

## Invited

## Electronic Structure and Defects of Lead-Zirconium Titanate (PZT) and Strontium Bismuth Titanate Ferroelectrics

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## 1 Introduction

Ferroelectrics are used as high dielectric constant films in the capacitor structures of DRAMs and in non-volatile memories [1]. These more sophisticated applications require a knowledge of their electronic behaviour (bands, defects), as well as their ferroelectric behaviour. We focus here on the perovskite-based ferroelectrics, PZT ( $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ ) and SBT ( $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ). We contrast the electronic and ferroelectric behaviour of these compounds whose A site ion  $\text{Pb}^{2+}$  or  $\text{Bi}^{3+}$  has not ionised its valence s electrons, with  $\text{BaTiO}_3$  whose A ion ( $\text{Ba}^{2+}$ ) has a closed valence shell. These valence s states are shown to amplify the ferroelectricity and to greatly affect the electronic behaviour. Much of the interest in SBT arose because it shows a much lower memory fatigue than PZT, and we suggest a possible origin for this in terms of less carrier trapping at defects.

## 2 Band Calculations

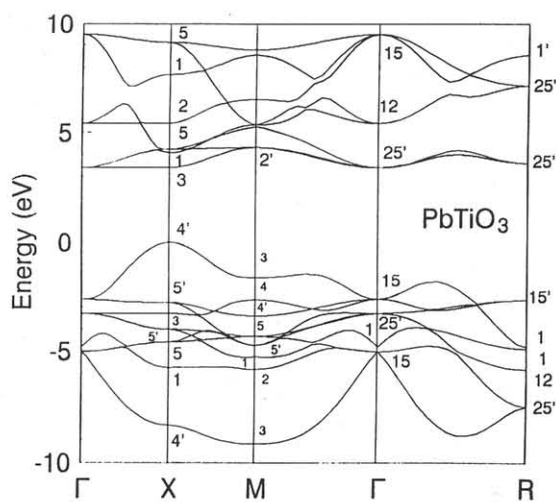
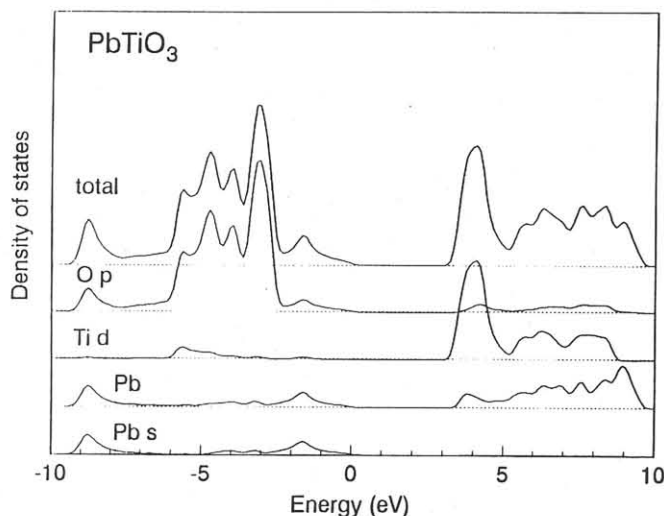
The band structure of PZT and SBT was calculated by the tight-binding method with a basis set of Pb s, p, O s, p and Ti/Zr d orbitals. The band structure of  $\text{PbTiO}_3$  is shown in Fig. 1. The valence band consists mainly of O 2p states plus the 6s states of the  $\text{Pb}^{2+}$  ion. The valence band edge state at X is actually a mixed Pb s/O p state [2]. The conduction band minimum is a  $\Gamma_{25'}$  Ti d state with the more dispersive Pb p states following immediately above. The density of states is shown in Fig. 2.

Substituting Zr for Ti changes little in the valence band but has a pronounced effect on the conduction band [3]. The atomic Zr d state lies about 2 eV above the Ti d state, so the  $\Gamma_{25'}$  d state rises rapidly and the conduction band minimum becomes the Pb p-like  $M_2'$  state. Thus, the band gap of PZT increases little across the alloy phase diagram, from 3.5 to 3.7 eV, despite the rise in the transition metal d state. This contrast with  $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ , where there is a strong rise in the band gap from 3.5 to 5.5 eV, because the A ion Ba has no low lying states in the conduction band.

The main source of ferroelectricity in perovskites is the polarization of the bond between B ion d states and O p states which drives the B ion off-centre. In  $\text{PbTiO}_3$  the Pb s valence states or 'lone pair' are also highly polarizable, and they act to amplify the ferroelectric behaviour of PZT [4]. Thus the A ion in PZT is not passive as it is in  $\text{BaTiO}_3$ .

$\text{SrBi}_2\text{Ta}_2\text{O}_9$  has a perovskite-based structure in which  $\text{TaO}_3$  units form perovskite blocks separated by puckered layers of  $\text{BiO}$  units [5]. The bands of SBT were calculated in a similar fashion [6]. One of the 'A' ions, Bi, like Pb retains its valence s electrons as a lone pair. The DOS in Fig. 4 shows that the Bi states lie mainly well inside the valence band, but a small fraction form the valence band edge with p states from the O in the  $\text{BiO}$  layer. Similarly, the Bi p states form the conduction band minimum state, while the Ta d states lie higher. We

therefore have the interesting situation that states on Bi and in the  $\text{BiO}$  layer form both band edges, while the Ta-O block creates the ferroelectric behaviour - a functional separation within the crystal.

Fig. 1. Band structure of  $\text{PbTiO}_3$ .Fig. 2. Total and partial density of states of  $\text{PbTiO}_3$ .

## 3 Defect States

The energies of defects can be calculated by the Greens function method to see if they form deep states. This method gives the energy of deep defects, as a function of the defect potential, which allows defects associated with a series of elements to be displayed as a single plot of chemical trends. In these calculations, the vacancy is represented as an infinity potential, while the trapped electron or hole is represented as the  $Z+1$  or  $Z-1$  element, respectively.

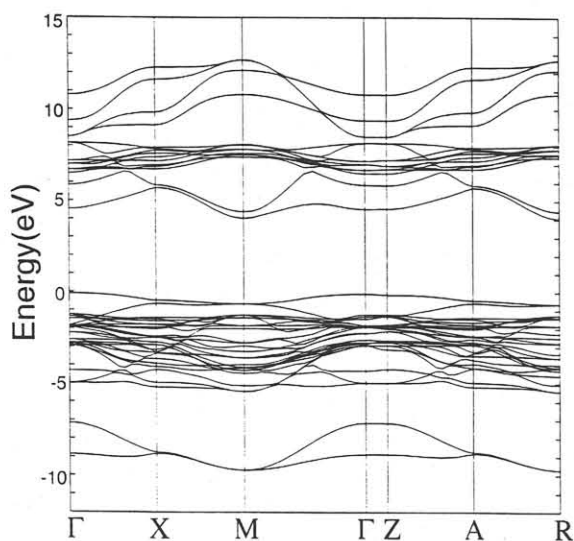


Fig. 3. Band structure of SBT

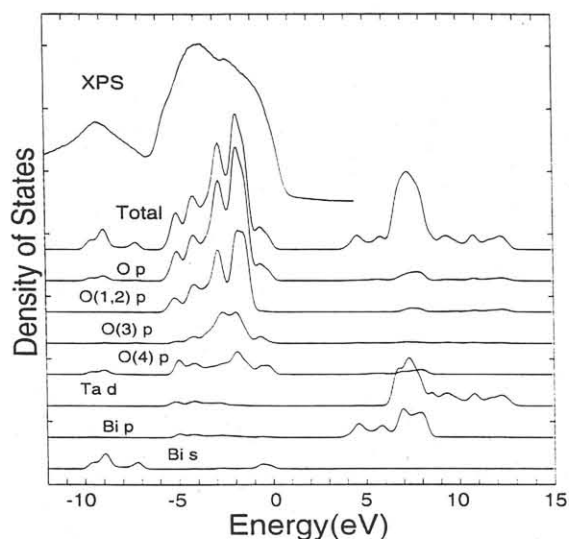


Fig. 4. Density of states of SBT

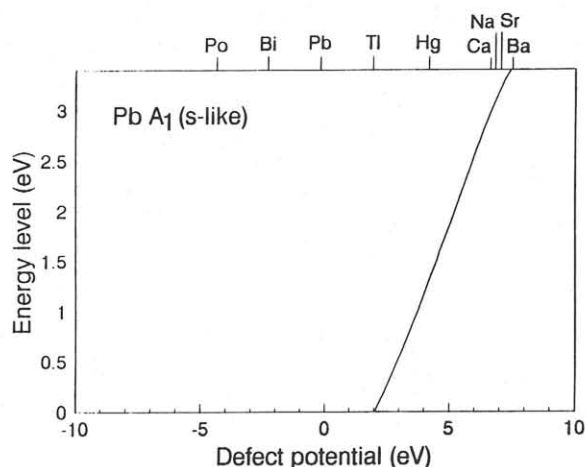


Fig. 5. Defect energy levels versus defect potential for substitutional defects at the Pb site.

Consider holes in PZT. These could be trapped either at the Pb site or at the oxygen site. Fig. 5 shows a plot of energy level above the valence band maximum versus defect potential for states of A1 symmetry trapped at the Pb site in PZT. This shows that the trapped hole state (at 'TI') is on borderline between a shallow and deep state. On the other hand Experimentally, the hole in PZT can be observed by electron spin resonance (ESR) and its thermal stability suggests that it is about 0.3 eV deep - borderline between deep and shallow. Transport data also suggest a hole trap depth of this size.

Contrasting this with  $\text{BaTiO}_3$ , the A ion cannot be further ionised, so hole can now only lie on the O p states. The O p states form a high effective mass valence band and the hole is trapped like in MgO.

Turning to SBT, the equivalent calculation finds that the hole state is shallower than in PZT. This is consistent with ESR, which no longer finds a long-lived hole signal.

#### 4 Discussion

The presence of lone pair s states and low lying conduction band p states from the A ion has the following effects; the s states give shallow hole traps. the s states amplify the ferroelectricity, and the p states limit the variation of the band gap in Zr-alloys.

It is interesting to finally consider the origin of the low fatigue of SBT, compared to PZT. Fatigue is the gradual decline in switchable polarization, over many switching cycles in a memory device. Fatigue is believed to occur by the trapping of charge carriers at domain poles, which pin domain walls into certain configurations and stop them switching [7]. In fact, nominally fatigue-free SBT does exhibit fatigue under UV illumination which creates electron-hole pairs [8], which shows that fatigue is fundamentally electronic in origin. The nature of potential pinning traps are few, and have been investigated here. The calculations suggest that SBT is fatigue-free in the dark because the hole traps in SBT are too shallow to pin domain walls.

#### Acknowledgements

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