

Nanometer-sized dielectric oxides : synthesis and properties

Ashok K Ganguli*, Pika Jha, Toker Ahmad and Padam R Arya

Department of Chemistry, Indian Institute of Technology,
Hauz Khas, New Delhi-110 016, India

E-mail : ashok@chemistry.iitd.ernet.in

Abstract : In recent years materials with nano-size particles have attracted wide attention from researchers. This is because the properties at nano-dimensions are quite different compared to their bulk counterparts. There have been tremendous efforts in understanding the optical and magnetic properties of nanomaterials. However very little research has been directed towards dielectrics with nanosized grains. With the recent advancements of electronics, the demand of capacitors with high volumetric efficiency, extended temperature ratings, smaller size and lower cost as required by multilayered capacitors, is constantly on the rise. Hence, it has become extremely important to synthesize dielectric materials with higher density and higher surface area, more uniform size distribution and less brittleness at elevated temperatures. This necessitates investigation of nanosized particles of well known dielectric materials. Using the polymeric citrate precursor route, we have synthesized monophasic dielectric oxides belonging to the families BST ($Ba_{1-x}Sr_xTiO_3$), BPT ($Ba_{1-x}Pb_xTiO_3$) and PZT ($PbZr_xTi_{1-x}O_3$) having particle sizes in the range of 40-80 nm as shown by TEM and X-ray line-broadening techniques. These nano-sized grains show no appreciable change in size even on sintering. Unlike their bulk counterpart, none of these oxides show ferroelectric properties.

Keywords : Metal oxide, quantum effects, dielectric properties

PACS Nos. : 61.46.+w, 61.10.Nz, 68.37.Lp, 77.22.-d

1. Introduction

The ferroelectric and dielectric properties of metal oxides with the perovskite structure are of utmost importance in the electronic industry. These materials include oxides like $BaTiO_3$, $PbTiO_3$, $SrTiO_3$ and their substituted derivatives.

Since, the properties of nanoparticles differ considerably from their bulk counterpart, they are inspiring a great deal of research attention. Quantum effects modify the overall properties of nano sized particles. This is especially in optical, magnetic and catalytic applications. The ferroelectric/dielectric properties of oxides depend considerably on the size and shape of the particles. Nanostructured materials can be dispersed in different types of matrix media to impart useful characteristics to the composite.

The microelectronic industry has been emphasizing on reduction in size of the device elements such as transistors, resistors and capacitors. However, there are practical difficulties to these achievements including the lack of ultra-fine precursors to manufacture these components, poor dissipation of the tremendous heat generated due to faster speeds, poor reliability, etc. Thus there is need to obtain ultra-pure materials of nanometer

size which have high energy density and better thermal conductivity.

The dielectric properties of many of the materials are seriously affected by the grain size, the grain boundaries, grain boundary motion etc, and detailed studies need to be carried out. Only a few studies have been reported on nano particles of dielectric oxides except for $BaTiO_3$ of which nanoparticles have been studied [1].

The nano-sized powders synthesized may be sintered into compacts of uniform size distribution and higher densities compared to commercial materials. Also, the exposed surface area will be high resulting in significant improvements by enhancing the volumetric efficiency, strength and service life of capacitors. The nano-sized ceramics are less brittle than micron or sub-micron sized powders at elevated temperatures.

Since long, $BaTiO_3$ and its related compounds are in extensive use as high dielectric constant capacitors, PTC resistors ferroelectric memories [2,3] and MLCC's, we focus our attention to the synthesis of nanometer-sized oxides like $Ba_{1-x}Sr_xTiO_3$ (BST), $Ba_{1-x}Pb_xTiO_3$ (BPT) and $PbZr_xTi_{1-x}O_3$ (PZT). There are tremendous applications already known for these three families of oxides and hence characterization of their nano-sized powder is of prime concern.

*Corresponding Author

These powders can be prepared by various methods [4-9] such as co-precipitation, oxalate, hydrothermal and sol-gel method. These methods are used to prepare these oxides at temperatures less than 1000°C. Traditional high temperature methods are not suitable for the preparation of these materials since they have a large particle size, low homogeneity and high impurity content. Low temperature routes lead to better chemical and structural homogeneity.

We have carried out detailed studies of the gel, precursor and the fine oxide powders using powder X-ray diffraction (PXRD), transmission electron microscopy (TEM) and dielectric measurements. We discuss our results on the synthesis and characterization of barium strontium titanates $Ba_{1-x}Sr_xTiO_3$ ($0 \leq x \leq 1$) (BST), barium lead titanates $Ba_{1-x}Pb_xTiO_3$ ($0 \leq x \leq 1$) (BPT) and $PbZr_{1-x}Ti_xO_3$ ($0.25 \leq x \leq 0.75$) (PZT) by the polymeric citrate precursor method and some preliminary results of some barium titanates ($BaTiO_3$ and Ba_2TiO_4) prepared by the reverse-micellar route.

2. Experimental

To ethylene glycol (Qualigens, SQ grade) titanium tetraisopropoxide (Acros) was added under nitrogen atmosphere in the ratio of 40 : 1. The contents were stirred to get a clear transparent solution and dried citric acid (Qualigens, SQ grade) was added to it (citric acid : ethylene glycol ratio was 10 : 40). The contents were stirred at room temperature till a clear solution was obtained. To this clear and viscous solution stoichiometric amounts of carbonates or nitrates of metals $BaCO_3$, $SrCO_3$, $Pb(NO_3)_2$ and zirconyl nitrate hydrate ($ZrO(NO_3)_2 \cdot xH_2O$) (which were previously dried in an oven at 110°C for 2 hours) were added and stirred till a clear solution was obtained. This viscous solution was kept in oven at $135 \pm 5^\circ C$ to evaporate the solvent and to promote polymerization. The solution changes to a dark color and becomes a viscous resin. This resin was further heated in an electrical muffle furnace for 2 hours at 300°C for charring and then allowed to cool at room temperature. The resin turns into a black mass, which was ground, to a powder in an agate mortar. The oxide powders of BST, BPT and PZT were formed by heating this precursor to temperatures of 500°C for 20 hours and then at 800°C for 8 hours. The oxides were compacted at a pressure of 4 ton and then sintered at 900°C for 12 hours (the BST samples were sintered at 1100°C for 3 hours).

The oxide powders were characterized by powder X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Ni-filtered $Cu-K\alpha$ radiation. X-ray line broadening studies (Scherrer's formula) were used to obtain the grain size of the powders. Transmission electron microscopy studies were carried out using a JEOL 200 CX electron microscope operating at 120 kV. Dielectric properties were measured on sintered disk coated with silver paste (dried at 90°C for 6 hours) using a Hewlett Packard multi frequency LCR meter (HP 4284L) in the frequency

range of 50 Hz to 500 kHz. The density of the sintered disks was found to be in the range of 92 to 95% of the theoretical density (Archimedes method).

3. Results and discussion

We have developed a rational synthesis of oxide nanoparticles using the polymeric citrate precursor method. Oxides of the type, $Ba_{1-x}Sr_xTiO_3$ were obtained after heating the precursors at 500°C and the PXRD patterns could be indexed on the basis of a cubic unit cell. It is seen that with increase in strontium substitution there is a decrease in the value of the 'a' lattice parameter (Figure 1). The crystalline cubic phases are obtained after heating at 500°C for all the compositions. For the composition with $x = 0.5$ a cubic phase with lattice parameter 'a' = 3.948(3) Å. For this composition the cubic symmetry is retained even after heating at 1100°C (Figure 2). The X-ray patterns of the oxides (BST) sintered at 1100°C appear to be cubic. However with more careful X-ray studies a weak tetragonal distortion is observed for $BaTiO_3$ (Figure 3). The lattice parameters were calculated as 'a' = 3.999(3) Å and 'c' = 4.0101(4) Å. However the other compounds were found to be cubic at this temperature.

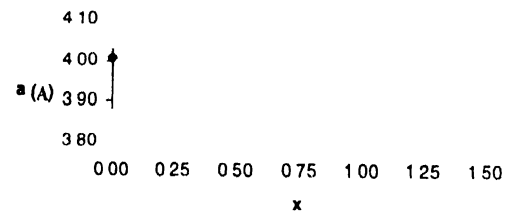


Figure 1. Plot of cubic lattice parameter 'a' vs x for $Ba_{1-x}Sr_xTiO_3$

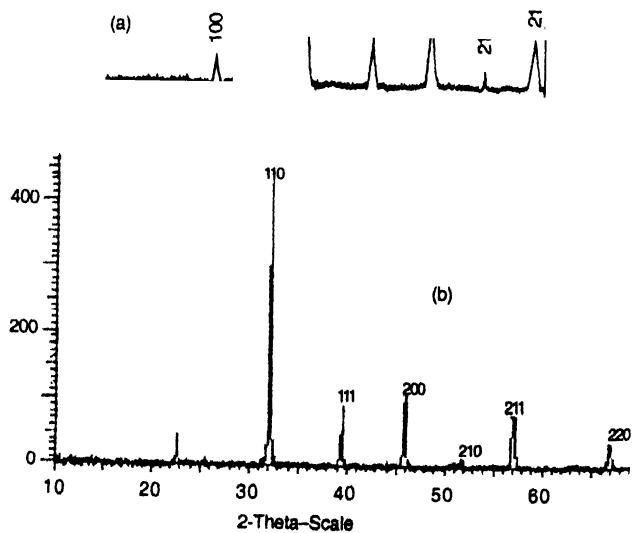


Figure 2. Powder X-ray diffraction pattern for the composition $Ba_{0.50}Sr_{0.50}TiO_3$ after being heated at (a) 500°C (b) 1100 °C.

Oxides of the type $Ba_{1-x}Pb_xTiO_3$ were obtained from the gel at 500°C show pure crystalline phases. The powder X-ray patterns could be indexed on the basis of a tetragonal cell for all

Transmission electron microscopy (TEM) studies (Figure 5) of the 500°C samples show a distribution of grain sizes with most of the grains in the range of 20 to 30 nm for $SrTiO_3$. The

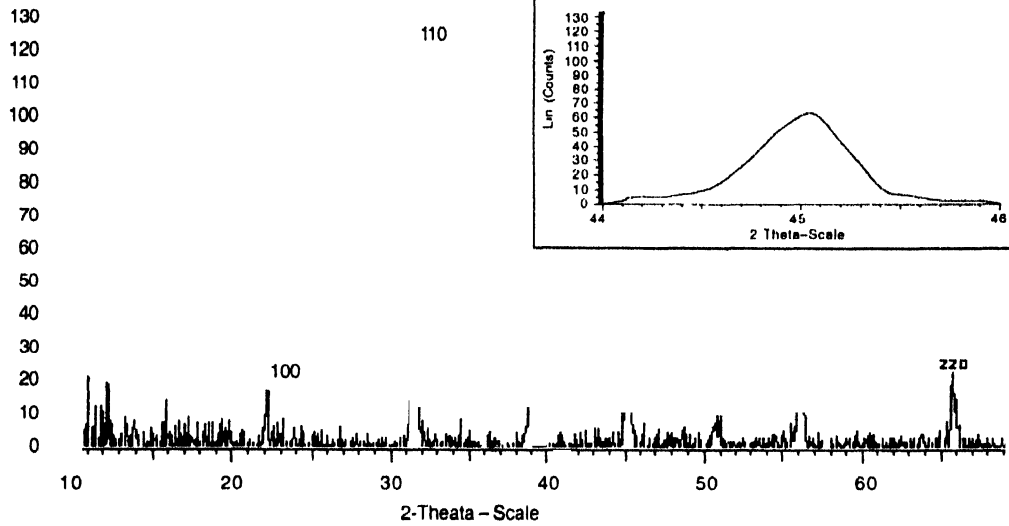


Figure 3. Powder X-ray diffraction pattern of $BaTiO_3$ sintered at 1100°C for 3 hours (inset shows the weak tetragonal distortion).

the compositions (Figure 4). For $PbTiO_3$ the tetragonal lattice parameters were ' a ' = 3.899(1) Å, ' c ' = 4.136(2) Å. The ' a ' parameter decreases whereas the ' c ' parameter increases with increase in lead content, c/a parameter increases with lead substitution.

grains are agglomerated. The particle size obtained at 1100°C from the Scherrer's formula 88 nm for $SrTiO_3$ [10]. This shows that with sintering there is only a marginal increase in grain size and the nano-size of the grains are retained even at a high temperature. There is an earlier report on nano-sized $Ba_{1-x}Sr_xTiO_3$ ($x = 0.0 - 0.3$) powders by Noh and coworkers [4] in which particle size of 10–40 nm has been obtained.

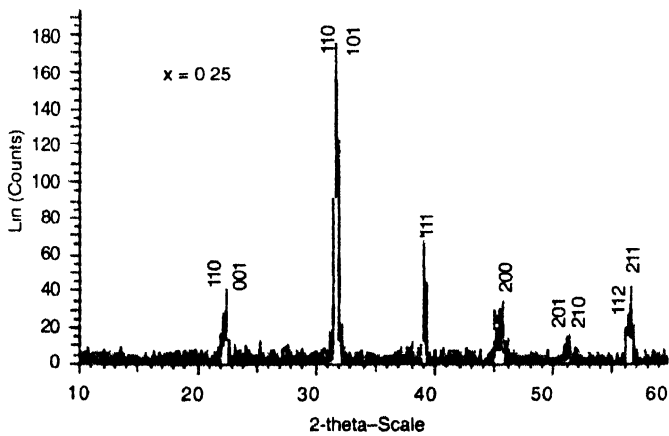


Figure 4. Powder X-ray diffraction pattern for the $x = 0.25$ composition of $Ba_{1-x}Pb_xTiO_3$.

Powder X-ray diffraction of the $PbZr_xTi_{1-x}O_3$ (PZT) oxides were carried out at room temperature. The sample belonging to $x = 0.50$ composition obtained at 800°C shows a broad peak. On sintering at 900°C, the reflections become much sharper and the splitting of the above reflections becomes very distinctly visible. The composition with $x = 0.25$ could be indexed on a tetragonal cell with ' a ' = 3.899(1) Å and ' c ' = 4.136(2) Å. However, the powder X-ray diffraction pattern for the composition of $x = 0.75$, was indexed on a rhombohedral unit cell with lattice parameter ' a ' = 4.089(3) and $\alpha = 89.73^\circ$.

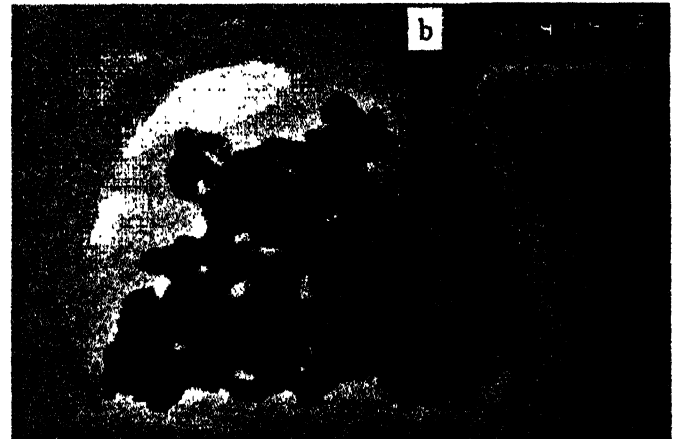


Figure 5. Transmission electron micrograph of $SrTiO_3$.

X-ray line broadening studies have been used to calculate the grain size of the BPT samples using the Scherrer's formula for samples sintered at 900°C. A grain size of 50 nm for $PbTiO_3$ (Figure 6(a)) is observed [11]. The particle size obtained from TEM (Figure 6(b)) are in the range of 40–60 nm for this compositions and corroborate well with the X-ray line broadening studies. The particle size obtained from the X-ray line broadening studies for PZT using the Scherrer's formula show that the particle sizes are in the range 48 nm for

$\text{PbZr}_{0.25}\text{Ti}_{0.75}\text{O}_3$. The particle size obtained from transmission electron microscopy are in the range of 50–60 nm.

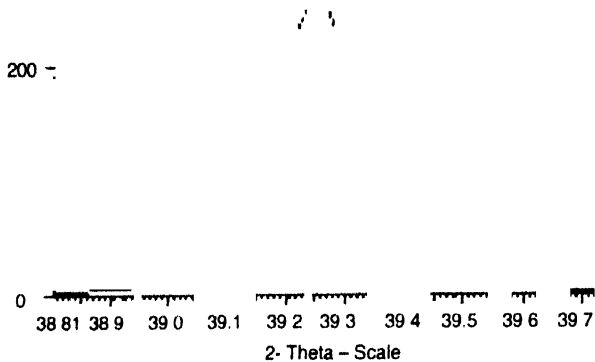


Figure 6. X-ray line broadening studies of PbTiO_3

The dielectric constant and the dielectric loss of the above family of oxides have been studied as a function of temperature and composition in the frequency range of 50 Hz to 500 kHz.

It is found that with increase in strontium substitution the dielectric constant decreases. The value of dielectric constant varies from 510 for BaTiO_3 to 190 for SrTiO_3 . The composition of $x = 0.5$, namely $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, the dielectric constant decreases in a regular fashion with increase in temperature from room temperature to 300°C . For BaTiO_3 the dielectric constant shows a very minor change with temperature till 150°C beyond which it shows a decrease. Figure 7 shows the variation of dielectric constant and dielectric loss at various temperatures for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ at 100 kHz. The dielectric constant also shows a very slight variation with frequency till 300 kHz. The dielectric loss also remains almost constant till 200 kHz beyond which it shows a considerable rise with increasing frequency. For $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, the dielectric constant shows negligible variation in the frequency range 100 to 500 kHz in the entire range of temperature studied. Similar behavior is seen for BaTiO_3 and SrTiO_3 . Also no peak has been observed in the dielectric constant *versus* temperature curve in the temperature range of 50°C to 150°C for BaTiO_3 (Figure 8). It has been pointed out earlier [12,13] that the cubic structure and absence of ferroelectricity for BaTiO_3 occurs for small grain sizes. As grain size decrease the polarization decreases and thus ferroelectricity is lost. Thus we may conclude that in our case the particle sizes

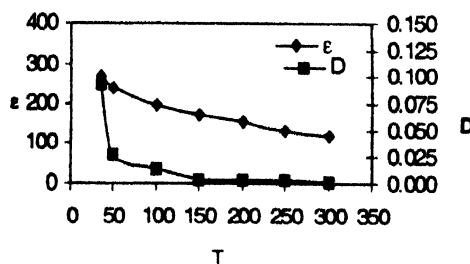


Figure 7. Variation of dielectric constant and dielectric loss with temperature for the composition $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (sintered at 1100°C) at 100 kHz.

are below the critical size and the tetragonal distortion is too weak to give rise to a ferroelectric transition.

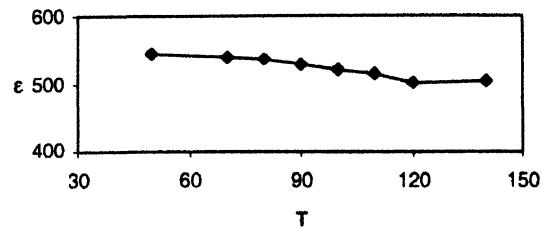


Figure 8. Variation of the dielectric constant with temperature (50°C to 140°C)

We have studied the dielectric constant and the dielectric loss of the sintered disks of barium lead titanates (BPT) as a function of composition and temperature. The dielectric constant for BaTiO_3 was found to be 430 at 100 kHz [10] and decreases drastically with lead substitution ($\epsilon = 30$ for $\text{Ba}_{0.75}\text{Pb}_{0.25}\text{TiO}_3$). Figure 9 shows the variation of dielectric constant and dielectric loss with frequency for PbTiO_3 . The dielectric constant remained almost constant in the frequency range of 10 to 500 kHz. The dielectric loss also shows a constant value till 400 kHz beyond which it shows a small increase. Depending on the composition the dielectric loss varies from 0.02 to 0.10. No ferroelectric transition is observed as in the BST oxides due to the small grain size obtained by the synthetic procedure employed.

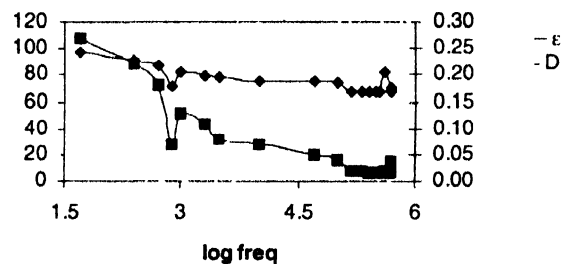


Figure 9. Variation of the dielectric constant and dielectric loss with frequency for PbTiO_3 at room temperature.

Similar studies on the PZT oxides show that the dielectric constant increases from 90 to 125 with increase in Zr content from $x = 0.25$ to $x = 0.75$. The dielectric constant is quite stable for the entire frequency range studied (100 Hz to 500 kHz). The dielectric loss also increase slightly with increase in Zr content from 0.01 at $x = 0.25$ to 0.02 at $x = 0.75$.

The absence of ferroelectricity in all the above oxides suggest that the grain size is much below the critical size required to maintain the ordered dipoles needed for ferroelectricity. Theoretically, it was calculated [14] that the critical size is around 44 nm for BaTiO_3 . However such a calculation based on the phenomenological Ginzburg-Landau theory does not take care of the lattice defects, which if present will affect the critical size. Several other attempts [15–18] have been made to understand the cubic to tetragonal transition (ordered to disordered) in these oxides. Yet a clear understanding is not available.

We have also synthesized nanoparticles of BaTiO_3 and Ba_2TiO_4 through reverse micellar route using tergitol as a surfactant. In both the cases we have found single phase at 800°C . X-ray line broadening studies showed particle size of 40 nm for BaTiO_3 and 42 nm for Ba_2TiO_4 . Transmission electron microscopic studies showed particle size of 35 nm for BaTiO_3 and 40 to 50 nm for Ba_2TiO_4 . Thus our TEM studies corroborates well with our X-ray line broadening studies. These particles had a high level of monodispersity and were uniform in size. Dielectric properties were measured on disks sintered at 900°C . The dielectric constant (ϵ) of BaTiO_3 was 215 and dielectric loss was found to be 0.02. The dielectric constant (ϵ) of Ba_2TiO_4 was 100 and dielectric loss was found to be 0.05.

4. Conclusion

We have obtained monophasic solid solutions of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, $\text{Ba}_{1-x}\text{Pb}_x\text{TiO}_3$ and $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ by the polymeric citrate precursor route at 500°C . For all the compositions studied nanometer sized particles have been obtained which are reasonably stable to sintering. Although the oxides have not shown as high dielectric constant as their bulk counterparts, their dielectric constant is still high and the dielectric loss effects have been substantially reduced for all these compositions. The ferroelectric properties that are observed in the micron sized grains are not observed in these cases due to the small size of the grains.

References

- [1] T Fukui, C Sakurai and M Okuyama *J. Mater. Sci.* **32** 189 (1997)
- [2] G H Hertling *J. Am. Ceram. Soc.* **82** 797 (1999)
- [3] F Selmi, S Komareni, V K Varadan and V V Varadan *Mater Lett* **10** 235 (1990)
- [4] T Noh, S Kin and C Lee *Bull. Korean Chem. Soc.* **16** 180 (1995)
- [5] C Beck, W Härtl and R Hempelmann *J. Mater. Res.* **13** 3174 (1998)
- [6] G R Fox, J H Adair and R E Newnham *J. Mater. Sci.* **25** 3634 (1990)
- [7] J B Blum and S R Gurkovich *J. Mater. Sci.* **20** 4479 (1985)
- [8] K Saegusa, W E Rhine and H K Bowen *J. Am. Ceram. Soc.* **76** 1495 (1993)
- [9] C K Kwok and S B Desu *J. Mater. Res.* **8** 339 (1993)
- [10] P R Arya, P Jha and A K Ganguli *J. Mater. Chem.* **13** 415 (2002)
- [11] P R Arya, P Jha and A K Ganguli *Mater. Res. Bull.* (in print)
- [12] M H Frey and D A Payne *Appl. Phys. Lett.* **63** 2753 (B) 1993
- [13] K Binder *Ferroelectrics* **35** 99 (1981)
- [14] Y G Wang, W L Zhong and P L Zhang *Solid State Commun.* **90** 329 (1994)
- [15] R C Garvie *J. Phys. Chem.* **82** 218 (1970)
- [16] B Begg, E R Vance and J Nowotny *J. Am. Ceram. Soc.* **77** 3186 (1994)
- [17] I P Batra, P Wurfel and B D Silverman *Phys. Rev. Lett.* **30** 384 (1973)
- [18] R Asiate, W Zhu, S A Akbar and P K Dutta *Chem. Mater.* **8** 226 (1996)