

# Effect of pre-sintering temperature on the structural and dielectric properties of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films deposited by sol–gel technique

Somnath C. Roy<sup>a</sup>, M.C. Bhatnagar<sup>a</sup>, G.L. Sharma<sup>a,\*</sup>, R. Manchanda<sup>b</sup>, V.R. Balakrishnan<sup>b</sup>

<sup>a</sup> Thin Film Laboratory, Department of Physics, Indian Institute of Technology Delhi, New Delhi 110016, India

<sup>b</sup> Solid State Physics Laboratory, New Delhi 110054, India

Received 1 September 2003; received in revised form 12 November 2003; accepted 13 January 2004

Available online 21 April 2004

## Abstract

$(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$  thin films have been deposited by sol–gel technique and the effect of pre-sintering temperature on the structural and dielectric properties has been studied. The sol was prepared from barium acetate and strontium acetate powders by dissolving them in acetic acid; while titanium isopropoxide was used as titanium source. Acetyl acetone, 2-methoxyethanol, and formamide were used as chelating agent, diluting reagent, and for getting crack free films, respectively. Two sets of films were prepared; one set pre-sintered at 400 °C while the other one at 600 °C. In all the cases, the final sintering temperature was kept fixed at 700 °C for 2 h. These films were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), dielectric constant, and loss measurements and AC conductivity studies. It has been found that with an increase in the pre-sintering temperature from 400 to 600 °C, the dielectric constant increases from 225 to 383 (measured at 100 kHz); whereas, the loss tangent remains nearly constant at 0.03–0.05. The XRD results show better crystallinity and enhanced grain growth in case of films pre-sintered at 600 °C. The FTIR spectra reveals that there is significant removal of organic materials in films with higher pre-sintering temperature as compared to that with lower pre-sintering temperature. The AC conductivity studies show a decrease in the frequency exponent 's' with an increase in the pre-sintering temperature which has been correlated with the reduction in oxygen vacancy densities in the sample with higher pre-sintering temperature.

© 2004 Elsevier Ltd and Techna S.r.l. All rights reserved.

**Keywords:** C. Dielectric properties; Sol–gel; Barium strontium titanate; AC conductivity

## 1. Introduction

$(\text{Ba},\text{Sr})\text{TiO}_3$  thin films are being extensively studied for their potential applications in high density dynamic random access memories (DRAM) [1], voltage tunable devices [2], IR [3], and humidity [4,5] sensors. Material properties like high dielectric constant, low dielectric loss, low leakage current, dielectric tunability, and rapid change in the dielectric constant in the vicinity of the transition temperature make BST films suitable for the above-mentioned applications.

The methods by which BST films are deposited include rf sputtering [6], metal–organic chemical vapor deposition [7], pulsed laser deposition [8], hydrothermal electrochemical technique [5], and sol–gel synthesis [4]. Among these, sol–gel method is one of the most important approaches which is being used for the preparation of complex oxide

thin films. The sol–gel processing has the advantage of delivering films with extremely uniform composition over large area, ease of dopant incorporation, and non-vacuum processing. But, at the same time, the sol–gel deposited films suffer from inherent disadvantage of having porous structure due to evolution of organic matter and gases during drying. It is well known that the structural and electrical properties of sol–gel derived thin films depend strongly on the thermal processing; both on the pre-sintering and final sintering temperatures. Although the effect of final sintering temperature on the structural and electrical properties of these films have been reported in the literature [9–11], a study on the role played by the pre-sintering temperature has been ignored. In the present paper, we have reported the effect of pre-sintering temperature on the structural and electrical properties of BST thin films. The BST films pre-sintered at relatively lower temperature (300–400 °C) suffer from large shrinkage during the final sintering which results in the development of micro-cracks and porosity due to the release of trapped organic matter. In the present work,

\* Corresponding author. Tel.: +91-11-2659-1332;  
fax: +91-11-2658-1114.

E-mail address: glsharma6@hotmail.com (G.L. Sharma).

the idea has been to perform pre-sintering at a temperature close to the final sintering temperature of the BST films. It was expected that in this process, there would be almost complete removal of organic matter from each deposited layer which could result in a final microstructure with much less porosity. Additionally, with each layer being dried at near to final sintering temperature, a much larger extent of initial grain growth was expected coupled with the release of stress during the drying process. Therefore, in this case, the shrinkage in the films during the final sintering could effectively be reduced. It has been observed that the pre-sintering temperature has a pronounced effect on the structural, dielectric, and electrical properties of BST thin films.

## 2. Experimental

Barium acetate [ $\text{Ba}(\text{CH}_3\text{COO})_2$ ] and strontium acetate [ $\text{Sr}(\text{CH}_3\text{COO})_2$ ] were taken in the molar ratio of 1:1 and dissolved in heated glacial acetic acid. Ti-isopropoxide [ $\text{Ti}(\text{OC}_2\text{H}_4\text{CH}_3)_4$ ] was mixed with acetyl acetone (chelating agent) under nitrogen atmosphere and then mixed with the acetate solutions drop by drop with constant stirring. 2-Methoxy-ethanol and formamide were added to adjust the viscosity of the sol. The transparent yellow sol was finally filtered using Whatman glass-microfiber filter paper and stored as the precursor solution.

BST films were deposited from this precursor sol onto Pt/Si substrates by spin coating technique. For studying the effect of pre-sintering temperature, two sets of films were deposited. In one set, the films were dried at 400 °C for 15 min after depositing each layer, while in the other set, the pre-sintering temperature was kept at 600 °C. All the films are finally sintered at 700 °C for 2 h in an air-furnace. The final thickness of films was 480 nm. Circular aluminum dots of 0.5 mm diameter were deposited onto the films using thermal evaporation by shadow mask technique. A part of film was etched off to expose the underlying platinum in order to form a planar MIM (metal–insulator–metal) structure for the electrical measurements.

The structural characterization of films was carried out with the glancing angle X-ray diffraction (GAXRD) using Rigaku glancing angle X-ray diffractometer (model Giegerflex-D/max-RB-RU200). The Fourier transform infrared spectroscopy (FTIR) was done using a Perkin-Elmer model Spectrum BX FTIR system in the range of 2000–500  $\text{cm}^{-1}$ . The capacitance and conductance measurements were performed using an HP 4192A LF Impedance Analyzer and in the range of 1 kHz–1 MHz.

## 3. Results and discussion

### 3.1. X-ray diffraction studies

Fig. 1 shows the X-ray diffractograms of the samples used in the present study. In this figure, part (a) depicts the XRD

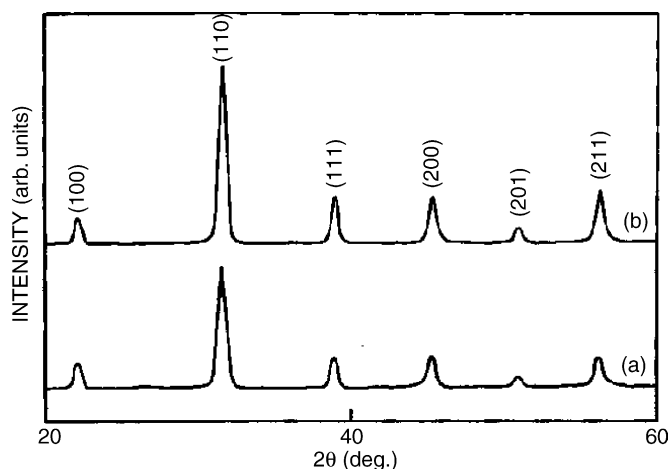


Fig. 1. X-ray diffractograms of samples: (a) pre-sintered at 400 °C and (b) pre-sintered at 600 °C (both are finally sintered at 700 °C).

pattern of sample pre-sintered at 400 °C and finally sintered at 700 °C, while part (b) represents the diffractogram of sample pre-sintered at 600 °C and finally sintered at 700 °C. The XRD patterns indicate that films are grown with cubic structure having good crystallinity in both the cases. But, it is also observed that with increase in pre-sintering temperature from 400 to 600 °C, the intensity of all the lines in Fig. 1b increases as compared to those in Fig. 1a. This observation points to the fact that films with better crystallinity are produced as we increase the pre-sintering temperature and also facilitates grain growth in the samples. To see the grain growth effect more closely, high-resolution X-ray scan of 110 peaks in the two samples was taken in the 2θ range from 30 to 34°. It has been found that with an increase in the pre-sintering temperature, the FWHM of 110 peak decreases from 0.745 to 0.643°. Thus, the narrowing of the peak indicates that with an increase in the pre-sintering temperature, the grain size in the films increases. The dielectric measurement reflects the consequences of better crystallinity with a substantial increase in the dielectric constant, which has been discussed later.

### 3.2. FTIR studies

Fig. 2a and b shows the FTIR spectra for the samples pre-sintered at 400 and 600 °C. The general feature of the spectra reveals that there is significant reduction in the both number of absorption bands and intensity of these bands for the sample pre-sintered at 600 °C. The entire spectra can be divided into two main regions, namely, from 500 to 1000  $\text{cm}^{-1}$  and from 1000 to 2000  $\text{cm}^{-1}$ . It is known that the absorption peaks which appear below 800 up to 400  $\text{cm}^{-1}$  are caused by the different kinds of metal oxygen bonds present in the sample [12]; whereas, the absorption peaks appearing beyond 800  $\text{cm}^{-1}$  are due to the different kinds of organic legands. It is seen that for the sample pre-sintered at 400 °C (Fig. 2(a)), there is a shallow peak appearing at

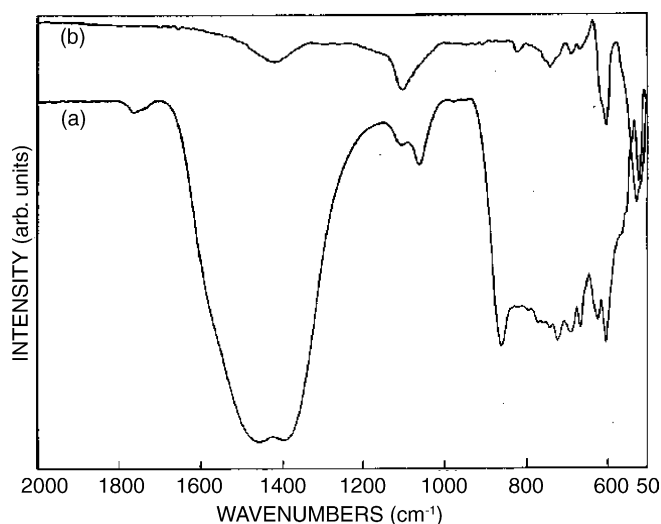


Fig. 2. FTIR spectra of samples: (a) pre-sintered at 400 °C and (b) pre-sintered at 600 °C.

1761  $\text{cm}^{-1}$  which disappears for the sample pre-sintered at 600 °C. This band has been assigned to the C=O stretching mode [13] which is present in the as deposited film with lower pre-sintering temperature. The intense and broad dual peaks in (a) at 1453 and 1387  $\text{cm}^{-1}$  are probably due to carbonate bands partially bonded to barium or strontium ions [14]. In the sample pre-sintered at 600 °C, a very shallow peak appears at 1422  $\text{cm}^{-1}$  which replaces the large band in the former case. This has been reported to be due to  $\text{CH}_2\text{--CO}$  bending vibrations [12]. There are two bands at 1101 and 1062  $\text{cm}^{-1}$  in spectrum (a) that could be due to vibrations of C–O bonds of alcohol legands [15]. For the spectrum (b) which is pre-sintered at 600 °C, only one remains at 1101  $\text{cm}^{-1}$ . In the lower wave-number range, from below 1000 to 500  $\text{cm}^{-1}$ , there also remain traces of organic materials along with the characteristic metal–oxygen bonds in spectrum (a). In this spectrum (a), the absorption bands present at 668 and 626  $\text{cm}^{-1}$  represent the presence

of deformation vibrations of O–C–O and bending modes of CH or COO, respectively [16,17]. But, these bands are absent in the sample pre-sintered at a higher temperature of 600 °C. Also, the shift in the Ti–O absorption band from 524 to 529  $\text{cm}^{-1}$  points to the fact that with an increase in the pre-sintering temperature, there is filling up of oxygen vacancies which then leads to the formation of oxygen octahedra, and consequently, the energy of the absorption band increases. Similar results have been reported in literature for  $\text{BaTiO}_3$  [18]. Thus, with an increase in the pre-sintering temperature from 400 to 600 °C, we observe a significant extent of reduction in the organic matter content in as deposited samples. Therefore, when the final sintering is performed, the sample with higher pre-sintering temperature forms relatively denser microstructure, whereas, the sample pre-sintered at lower temperature has a possibility of having porous structure owing to the evolution of leftover organic matters. The denser microstructure and better crystallinity is reflected and supported through the XRD patterns and dielectric measurements.

### 3.3. Dielectric constant and dielectric loss

Fig. 3 shows the variation of dielectric constant with frequency ranging from 1 kHz to 1 MHz. Two samples have been studied; the first one pre-sintered at 400 °C and the second sample at 600 °C, while the sintering temperature was kept at 700 °C. As it is observed from the figure, the dielectric constant increases from 225 to 383 (at 100 kHz) with the increase in pre-sintering temperature from 400 to 600 °C.

The variation of the dielectric loss tangent with respect to frequency for the above two samples is shown in Fig. 4. It is observed that the loss tangent values are 0.03 and 0.05 (measured at 100 kHz) for the films presintered at 400 and 600 °C, respectively.

The increase in the value of dielectric constant with pre-sintering temperature can be linked with the grain growth during the drying of the films. It is known that in the sol–gel process of film deposition, multiple coatings are carried out in order to achieve the desired thickness. After the deposition of individual layers, the films are dried at some elevated temperature (usually 300–400 °C for BST films) in order to drive out the organic solvents from the gelling layer. When this drying process is performed at a temperature of 300–400 °C, the resultant dried layer is essentially amorphous in nature with nil or very little grain growth. In this case, the final sintering process actually defines the nature of grain growth and followed by crystallization into desired phase. But, when the films are dried (after coating of individual layers) at a temperature (600 °C) which is close to the sintering temperature (700 °C for BST), there is a significant extent of initial grain growth and much higher degree of densification of the forming gel. So after final sintering, the film pre-sintered at 600 °C shows higher value of dielectric constant than that for the film pre-sintered at 400 °C.

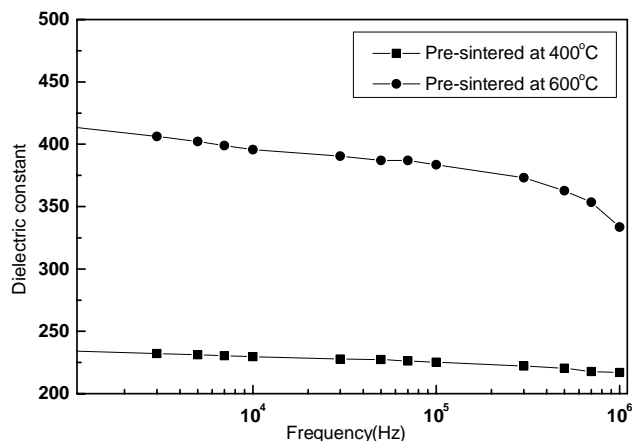


Fig. 3. Variation of dielectric constant with frequency for samples pre-sintered at 400 and 600 °C.

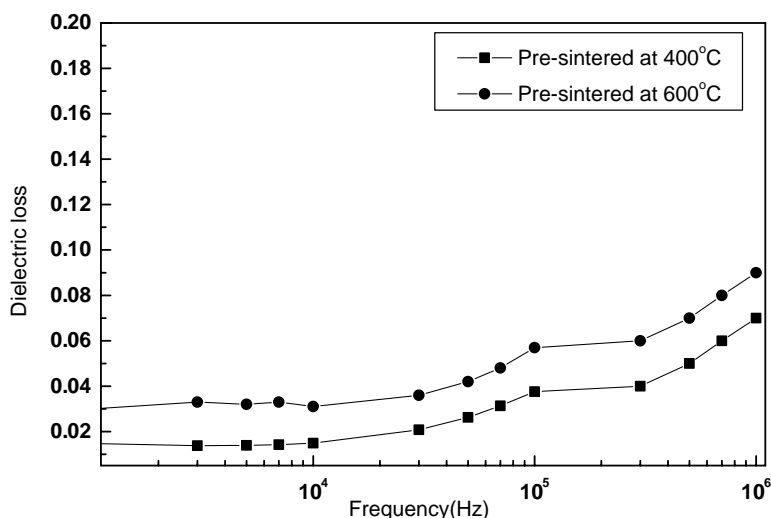


Fig. 4. Variation of dielectric loss with frequency for samples pre-sintered at 400 and 600 °C.

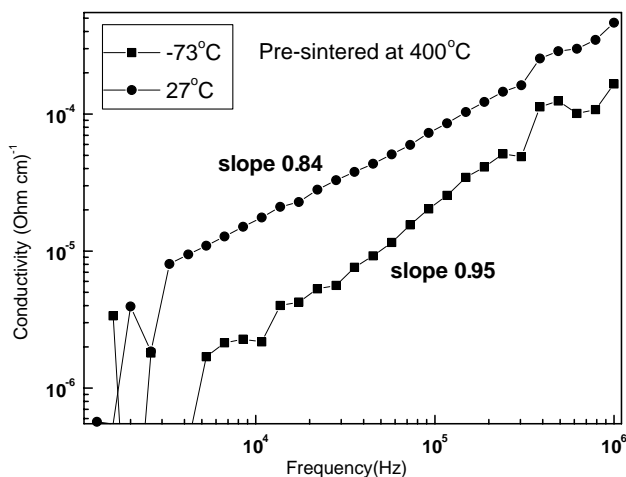


Fig. 5. Frequency dependent AC conductivity for sample pre-sintered at 400 °C (at two different temperatures).

### 3.4. AC conductivity

Figs. 5 and 6 show the AC conductivity data of the films at  $-73^{\circ}\text{C}$  (200 K) and  $27^{\circ}\text{C}$  (300 K), where the frequency was varied from 1 kHz to 1 MHz. We observe that the conductivity is higher for higher temperature and also the slope of the curve (or the frequency exponent,  $s$ ) decreases as the temperature increases. Moreover, it is seen that the frequency exponent changes from 0.95 to 0.77 (at  $-73^{\circ}\text{C}$ ) and from 0.84 to 0.65 (at  $27^{\circ}\text{C}$ ) with an increase in pre-sintering temperature from 400 to 600 °C (final sintering temperature 700 °C). The different values of the frequency exponent ' $s$ ' are shown adjacent to the respective graphs.

The frequency dependent conductivity in amorphous and polycrystalline materials is known to follow relation given by  $\sigma_{ac} = A\omega^s$ . Here,  $A$  is a pre-exponential factor,  $\omega$  is the angular frequency, and  $s$  is the frequency exponent which usually takes the value  $\leq 1$ . The power law nature of conduc-

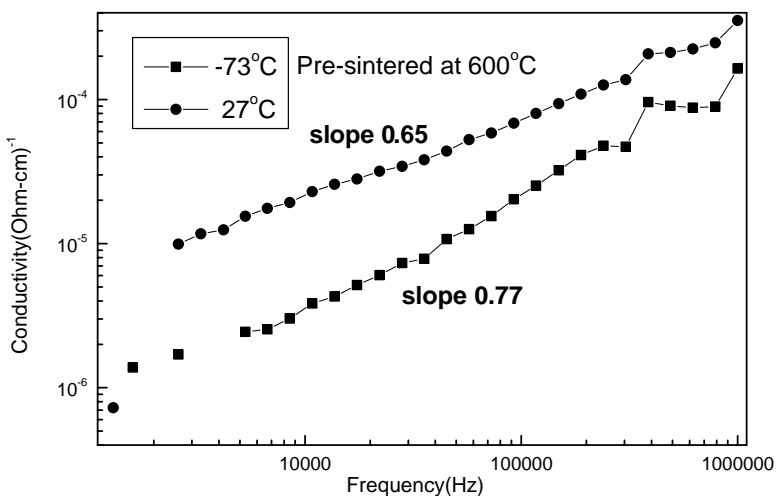


Fig. 6. Frequency dependent AC conductivity for sample pre-sintered at 600 °C (at two different temperatures).

tivity is a universal behavior which arises from the electron hopping through the trap sites present in the band gap of the material [19]. Also, the magnitude of the frequency exponent ' $s$ ' represents the extent of many body interactions among electrons, impurities, and other charged defects. Since these interactions are strongly dependent on temperature, the frequency exponent ' $s$ ' is also temperature dependent. The perovskite type materials are known to contain large number of doubly charged oxygen vacancies [20] which act as the trap sites needed for the AC conduction. Electrons are trapped and released from these traps through the process of hopping known as the "Correlated Barrier Hopping" (CBH) phenomena [19,21]. In this model, the frequency exponent  $s$  is predicted to be temperature dependent with  $s$  increasing towards unity as  $T > 0$  K. Therefore, for a particular sample, the decrease in ' $s$ ' with increase in temperature from  $-73$  to  $27^\circ\text{C}$  results from the 'CBH' phenomena in AC conduction. However, in the present case, we also observe a decrease in ' $s$ ' when pre-sintering temperature is increased from  $400$  to  $600^\circ\text{C}$ . Since, it has already been mentioned that the power law dependence of AC conductivity is an essential and unique feature of trap controlled conduction, the decrease in ' $s$ ' in the present case points to the possibility of relative decrease in the trap densities (oxygen vacancies) in the sample pre-sintered at  $600^\circ\text{C}$ . As for both the samples, the final sintering is done at the same temperature of  $700^\circ\text{C}$ ; the pre-sintering temperature makes the difference in terms of oxygen vacancies in these samples. It has been reported that [22] when BST films are treated at temperatures of  $350$ – $400^\circ\text{C}$ , large concentration of mobile oxygen ions and vacancies are produced. But, at temperatures above  $500^\circ\text{C}$ , these ions get into their normal sites and fill up the oxygen vacancies. Therefore, in the sample with higher pre-sintering temperature ( $600^\circ\text{C}$  as compared to  $400^\circ\text{C}$ ), there is greater extent of filling up of oxygen vacancies even in the as deposited condition. So, when the final sintering of both the samples are carried out under similar conditions and at same temperature, the comparative difference in the initial vacancy density contributes towards the observed difference in AC electrical conductivity in these samples.

#### 4. Conclusions

The effect of an increase in the pre-sintering temperature on structural and electrical properties of sol–gel derived  $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$  thin films have been demonstrated. It has

been observed that with an increase in the pre-sintering temperature from  $400$  to  $600^\circ\text{C}$ , the dielectric constant enhanced from  $225$  to  $383$  (measured at  $100\text{ kHz}$ ); whereas, the loss tangent remains nearly constant at  $0.03$ – $0.05$ . This results from better crystallinity in the samples with higher pre-sintering temperature and also due to almost complete removal of organic materials during the pre-sintering step. The AC conductivity studies show a decrease in the frequency exponent ' $s$ ' with increase in pre-sintering temperature which can be correlated with reduction in oxygen vacancy densities in the sample with higher pre-sintering temperature.

#### References

- [1] S. Ezhilvalavan, T.Y. Tseng, *Mater. Chem. Phys.* 65 (2000) 227.
- [2] J. Im, O. Auceillo, S.K. Streiffer, *Thin Solid Films* 413 (2002) 243.
- [3] K. Hashimoto, H. Xu, T. Mukaigawa, R. Kubo, H. Zhu, M. Noda, M. Okuyama, *Sens. Actuators A* 88 (2001) 10.
- [4] S. Agarwal, G.L. Sharma, R. Manchanda, *Solid State Commun.* 119 (2001) 681.
- [5] S. Agarwal, G.L. Sharma, *Sens. Actuators B* 85 (2002) 205.
- [6] E.J. Cukauskas, S.W. Kirchoefer, W. Chang, *J. Cryst. Growth* 236 (2002) 239.
- [7] J. Petzelt, T. Ostapchuk, A. Pashkin, I. Rychetsky, *J. Eur. Ceram. Soc.* 23 (2003) 2627.
- [8] S.G. Lu, X.H. Zhu, C.L. Mak, K.H. Wong, H.L.W. Chan, C.L. Choy, *Mater. Chem. Phys.* 79 (2003) 164.
- [9] Y.L. Cheng, Y. Wang, H.L.W. Chan, C.L. Choy, *Microelectron. Eng.* 66 (2003) 872.
- [10] H.-Y. Tian, J. Choi, K. No, W.-G. Luo, A.-L. Ding, *Mater. Chem. Phys.* 78 (2002) 138.
- [11] M. Nayak, S.-Y. Lee, T.-Y. Tseng, *Mater. Chem. Phys.* 77 (2002) 34.
- [12] H.-Y. Tian, W.-G. Luo, X.-H. Pu, P.-S. Qiu, X.-Y. He, A.-L. Ding, *Thermochim. Acta* 360 (2000) 57.
- [13] P. Duran, D. Gutierrez, J. Tartaj, M.A. Banares, C. Moure, *J. Eur. Ceram. Soc.* 22 (2002) 797.
- [14] M. M-Silvan, L. F-Cobas, R.J. M-Palma, M. H-Velez, J.M. M-Duart, *Surf. Coat. Technol.* 151–152 (2002) 118.
- [15] L. Weng, X. Bao, K. S-Crentsil, *Mater. Sci. Eng. B* 96 (2002) 307.
- [16] M.T. Tsai, *J. Non-Cryst. Solids* 298 (2002) 116.
- [17] K. Kitaoka, H. Kozuka, T. Yoko, *J. Am. Ceram. Soc.* 81 (5) (1998) 1189.
- [18] U. Hasenkox, S. Hoffman, R. Waser, *J. Sol–Gel Sci. Technol.* 12 (1998) 67.
- [19] S.R. Elliott, *Philos. Mag.* 36 (6) (1977) 1291.
- [20] W.L. Warren, K. Vanheusden, D. Dimos, G.E. Pike, B.A. Tuttle, *J. Am. Ceram. Soc.* 79 (2) (1996) 536.
- [21] S.R. Elliott, *Adv. Phys.* 36 (2) (1987) 135.
- [22] M. Shen, Z. Dong, Z. Gan, S. Ge, W. Cao, *Appl. Phys. Lett.* 80 (2002) 2538.