Letters

Inhibition of reduction of BaTiO$_3$

The use of base metal electrodes (e.g. Ni) in place of the expensive Pd or Pd–Ag alloys on titanate capacitor materials requires sintering in reducing atmospheres [1, 2]. This normally leads to the reduction of BaTiO$_3$ by converting Ti^{4+} to Ti^{3+} ions, causing enhanced electrical conductivity in the material, but this can be prevented or minimized under appropriate conditions by the incorporation of some impurity ions (e.g. Mn [1–4] or Ga [5, 6]) into BaTiO$_3$. A variety of other ions were also found to be effective to varying extents. For example, Burn and Maher [7] found that the efficiency of the various ions in this respect increases in the order: Fe, Ga, Cr, Mg, Co and Mn. Since no explanation seems to have been put forth for this observed trend, a plausible basis is suggested here.

BaTiO$_3$ when heat-treated in a reducing atmosphere becomes highly conductive, due to the conversion of Ti^{4+} ions into Ti^{3+} ions accompanying the formation of oxygen vacancies, according to

$$\mathrm{BaTi^{4+}O_3} \xrightarrow{\text{reduction}} \mathrm{BaTi^{4+}_{1-2x}Ti^{3+}_{2x}O_{3-x}} + \frac{x}{2}\mathrm{O_2}. \tag{1}$$

The free electrons which become available when BaTiO$_3$ is reduced can be trapped by the positive ions (Ba, Ti) of the base material or by additives (M^{4+}, M^{3+}, M^{2+} or M^{+} at Ti sites and M^{3+}, M^{2+} or M^{+} at Ba sites). Other potential trapping sites are negative ion vacancies (oxygen of the base material) or halogen impurity anions.

The highest probability of electron trapping by an ion arises when the decrease in lattice energy is a maximum. Following Mott and Littleton [8], the energy (ΔW) involved in electron trapping by a cation M^{m+} going to M^{n+} is given by

$$\Delta W = \mathrm{B.E.}_{\mathrm{M}^{m+}} - \mathrm{B.E.}_{\mathrm{M}^{n+}} - I_{\mathrm{M}^{n+} \to \mathrm{M}^{m+}}, \tag{2}$$

where B.E. is the binding energy of the particular ion concerned and I is the ionization potential for the specific case. Thus ΔW values are indicative of the efficiency of a particular ion for trapping electrons.

The binding energy of some ions in the BaTiO$_3$ lattice has been estimated by Coufova [9], whose approach has been extended in the following to cover other ions of interest in the present context. The binding energy calculations are made on the assumption that BaTiO$_3$ is cubic with $a = 4.102$ Å, the ionic charges correspond to the idealized ionic bond i.e. Ba^{2+}, Ti^{4+}, O^{2-} and for additives 1+ to 4+, and ignoring the size differences of the additive ions. The potential energy, E, of two ions i and j spaced r_{ij} apart can be written as

$$E = \frac{e_i e_j}{r_{ij}} + \frac{\lambda_{ij}}{r_{ij}^n} - \frac{\mu_{ij}}{r_{ij}^6}, \tag{3}$$

where the three terms on the right are coulombic, repulsive and Van der Waals energies, respectively. Since the last two terms do not directly depend on the magnitude of the charges and rapidly diminish with distance of the ions in question, one may consider them as equal for all the ions at a particular lattice site, i.e. for any M^{n+} at the Ba site and for any M^{m+} at the Ti site. With this simplification, Equation 3 will have only the coulombic term. This is summed over four unit cells instead of to infinity, since the contribution of other ions is assumed to be small. The binding energy values computed in this manner are listed in Table I together with those of Coufova [9]. The slight difference in the two sets of values is due to the fact that a cubic unit cell parameter of 4.102 Å was used in the present work, compared to 4.00 Å employed by Coufova. Incorporating these and the standard ionization poten-

TABLE I Binding energy values for various ions in BaTiO$_3$ lattice

Site	Ions	Binding energy (eV)	
		Present work	[9]
Ba Site	M^{3+}	55.12	
	Ba^{2+} or M^{2+}	37.42	37.54
	Ba^{+} or M^{+}	18.69	18.75
Ti Site	Ti^{4+} or M^{4+}	105.38	105.70
	Ti^{3+} or M^{3+}	65.40	65.60
	M^{2+}	43.67	43.80
	M^{+}	21.23	
O Site	O^{2-} or X^{2-}	38.68	38.38
	X^{-}	19.14	19.20

0022–2461/80/082113–03$02.30/0

tials in Equation 2, the ΔW values for the various ions changing valency are computed and listed in Table II which includes Coufova's results for comparison. A sample calculation for $Mn^{4+} \rightarrow Mn^{2+}$ consists of

$$\begin{aligned} \Delta W &= \mathrm{B.E.}_{\mathrm{M}^{m+}} - \mathrm{B.E.}_{\mathrm{Mn}^{2+}} - I_{\mathrm{Mn}^{2+} \rightarrow \mathrm{Mn}^{4+}} \\ &= 105.38 - 43.67 - (36.67 + 51.20) \qquad (4) \\ &= 26.16\,\mathrm{eV} \end{aligned}$$

where Mn^{2+} is assumed to occupy a Ti site.

The effectiveness of the various ions as reduction-inhibitors may now be compared on the basis of the ΔW values and the acceptor nature of the ions. The formation of Ti^{3+} ions can be prevented in two ways: (i) by compensating the non-stoichiometry with acceptors, as in

$$\mathrm{Ba(Ti^{4+}_{1-2x}M^{3+}_{2x})O_{3-x}}$$

$$\text{or} \quad \mathrm{Ba(Ti^{4+}_{1-x}M^{2+}_{x})O_{3-x}} \qquad (5)$$

$$\text{or} \quad \mathrm{(Ba_{1-2x}M^{+}_{2x})Ti^{4+}O_{3-x}},$$

or (ii) by introducing dopants which will trap the free electrons (available under reducing conditions) more effectively than by Ti^{4+} and remain in the lattice, as in

$$\begin{aligned} \mathrm{BaTi^{4+}_{1-x}M^{3+}_{x}O_3} &\rightarrow \mathrm{Ba(Ti^{4+}_{1-x}M^{3+}_{x})O_{3-(x/2)}} + \frac{x}{4}\,\mathrm{O_2} \\ &\rightarrow \mathrm{Ba(Ti^{4+}_{1-x}M^{2+}_{x})O_{3-x}} + \frac{x}{2}\,\mathrm{O_2} \\ &\rightarrow \mathrm{Ba(Ti^{4+}_{1-x}M^{+}_{x})O_{3-(3x/2)}} + \frac{3x}{4}\,\mathrm{O_2}. \end{aligned} \qquad (6)$$

Taking into account Equations 5 and 6 and the ΔW values (Table II), the various ions which can inhibit reduction of $BaTiO_3$ may be classified into three types, depending upon whether they act purely as electron traps or purely as acceptors and compensating for the oxygen vacancies or in both the roles.

Type I: those ions which have $\Delta W \leqslant -3.26\,\mathrm{eV}$ (ΔW for $Ti^{4+} \rightarrow Ti^{3+}$) cannot act as effective electron traps: e.g. Li^+, Mg^{2+}, In^{3+}, Sc^{3+} and Al^{3+} at Ti sites and alkali ions at the Ba site. But some of these ions may prevent formation of Ti^{3+} ions if they can act as acceptors and thus form oxygen vacancies.

Type II: those ions which act as electron traps but not as acceptors (i.e. cannot compensate for oxygen vacancies) fall in this category, e.g. Mn^{4+} with $\Delta W = -11.26$ and $-26.16\,\mathrm{eV}$ for Mn^{3+} and Mn^{2+} conversion, respectively, which is very high compared to $\Delta W = -3.26\,\mathrm{eV}$ for $Ti^{4+} \rightarrow Ti^{3+}$.

Type III: all the other ions in Table II can act both as acceptors and effective electron traps. By comparing the ΔW values, one can arrange them in the order of efficiency in preventing reduction of $BaTiO_3$ as follows: $Zn^{2+} > Ni^{3+} = Cu^{2+} > Mn^{3+} > Co^{3+} > Cr^{3+} > Fe^{3+} > V^{3+} > Ga^{3+} > Tl^{3+}$. Zn^{2+}, Ni^{3+} and Cu^{2+} are all readily reduced to the metallic state for the experimental conditions under consideration and may, therefore be excluded. This sequence compared quite well with that found by Burn and Maher [7], namely

$$\mathrm{Mn > Co > Mg > Cr > Ga > Fe}$$

except for the relative positions of Ga and Fe. Considering the simplicity of approach and the assumptions involved, this agreement is indeed

TABLE II Energy change due to change of oxidation state of the dopant in $BaTiO_3$ cubic lattice

Dopant and change of oxidation state	Energy change (eV)	
	Present work	[9]
At the Ti site:		
$Li^+ \rightarrow Li$	+ 15.84	
$Mg^{2+} \rightarrow Mg^+$	+ 7.41	
$In^{3+} \rightarrow In^+$	− 2.72	
$Sc^{3+} \rightarrow Sc^{2+}$	− 3.02	
$Al^{3+} \rightarrow Al^+$	− 3.09	
$Ti^{4+} \rightarrow Ti^{3+}$	− 3.26	− 3.13
$Tl^{3+} \rightarrow Tl^+$	− 6.05	
$Ga^{3+} \rightarrow Ga^+$	− 7.10	
$V^{3+} \rightarrow V^{2+}$	− 7.58	
$Fe^{3+} \rightarrow Fe^{2+}$	− 8.91	− 8.84
$Cr^{3+} \rightarrow Cr^{2+}$	− 9.22	
$Mn^{4+} \rightarrow Mn^{3+}$	−11.26	
$Co^{3+} \rightarrow Co^{2+}$	−11.76	−10.69
$Mn^{3+} \rightarrow Mn^{2+}$	−11.94	
$Cu^{2+} \rightarrow Cu^+$	−14.39	
$Ni^{3+} \rightarrow Ni^{2+}$	−14.43	−14.36
$Zn^{2+} \rightarrow Zn^+$	−17.26	
$Mn^{4+} \rightarrow Mn^{2+}$	−26.16	
At the Ba site:		
$Cs^+ \rightarrow Cs$	+ 14.80	
$Rb^+ \rightarrow Rb$	+ 14.51	
$K^+ \rightarrow K$	+ 14.35	+ 14.43
$Ba^{2+} \rightarrow Ba^+$	+ 8.73	+ 6.77

good. It has been assumed that all the ions considered are soluble to an adequate extent in the $BaTiO_3$ which may not necessarily be true.

The minimum concentration of the various dopants needed to prevent the reduction of $BaTiO_3$ is dependent upon the value of x in Equation 1, which, in turn, is a function of the reducing conditions employed. Estimates of x have been made by Arend and co-workers [10, 11] and utilized by Burn and Maher [7] to compute the dopant level needed. The amount of dopant needed exceeds the calculated value if the dopant can exist in more than one oxidation state (e.g. 2+, 3+ and 4+ in the case of Mn) under the conditions of temperature and P_{O_2} employed or if the dopant can occupy more than one type of lattice site (e.g. Mn^{2+} occupying Ba site, while Mn^{2+}, Mn^{3+} and Mn^{4+} can occupy the Ti site).

Based on lattice energy decrease due to the presence of various ions in the $BaTiO_3$ lattice, it was shown that the effectiveness of inhibiting reduction of $BaTiO_3$ in a reducing atmosphere is in the order

$$Mn > Co > Cr > Fe > V > Ga$$

which is in good agreement with experimental results.

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Received 2 October
and accepted 5 December 1979

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Eutectic alloys of thorium–niobium and thorium–titanium

Eutectic alloys of niobium–thorium solidify with a rod eutectic morphology, and consequently directionally solidified alloys produce aligned filaments of Nb in a Th matrix. The solid solubility in both phases is quite low and, therefore, such alloys are excellent model systems for studying superconducting properties at superconducting–normal interfaces. In addition, thorium–titanium also forms a eutectic system with very low solid solubility in the constituent phases, so that one has the potential of preparing aligned Nb–Ti filaments by directional solidification from ternary Nb–Ti–Th alloys. Such alloys would provide an

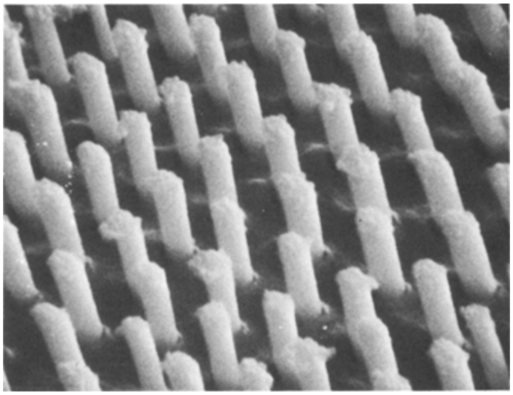

Figure 1 Transverse section of directionally solidified Nb–Th eutectic alloy, deep etched to illustrate aligned structure of Nb filaments. Solidification rate = 45 $\mu m\ sec^{-1}$ × 17 200.

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