and 1200 K, only the $g = 1.963$ signal is observed at 300 K, while the $g = 1.997$ appears above T_c with much lower intensity than that of the donor-doped specimens. We have identified that the $g = 1.963$ signal originates from the $Ti^{3+} - V_O$ defect complex whereas $g = 1.997$ arises from singly ionised V'_{Ba} (Kutty *et al* 1984). In the tetragonal phase, the Ba-vacancies are either neutral or doubly ionised (V''_{Ba} , He-like) and hence, do not show EPR signals. If V''_{Ba} were present in the tetragonal phase, the conversion to V'_{Ba} ($V''_{Ba} = V'_{Ba} + e'$) should enhance the conduction. Since the reverse is the case (figure 5), neutral V_{Ba} should be the right choice. The appearance of the $g = 1.997$ signal is reversible across the phase transition. Its disappearance in the tetragonal phase may be related to the crystal structure changes or due to the existence of spontaneous polarisation. The EPR spectra recorded at lower temperatures indicate that $g = 1.997$ acquires intensity in the rhombohedral phase as well (figure 6). Since the rhombohedral phase is also ferroelectric, the appearance of the $g = 1.997$ signal depends on the crystal structure changes and not on the spontaneous polarisation. Considering the difference in intensity of the $g = 1.997$ signal in donor-doped BaTiO₃ when compared to that of

Figure 4. EPR signals of La-doped BaTiO_3 (a) at 400 K, (b) at 350 K and (c) BaTiO_3 sample annealed at $p_{\text{O}_2} \sim 10^{-20}$ atm and 1200 K.

Figure 5. Electrical resistivity of La-doped as well as H_2 -annealed BaTiO_3 .

Figure 6. Variation in intensity of V'_{Ba} EPR signal for La-doped as well as H_2 -annealed BaTiO_3 .

BaTiO_3 annealed in low p_{O_2} , it can be concluded that the concentration of V_{Ba} is very much higher in donor-doped materials.

Corresponding changes in electrical resistivity (figure 5) indicate that the Ba-vacancies are neutral in tetragonal and orthorhombic phases whereas they are singly ionised in the cubic and rhombohedral phases. The change over of $V_{\text{Ba}} + e' \rightleftharpoons V'_{\text{Ba}}$ leads to the trapping of charge carriers which are therefore not available for conduction and hence increase in electrical resistivity. These observations lead to a new explanation for the PTCR effect in BaTiO_3 ceramics (Kutty *et al* 1985). Although the sign of the temperature coefficient of resistivity across the rhombohedral-orthorhombic phase transition is in accordance with that for any semiconductor, the magnitude of resistivity change is large in a short temperature interval and probably arises from the charge redistribution between the acceptor states arising from Ba-vacancies. It is evident from figures 5 and 6 that V'_{Ba} has higher stability in the cubic as well as the rhombohedral phases.

It is known that 3d-metal ions in concentrations < 0.1 atom %, enhance the PTCR property and improve the grain-boundary layer capacitance (Brauer 1974; Ueoka 1974). At higher concentration ranges, 3d-ions enhance the resistivity of BaTiO_3 even when sintered at lower p_{O_2} atmospheres. The magnetic susceptibility measurements of such samples showed that the valencies of Cr, Mn, Co dopants change with p_{O_2} , whereas that of Fe, Ni, Zn remain unchanged (Hagemann and Ihrig 1979). Therefore the nature of Mn and Fe at concentrations < 0.1 atom % in BaTiO_3 has been investigated. Mn enhances the PTCR around T_c and also the resistivity across the orthorhombic-rhombohedral phase transition (figure 5). For BaTiO_3 doped with 0.25 atom % La and 0.01–0.03 atom % Mn, no EPR signals from Mn are noticed at 300 K. Above T_c , a 6-line

spectrum with $g = 2.0024$ and hyperfine splitting constant $A = 80 \times 10^{-4} \text{ cm}^{-1}$ is noticed. This spectrum is identified as that arising from the $|+\frac{1}{2}M_I\rangle \rightarrow |-\frac{1}{2}M_I\rangle$ transition of Mn^{2+} occupying Ti^{4+} sites (Kutty and Murugaraj 1985). The appearance of the 6-line Mn^{2+} signal is reversible across the phase transformation. When recorded at lower temperatures, the Mn^{2+} -signal appears only in the rhombohedral phase. Figure 7 shows that the Mn^{2+} signal is not observed in the orthorhombic and tetragonal phases. When the concentration of Mn is increased to 0.05 atom %, two sets of signals of $g = 2.0024$ and 2.0028 are observed with low intensity in these two phases. Above T_c only one set of 6-line signal is noticed with $g = 2.0024$ and 100-fold increase in intensity (figure 7). The two sets of 6-line signals arise from the anisotropy of the g -factor in the tetragonal phase. The EPR of BaTiO_3 : 0.02 atom % Mn reduced in H_2 shows the same temperature variation features as those of BaTiO_3 : 0.25 La, 0.02 Mn sintered in air. When BaTiO_3 : 0.05 atom % Mn is annealed in O_2 at 1200 K, no signal from Mn is noticed in all the phases of BaTiO_3 .

The EPR of Mn^{4+} ions is observed at room temperature in SrTiO_3 , TiO_2 and PbTiO_3 indicating a larger relaxation time for this d^3 -ion (Müller 1959; Anderson 1960; Hennings and Pomplun 1974). There is no reason why Mn^{4+} should have a shorter relaxation time in BaTiO_3 at room temperature. Obviously, Mn does not exist in the tetravalent state, whereas Mn^{3+} (d^4) with its short relaxation time should be the species whose EPR signal can be observed only at very low temperatures ($\sim 10 \text{ K}$). Therefore, the absence of a Mn signal in the tetragonal and orthorhombic BaTiO_3 can be attributed to the existence of Mn as Mn^{3+} ions. For the same sample, Mn exists as Mn^{2+} in the cubic and rhombohedral phases indicative of the crystal-structure-dependent $\text{Mn}^{3+} + e' \rightleftharpoons \text{Mn}^{2+}$ conversion, whereby Mn^{3+} traps electrons and augments the effect of $V_{\text{Ba}} + e' \rightleftharpoons V'_{\text{Ba}}$ in lowering the number of charge carriers. This

Figure 7. Change in intensity of Mn^{2+} EPR signal for various concentrations of Mn in La-doped BaTiO_3 .

leads to enhanced resistivity jump around the two-phase transition temperatures (figure 5).

Incorporation of 0.01–0.1 atom % Fe^{3+} ions in BaTiO_3 also enhances the PTCR effect but to a lesser extent than that of Mn. EPR spectrum of $\text{BaTiO}_3:0.25 \text{ La}, 0.01 \text{ Fe}^{3+}$ showed two additional signals of $g = 5.542$ and 11.831 which are identified as arising from the anisotropic g -factor components of $\text{Fe}^{3+}-V_{\text{O}}$ defect complex in the tetragonal phase (Murugaraj and Kutty 1986). When the concentration of Fe^{3+} is increased to 0.05 atom %, an additional signal of $g \approx 2.00$ is observed at 300 K which originates from $\text{Fe}_{\text{Ti}}^{3+}$. In the orthorhombic phase, there are three signals of $g = 4.437, 5.54$ and 11.831 due to the non-equivalence of the $\text{Fe}^{3+}-V_{\text{O}}$ defect complex. The temperature variation of the combined intensities of $\text{Fe}^{3+}-V_{\text{O}}$ signals is shown in figure 8. The signals vanish as the temperature approaches T_c , as does the orthorhombic-rhombohedral transition at low temperatures. This may either correspond to the dissociation of $\text{Fe}^{3+}-V_{\text{O}}$ or the capture of an electron to form $\text{Fe}^{3+}-V_{\text{O}}(e')$, whereby the five unpaired electrons of the high spin Fe^{3+} may couple with the captured electron at the oxygen vacancy to an effective even-spin state, and hence not observable by EPR. If thermal dissociation is the cause, there is no reason why the signals should vanish in the low temperature rhombohedral phase. Further, optical illumination with blue light does not affect $\text{Fe}^{3+}-V_{\text{O}}$ signals and hence does not involve other oxidation states of Fe (Berney and Cowan 1981). Therefore, the disappearance of these signals is due to the formation of $\text{Fe}^{3+}-V_{\text{O}}(e')$. It has been shown that the Fe^{3+} ion moves towards the oxygen vacancy of the defect complex which reduces the rotation of the $\text{Fe}^{3+}-V_{\text{O}}$ centre by 1.6 times as compared to the intrinsic value for TiO_6 octahedra (Müller 1981). Since the coordination polyhedra are nearly undistorted in the rhombohedral BaTiO_3 , the structural changes across T_c are identical to those of a orthorhombic-rhombohedral transition.

With SrTiO_3 , the EPR signals arising from V'_{Sr} and Mn^{2+} are observable at room temperature (figure 9) which is in agreement with the results from cubic BaTiO_3 . However Mn shows more complicated EPR spectrum. Oxygen annealed $\text{SrTiO}_3:0.01 \text{ atom \% Mn}$ shows the 6-line signal of $g = 1.997$ arising from Mn^{4+} (Müller 1959). When the same is reduced in H_2 , other signals arising from Mn^{2+} ($g = 2.0024$) and $\text{Mn}^{2+}-V_{\text{O}}$ ($g = 2.001$) are noticed. As the reduction temperature is increased, the Mn^{4+}

Figure 8. Intensity variation of $\text{Fe}^{3+}-V_{\text{O}}$ EPR signal in $\text{BaTiO}_3:0.25 \text{ La}, 0.01 \text{ Fe}^{3+}$ (atom %).

Figure 9. EPR spectra of SrTiO_3 doped with 0.01 atom % Mn and annealed at different conditions.

signal vanishes and the intensity of the $\text{Mn}^{2+}-V_{\text{O}}$ signal increases. The identity of $\text{Mn}^{2+}-V_{\text{O}}$ is further confirmed by the fact that the $g_{\parallel}$ component ($= 5.749$) appears in the deeply reduced samples. Figure 10 shows the variation in intensity of these signals with temperature. The intensity of V'_{Sr} signal of SrTiO_3 annealed at 1400 K, increases with temperature. Around the cubic-tetragonal phase transition (~ 108 K), the intensity increases and at lower temperature it falls off. Whereas the intensities of Mn^{4+}

Figure 10. Variation in intensity of the various signals in SrTiO_3 with temperature.

and $\text{Mn}^{2+}-V_{\text{O}}$ signals remain nearly unchanged, that of Mn^{2+} continuously decreases with lowering temperature. The Mn^{2+} signal vanishes around 108 K. The decrease in intensity of the Mn^{2+} signal is not accompanied by line broadening since the half-band width remains unchanged all through the observed temperature range. Therefore the disappearance of the Mn^{2+} signal cannot be due to change in the rotational order parameter but is due to a change in the valence state as in the case of BaTiO_3 except that the $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+} + e'$ conversion occurs continuously as the temperature is lowered. From the slope of the $\log I_{\text{Mn}^{2+}}$ vs $1/T$ curve (figure 10) the activation energy is found to be ~ 0.065 eV which corresponds to one of the transverse optical (TO) soft modes of SrTiO_3 (Servain *et al* 1980). Optical illumination (infrared) does not affect the EPR signals at low temperature, possibly due to the fact that the frequency of the corresponding vibrations is not coincident with that of some point on the dispersion curve and hence cannot be transmitted underdamped.

The resistivity of SrTiO_3 reduced at $p_{\text{O}_2} \approx 10^{-20}$ atm and 1400 K increases with temperature (figure 11), whereas those of SrTiO_3 samples annealed at $p_{\text{O}_2} 10^{-10}$ atm and 1100 K show the usual semiconductor behaviour. Around the cubic-tetragonal transition temperature, the resistivity of the deeply reduced samples shows reversal in temperature coefficient. The correlation in temperature variations of EPR signals of the acceptor centres and the resistivity indicates that the metallic behaviour arises from the increased trapping of electrons at the defect sites. It can be inferred, therefore, that the charge redistribution between the various acceptor states in SrTiO_3 is different from that observed in BaTiO_3 . The underdamped soft modes of SrTiO_3 may facilitate continuous redistribution at structurally favourable acceptor centres.

Figure 11. The electrical resistivity of SrTiO_3 (a) annealed at $p_{\text{O}_2} \sim 10^{-20}$ atm and 1400 K; (b) annealed at $p_{\text{O}_2} \sim 10^{-10}$ atm and 1100 K, (c) SrTiO_3 single crystal annealed at $p_{\text{O}_2} \sim 10^{-20}$ atm and 1400 K.

5. Photoelectrochemical properties

The junction between the semiconducting SrTiO_3 or BaTiO_3 and aqueous redox systems shows photon-assisted electric current when illuminated with light of band gap energy. However, BaTiO_3 electrodes show response to visible light of lesser intensity than when illuminated with uv, which is attributed to the existence of sub-band gap states in the forbidden gap (Chang *et al* 1983) (figure 12), whereas no visible light response is observed for SrTiO_3 . The flat band (f.b.) potential (V_{fb}) for BaTiO_3 doped with La is ≈ -0.85 V (vs SCE) in the uv and the apparent flat band potential (V'_{fb}) in the visible is ≈ -0.5 V. Therefore the mid-band gap states should be located around 0.28 V ($V_{fb} - V'_{fb}$) below the Fermi level. This mid-band gap cannot arise from acceptor type centres whereas they arise from donor-type states which may arise from $\text{Ti}^{3+}-V_o$ centres. Since the Fermi level in BaTiO_3 itself is located ~ 0.3 eV below the conduction band edge (Butler *et al* 1981), the $\text{Ti}^{3+}-V_o$ sub-band should be located around 0.6 eV below the conduction band. This energy value coincides with that of the broad absorption maximum noticed in the infrared region for donor doped BaTiO_3 and whose intensity increases with conductivity (Berglund and Braun 1967).

The difference in photoresponse between the tetragonal BaTiO_3 and cubic SrTiO_3 has been explained on the basis of a band model (figure 13) (Kutty and Gomathidevi 1985). The cation vacancies disrupt the chemical bonds with oxygen and thereby perturb the filled valence band (made of the $2p^6$ orbitals of O^{2-} ions) creating acceptor states. If these states are not lifted out of the valence band, they will remain neutral. In the cubic phase, due to crystal structure changes, the whole of the V_{Ba} acceptor states are lifted out of the valence band so as to form discrete levels within the band gap and can capture electrons from the conduction band to become V'_{Ba} . This will happen around T_c for BaTiO_3 whereas for SrTiO_3 the ionised acceptor states exist at room temperature itself. Correspondingly, the electronic states of other acceptors are also affected in the two phases. The electrons are photoexcited from the valence band to the $\text{Ti}^{3+}-V_o$ sub-band from where they will tunnel into the conduction band. The photogenerated holes may travel uphill, finding their way into neutral V_{Ba} states and will be available at the

Figure 12. Visible light photocurrent vs applied potential for (a) SrTiO_3 ; (b) H_2 annealed BaTiO_3 ; (c) La-doped BaTiO_3 .

Figure 13. Schematic changes in energy level for tetragonal and cubic phases of BaTiO_3 . Possible energy levels of Mn and $\text{Fe}^{3+}-V_O$ are also shown.

interface in response to the depletion layer. In the cubic phase, mobility of photogenerated holes into the V'_{Ba} states is restricted and hence the difference in response to visible light.

6. Discussion

The results indicate that charge redistribution among the acceptor states takes place at lower temperatures and is dependent on the structural changes in the lattice. The results also demonstrate that the same impurity can be present in more than one type of defect centre so that the shift from insulating to conducting state cannot be accounted for in terms of the concentrations of acceptor and donor simultaneously present. The charge redistribution of the acceptor can be represented by one of the two alternatives:

These boundary limits are functions of the electronic deformation and polarization energy, E_{dp} as well as the electron affinity of the bulk crystal, E_A . Additionally, if the acceptors are transition metal ions, the crystal field (CF) energy E_{CF} and the impurity Jahn-Teller (JT) energy, E_{JT} are also to be considered. The present findings imply that the dominance of one or the other of these parameters is dependent on the structural features of the crystal.

According to the EPR results, the neutral M -vacancies are stable in the tetragonal and orthorhombic phases where the MO_{12} polyhedra can be expected to be more distorted than those of rhombohedral and cubic phases. The perturbations on the oxygens, and hence of the valence band, by the absence of M -ions may lead to smaller ΔE_{dp} values when the polyhedra are more distorted so that the corresponding energy levels are continuous and overlapping with those of the valence band. When these polyhedra are undistorted, the corresponding ΔE_{dp} values are larger and hence the energy states are discontinuous and nonoverlapping with those of the valence band. This leads to the difference in energy level distribution as shown in figure 13.

In BaTiO_3 , the changeover of $\text{Fe}^{3+}-V_{\text{O}}$ to $\text{Fe}^{3+}-V_{\text{O}}(e')$ takes place when the lattice acquires higher symmetry i.e. the coordination polyhedra are nearly undistorted (figure 8). Since the local symmetry of the $\text{Fe}^{3+}-V_{\text{O}}$ centre (C_{4v}) continues to be less than that of the surroundings, even in the cubic phase, the contribution from E_{CF} of Fe^{3+} is less significant in the above charge redistribution when compared to that of electronic deformation of the surrounding oxygen ions. Therefore, the behaviour of $\text{Fe}^{3+}-V_{\text{O}} + e' \rightleftharpoons \text{Fe}^{3+}-V_{\text{O}}(e')$ follows a similar trend to that of $V_{\text{Ba}} + e' \rightleftharpoons V'_{\text{Ba}}$. Influence of the soft modes in the former case is evident from the fact that the charge redistribution occurs not exactly at the phase transition temperature but as the system approaches the tetragonal to cubic or orthorhombic to rhombohedral phase boundary. Besides, the prevalence of $\text{Fe}^{3+}-V_{\text{O}}$ in cubic SrTiO_3 (Müller 1981) indicates that the situation in crystals with underdamped soft modes cannot be the same in BaTiO_3 with overdamped soft modes.

The variations in the valence states of transition metal ions, as illustrated by Mn indicate the important role of E_{JT} . In the tetragonal and orthorhombic phases, the TiO_6 octahedra are distorted along the c -axis so that the Ti^{4+} ion can have effective displacements. In the same surroundings, $\text{Mn}^{2+}(d^5)$ ion, with its preference to cubic symmetry shifts to a $\text{Mn}^{3+}(d^4)$ state with gain in E_{JT} , which is sufficiently large to offset the electrostatic potential, whereas, in the cubic and rhombohedral phases, the undistorted or nearly undistorted octahedral surroundings stabilise Mn^{2+} . Thus the choice of the alternatives in (16) is dictated by the symmetry of the TiO_6 octahedron. Similar conclusions can be drawn for Cu and that is why Mn and Cu are the most effective dopants in enhancing the PTCR property. The $\text{Mn}^{2+}-V_{\text{O}}$ complex does not show similar variations as $\text{Mn}_{\text{Ti}}^{2+}$ since it is locally distorted even in the cubic and tetragonal phases. $\text{Fe}_{\text{Ti}}^{3+}$, though a d^5 ion, will not behave as Mn^{2+} since Fe^{2+} is not a Jahn-Teller active ion. When the concentration of Mn is enhanced, the higher population of impurity may locally distort the lattice and stabilise part of Mn as Mn^{2+} in the tetragonal phase as well.

7. Conclusions

If one tries to identify the above mentioned soft modes with specific types of vibrations, as chemists would like to do, Last's S_2 mode of M^{2+} vibrating against the ' TiO_3 frame' (Last 1957) is one of the alternatives, the other being Slater's S_1 mode of Ti^{4+} vibrating against the oxygen octahedra (Harada *et al* 1970). Slater's S_1 mode is favoured in SrTiO_3 whereas a mixed situation of S_1 and S_2 is said to prevail in BaTiO_3 (Shirane *et al* 1970). The charge redistributions among acceptor states arising from Ba-vacancies as well as Ti-site occupants indicate the involvement of both S_1 and S_2 modes.

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