

Sol-gel processing and characterization of nanometersized (Ba,Sr)TiO₃ ceramics

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ABSTRACT

Ba_{0.5}Sr_{0.3}TiO₃ (BST 70/30) nanopowders have been prepared by the modified sol-gel method using barium acetate, strontium acetate and titanium isopropoxide as the precursor. The formation mechanism, phase evolution, and particle size have been investigated using TG/DTA, XRD, and SEM. The fine particles of the nano-powders calcined are homogeneous and well-dispersed and their narrow size distribution is about 15–25 nm. The as-formed gel was dried at 200^o C and then calcined in the temperature range 650^o C to 850^o C for crystallization. Phase evolution during calcination was studied using X-ray diffraction (XRD) technique which exhibited cubic crystal structure with perovskite phase. Sintering of the pellet was performed at 950^o C and the study on the dielectric relaxation and the ac electrical conductivity behavior of modified Barium titanate, Ba_{0.7}Sr_{0.3}TiO₃ ferroelectric ceramic exhibit that these are thermally activated process. Copyright © 2011 VBRI press.

Keywords: BST; Sol-gel; XRD; SAED.



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Introduction

Ferroelectric materials with perovskite structure have a wide range of applications, as dielectric, piezoelectric, pyroelectric, electro-optical material. Barium titanate is the earliest known perovskite-type ferroelectric materials used in electronics. Barium titanate and related compounds have been extensively used in the preparation of high dielectric constant capacitors, PTC resistors, transducers and ferroelectric memories [1]. BaTiO₃-SrTiO₃ (BST) has been studied widely in recent years [2, 3]. It is known to form solid solutions across the entire compositional range due to their similar crystal structure and comparable ionic radii [4-5] and the addition of strontium is usually employed to lower the Curie point and maintain a relatively low temperature dependence of the dielectric constant. As a result, BST compounds are now being investigated with regard to various electronic applications. It has been found that BST has applications in piezoelectric sensors, dynamic random access memories (DRAM), microwave phase shifters, tunable filters and uncooled infrared detectors for its high dielectric, ferroelectric, and pyroelectric properties [6-8]. Since all these properties are strongly related to the microstructure of the ceramics, the homogeneity of the materials is important. Traditionally, BSTs are prepared by the ceramic method, in which the carbonates of barium, strontium, and titanium oxide are calcined at high temperature (1200^oC) [9, 10]. However, the ceramic method is not very useful for the preparation of high

performance ceramics because the materials have very large particle sizes, are non-homogeneous and have high impurity contents [11-13]. So many studies have been focused on various chemical methods for the synthesis of BST powders, for example sol-gel, co-precipitation, hydrothermal, spray pyrolysis, and modified citrate gel [14-17]. Conventional hydrothermal methods have been successfully used for the synthesis of BST powders [18]. In particular, the microwave hydrothermal synthesis can avoid high temperature heat treatment that can lead to the particle growth and agglomeration. However the use of large excess of barium and strontium precursors and low yield are two major drawbacks of the method. In addition, co-precipitation method for synthesis of BST powders has been reported, in which Barium strontium titanate $[Ba_{1-x}Sr_xTiO(C_2O_4)_2 \cdot 4H_2O]$ are prepared firstly and then the BST powders are produced by the pyrolysis of BST at high temperature in air [19]. The route is simple and can produce stoichiometric, sub-micron-sized, almost unagglomerated BST powders. However, the process adds some unwanted ionic species and pH value is different in the steps. So the co-precipitation method suffers from two major problems, i.e., contamination of final precipitate with Cl^- ions and very stringent control of pH value. Sol gel synthesis of tunable, non-linear dielectric materials offer advantages like low temperature synthesis case in controlling the composition variation and low cost [17-23]. It was reported that $Ba_{1-x}Sr_xTiO_3$ ceramics solid solution with the composition of $x \leq 0.8$ exhibited normal ferroelectric behavior while a relaxor characteristic was observed in the $SrTiO_3$ rich region $x > 0.8$ [24]. Mao et. al reported the nonhydrolytic sol-gel synthesized pure phase BST70/30 powder with average size of 170 nm [25]. BST-glass ceramic system with increased dielectric constant was synthesized by sol-gel process leading to diffused phase transition in dielectric characteristics [26]. Somani et al [27] were able to synthesize BST at 1100°C and 1450°C by sol-gel technique. The present paper describes the study on the sol-gel synthesis, phase evolution, structural and electrical characterization of BST 70/30 powder.

Experimental

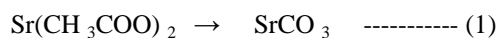
BST 70/30 powder was synthesized by using barium acetate, strontium acetate and titanium (IV) iso-propoxide as a precursor for barium, strontium and titanium respectively. Acetic acid was used as solvent and 2-methoxy ethanol was used to stabilize Titanium (IV) iso-propoxide. Stoichiometric proportion of barium acetate and strontium acetate powder was dissolved in 10 and 5ml of acetic acid, respectively by continuous magnetic stirring at 60° for half an hour. The two solutions were then mixed and refluxed at 110° C for 2h. 2-methoxy ethanol (2- 4 ml) was added in Titanium (IV) isopropoxide (0.11mol) to form a separate solution at room temperature. Ba-Sr solution was added drop by drop, into Ti solution and pH of the solution was maintained in the range of 2.5 to 4.0 by adding buffering agents. Refluxing the mixture again resulted in the formation of a thick white gel. Distilled water was added to the gel and the solutions were mixed by stirring on a hot plate with a magnetic stirrer. It was kept in the oven and heated to 200°C for 2h. This resulted in the formation

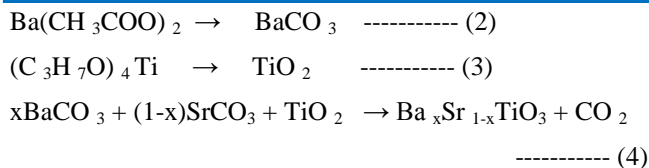
of amorphous powder of BST 70/30. The amorphous powder was then calcined at 650°C, 750°C, 800°C and 850°C, separately in a muffle furnace. The calcined powder was ground in a mortar pestle to obtain fine powder. The fine powders were used to characterize the structural and microstructural properties of the compound. The X-ray diffraction pattern of the compounds were recorded at room temperature using X-ray powder diffractometer with CuK_{α} ($\lambda = 1.5418\text{\AA}$) radiation (Rigaku Miniflex, Japan) in a wide range of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 70^\circ$) at a scanning rate of 2°min^{-1} . The differential thermal analysis (DTA-TG, Setaram Labsys, Setaram Instrumentation, Caluire, France) of thick gel was carried out in air from room temperature to 800 °C with different heating rates of $5^\circ \text{C min}^{-1}$. The microstructure was observed using a Transmission electron microscope (TEM). Bulk densities ρ (gm/cm^3) were measured by Archimedes' method.

The powder samples were uni-axially pressed into cylindrical pellets using a hydraulic press at a pressure of 10MPa. The sintering of the green pellets were carried out at 950°C for 4h in an air atmosphere. Silver painted electrodes were applied to the opposite faces of sintered samples. The dielectric properties were studied in the frequency range 1-1000 kHz and in the temperature range 25 to 500°C using an impedance analyzer PSM1735.

Results and discussion

Fig. 1(a) shows the X-ray powder diffraction of the precursor and powder of BST (70/30) sample calcined at 650,750, 800 and 850°C respectively. X-ray diffractograms of BST (70/30) system reveal the perovskite structure. X-ray diffraction pattern was indexed on the basis of a cubic cell structure. The gel was formed after 120°C and the precursor formed after 200°C show amorphous nature as observed from the X-ray diffraction study. Thermal heat treatment with particular time and temperature allows the amorphous phase to crystallize because the amorphous phase is thermodynamically metastable state. The reflection becomes narrower and sharper with higher temperature (calcined at 650, 750, 800 and 850°C) as can be seen clearly from the high angle (211) reflection. The peaks observed in XRD pattern appear slightly shifted towards higher 2θ angles. This may be due to the decreased inter-atomic spacing of the small BST nanoparticles. The increased internal pressure in nanoparticles results in an elastic, compressive volume strain and hence, in a linear strain. This may sometimes lead to a reduced lattice parameter or interplanar spacing [28]. Fig. 1(a) shows extra weak diffraction peaks besides the peaks of cubic BST. It has been earlier reported that during sol-gel synthesis of barium titanium oxides several intermediate phases form before the transformation of the amorphous phase into perovskite phase [27, 29]. The peaks were identified, as $(Ba,Sr)CO_3$ (herein after, BSC) including $BaCO_3$, $SrCO_3$ [30] and intermediate phases of the $(Ba,Sr)_2Ti_2O_5CO_3$ (herein after BSTOC) including $Ba_2Ti_2O_5CO_3$ [31]. Based on these results the chemical equation leading to BST (70/30) phase evolution is:





The particle size of the calcined powder was determined using Scherrer equation:

$$\beta = 0.9\lambda/d \cos \theta \quad \text{----- (5)}$$

where λ = wavelength of CuK_α radiation, θ = angle of diffraction, d = the average particle size and β = the full width at half maximum from the recorded XRD patterns and was found to be $\sim 22\text{nm}$. **Fig. 1(b)** shows the XRD pattern of the sample sintered at 950°C . The diffraction lines of characteristic (100), (110), (111), (200), (210), (211) and (220) planes of the cubic structure BST (70/30) powder is clearly observed. The crystalline phase was identified as single phase cubic perovskite with lattice parameter $a = 3.978\text{\AA}$ (**Table 1**).

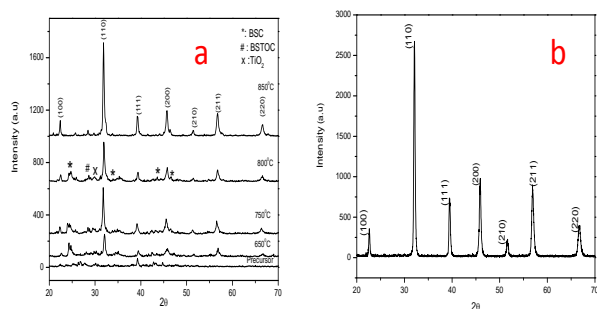


Fig. 1. (a) XRD pattern of the precursor and BST 70/30 calcined at $650, 750, 800$ and 850°C , (b) XRD pattern of the BST70/30 sintered at 950°C .

Table 1. Structural and dielectric data for BST70/30 compound

A	Volume	Relative	ϵ' (25°C)	ϵ'' (25°C)	E_a	Particle	Particle
(\AA^3)	(\AA^3)	density(%)			(eV)	size(TEM)	size(XRD)
						(nm)	(nm)
3.9908	63.56	95.5	7000	1500	0.355	18	22

Fig. 2(a) shows the thermogravimetric (TG) and differential thermal analysis (DTA) of the BST gel. The endothermic peak in DTA curve at 200°C - 250°C represents the loss of water. There was a large mass loss at 250°C - 450°C about 50% owing to the high percentage of organics in the precursor. The mass loss continues until 600°C . **Fig. 2(b)** shows the TEM image of the BST (70/30) nanoparticles. The powder was observed to be in form of agglomerates in the dispersed solution and the shape of the powder was not uniform. The average particle size of the powder was found to be $\sim 18\text{nm}$. The particle size of the nanoparticles determined from the recorded XRD patterns was found to be in line with TEM investigation. By adjusting the growth parameters, such as reaction time, initial concentration, the size of these nanostructured BST is controllable to be 18–25 nm in diameters. As reaction time and temperature and the precursor concentration are controlled, the size of the nanoparticles is decreased which

is in agreement with the results obtained by others [32, 33]. **Fig. 2(c)** shows Selected Area Electron Diffraction (SAED) pattern of the BST nanopowder. Presence of concentric rings in the diffraction pattern confirms the polycrystallinity of BST 70/30 nano powder. **Fig. 2(d)** shows results from EDAX spectra of as-prepared BST (70/30) nanoparticles and it contains Ba, Sr, Ti, and O species. Peaks for Cu and C are from the grid used in TEM experiment. The density of the sintered samples measured by Archimede's method was 95-96% of the theoretical value.

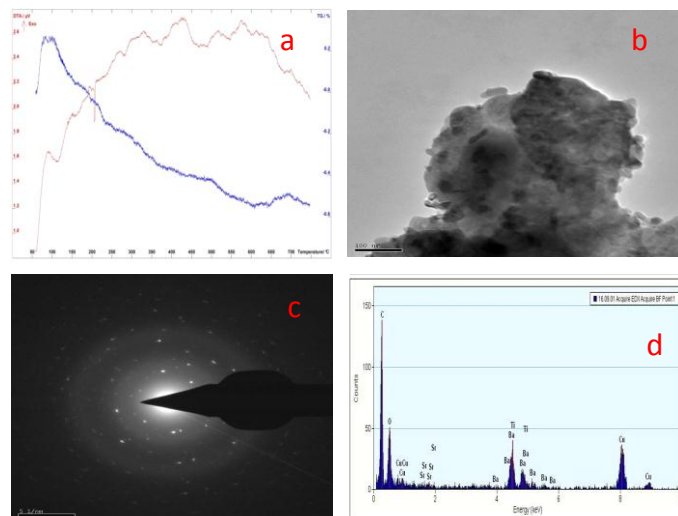


Fig. 2. (a) TG-DTA curves of the precursor of BST70/30, (b) TEM micrograph, (c) SAED micrograph and (d) EDAX spectrograph of BST70/30 sample calcined at 850°C .

The dielectric constant of sintered sample of barium strontium titanates as a function of frequency is shown in the **Fig. 3**. Dielectric frequency curves shows that there is a decrease of ϵ' with increase in frequency. The dielectric constant decreases with increase in frequency upto 10 kHz, beyond which it remains almost constant. At low frequencies electronic, ionic, dipolar and interfacial/surface polarizations contribute to the dielectric constant. But for frequencies above 10 kHz the contribution from interfacial/surface polarization gets minimized. The interfacial/surface polarization can be explained by using a Maxwell-Wagner [34] mechanism and a Shockley-Read [35] mechanism. The Maxwell-Wagner mechanism was concerned with interfacial polarization due to ionic motion in presence of an electric field. At low frequencies the mobile charges, usually impurity ions diffuse under the influence of the applied field up to the interface and build-up the surface charge until the applied field reverses with the alternating voltage. These ionic motions are sensitive to the frequency of the alternating field and cannot follow the field variations at very high frequencies. Again for low and middle order frequencies and at high temperatures the impurity ions in the bulk crystals capture the surface electrons causing the space charge polarization at the surface. The electron capture process increases with increase in temperature. This type of surface polarization can be accounted by the statistics proposed by Shockley and Read [35] and this mechanism in dielectrics and

semiconductors is popularly known as Shockley-Read mechanism. Due to the Shockley-Read mechanism ϵ increases with increasing temperature in the high temperature region.

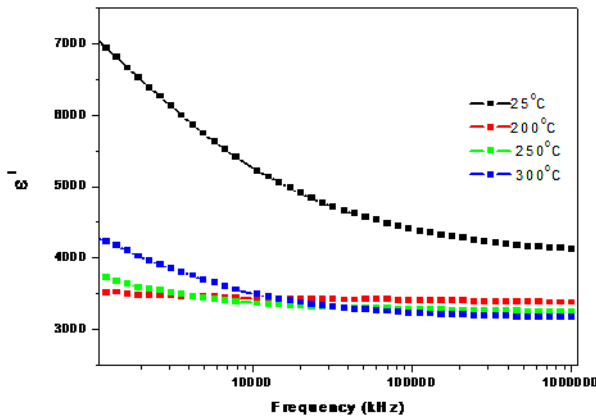


Fig. 3. Variation of dielectric constant with frequency at different temperature of BST70/30.

Fig. 4 shows the frequency dependence of the dielectric loss of BST (70/30) ceramic at different temperature. The decrease in ϵ'' for increase in frequency imply that up to a frequency of 10kHz the ionic conduction(Maxwell-Wager mechanism) and the electron capture process(Shockley-Read mechanism) contributes to the polarization process. The interfacial polarization is likely to occur at frequencies much lower than that corresponding to the dipolar polarization peak. So at frequencies 100 kHz or more the main contribution are due to dipolar polarization.

Fig. 5 shows the frequency dependence of the electrical conductivity for the studied composition in the paraelectric state, at different temperatures. A convenient formalism to investigate the frequency behavior of conductivity in a variety of materials is based on the power relation proposed by Jonscher [36] $\sigma_T(\omega) = \sigma_0 A\omega^s$, here σ_T is the total conductivity, σ_0 is the frequency independent conductivity, and the coefficient A and exponent s are temperature and material dependent [37].

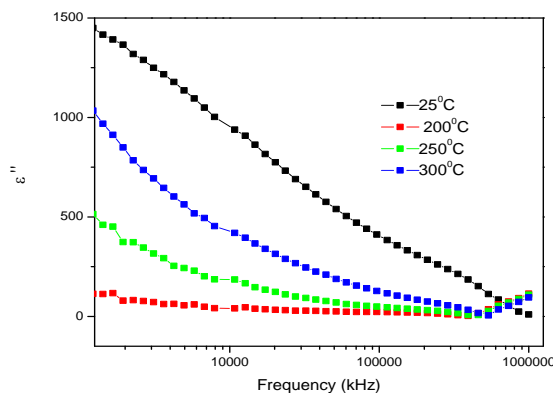


Fig. 4. Variation of dielectric loss with frequency at different temperature of BST70/30.

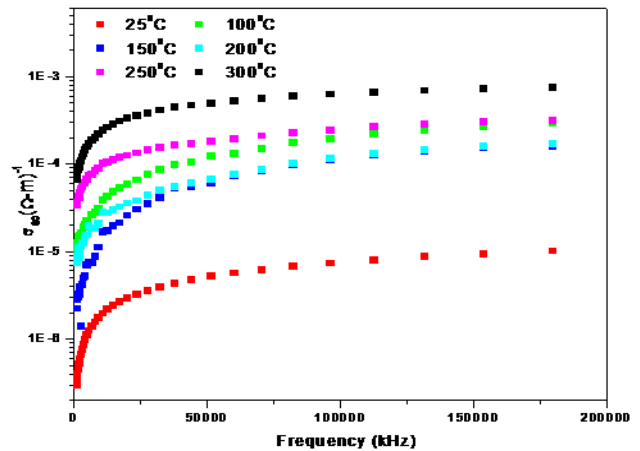


Fig. 5. Variation of ac conductivity with frequency at different temperature of BST70/30.

The term $A\omega^s$ contains the ac dependence and characterizes all dispersion phenomena. The exponent s has been found to behave in a variety of forms [38-41] a constant, decreasing with temperature, increasing with temperature, etc., but always within $0 < s < 1$. This indicates that the conduction process is a thermally activated process. From the graph it is seen that the exponent as depicted by the slope of the variation is a function of temperature. To calculate the ac conductivity the following relation have been used [42].

$$\epsilon'' = \epsilon \tan \delta = \sigma_{ac} / (\omega \epsilon_0) + (\epsilon_s - \epsilon_\infty) \omega \tau / (1 + \omega^2 \tau^2) \tag{6}$$

where ϵ'' is the imaginary part of the complex dielectric constant, ϵ_s is the low frequency static dielectric constant, ϵ_∞ is the very high frequency dielectric constant for which ionic polarization becomes negligibly small and τ is the relaxation time. At low frequencies the first term which represents the surface polarization due to ionic conductivity is dominant one. Hence the ac conductivity is dominant one. The ac conductivity is obtained from the formula

$$\sigma_{ac} = \epsilon \epsilon_0 \omega \tan \delta \tag{7}$$

where ω is the angular frequency and ϵ_0 is the dielectric constant in free space. The ac conductivity at different temperatures is studied by measuring the dielectric constant and the loss tangent at those temperatures. The variation of electrical conductivity with respect to the temperatures is governed by the relation

$$\sigma_{ac} = \sigma_0 \exp [-E_a / K_B T] \tag{8}$$

where E_a is the activation energy of the impurities of the samples. The temperature variation of $\ln \sigma_{ac}$ is shown in Fig. 6. E_a was calculated from the slope of the curve and was found to be 0.35eV at 100kHz. The possible explanation for the small value of E_a in the paraelectric region (higher temperature) may be given as follows (i) typical ionic solids, in contrast, possess limited numbers of mobile ions which are hindered in their motion by virtue of being

trapped in relatively stable potential wells. Due to rise in temperature the donor cations are taking a major part in conduction. The donors created a level (Band-Donor level) which is much nearer to the conduction band. Therefore to activate the donors a small amount of energy is required and (ii) a slight change in stoichiometry (i.e the metal to oxygen ratio) in multi metal complex oxides causes the creation of large number of donors or acceptors which may create donor or acceptors like states in the vicinity of conduction or valence band. These donors or acceptors may also be activated with less energy [43]. In ferroelectrics, the dielectric relaxation phenomenon reflects the delay (time dependence) in the frequency response of a group of dipoles subjected to an external applied field. When an alternating current is applied to a sample, the dipoles responsible for the polarization are no longer able to follow the oscillations of the electric field at certain frequencies. The field reversal and the dipole reorientation become out of phase, giving rise to a dissipation of energy. Over a wide frequency range, different types of polarization cause several dispersion regions, and the critical frequency characteristic of each contributing mechanism depends on the nature of the dipoles. For ferroelectric materials the dielectric relaxations are very sensitive to both external (temperature, electric field, ionic substitution, etc) and intrinsic (defect, domain configuration, etc) modifications because the polarization is greatly affected. The defects depend on either intrinsic or extrinsic heterogeneities due to special heat treatments (quenching, annealing, etc), ionic substitutions, grain size additives, and grain boundary nature. Defects may cause modifications of the short- and/or long-range interactions in ferroelectrics.

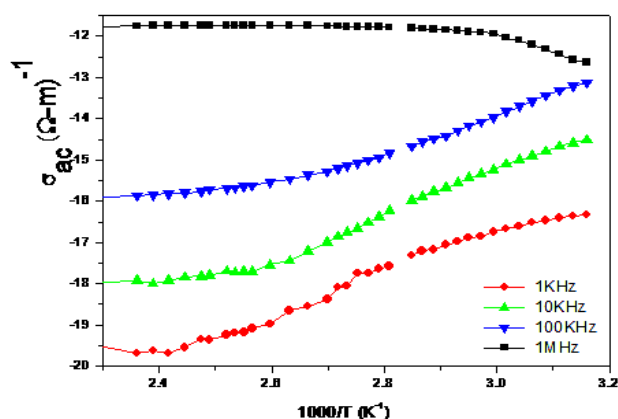


Fig. 6. Variation of ac conductivity with temperature at different frequency of BST70/30

Conclusions

Nanocrystalline BST70/30 powder of average size 18nm was synthesized via sol-gel route. Processing parameters were optimized and the phase evolution during synthesis was studied. It was found that the carbonates of the starting chemicals react to form $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ phase at around 650°C . Complete crystallization was achieved at 850°C where the phase composition is predominantly $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ with a small fraction of carbonates, oxycarbonates and titanium dioxide. Grain size calculated

from the XRD pattern was 18nm, in line with our TEM investigation. Ac conductivity process is a thermally activated process and the activation energy as calculated is 0.35eV.

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Reference

- Haertling, G.H. *J. Am. Ceram. Soc.* **1999**, 82, 797.
DOI: [10.1111/j.1151-2916.1999.tb01840.x](https://doi.org/10.1111/j.1151-2916.1999.tb01840.x)
- Jaffe, B.; Cook, W.R.; Jaffe, H. *Piezoelectric Ceramics*, Academic Press, London, **1971**.
- Smolenskii, G.A.; Bokov, V.A.; Isupov, V.A.; Krainik, N.; Pasynkov, R.E.; Sokolov, A.I.; *Ferroelectric and Related Materials*, Gordon and Breach, New York. **1984**.
- Waser, R. *J. Eur. Ceram. Soc.* **1999**, 19, 655.
DOI: [10.1016/S0955-2219\(98\)00293-3](https://doi.org/10.1016/S0955-2219(98)00293-3)
- Rai, R.; Sharma, S. *Adv. Mater. Lett.* **2010**, 1, 269.
DOI: [10.5185/amlett.2010.7140](https://doi.org/10.5185/amlett.2010.7140)
- Mahani, R.M.; Battisha, I.K.; Aly, M.; Abou-Hamad, A.B. *J. Alloy. Compd.* **2010**, 508, 354.
DOI: [10.1016/j.jallcom.2010.05.060](https://doi.org/10.1016/j.jallcom.2010.05.060)
- Wu, Y.J.; Wang, N.; Wu, S.Y.; Chen, X.M. *J. Amer. Ceram. Soc.* **2011**, 94, 1343.
DOI: [10.1111/j.1551-2916.2011.04507.x](https://doi.org/10.1111/j.1551-2916.2011.04507.x)
- Kong, L.B.; Li, S.; Zhang, T.S. Zhai, J.W.; Boey, F.Y.C. *Progress in Materials Science* 2010, 55, 840.
DOI: [10.1016/j.pmatsci.2010.04.004](https://doi.org/10.1016/j.pmatsci.2010.04.004)
- Bauger, A.; Moutin, J.C.; Niepce, J.C. *J. Mater. Sci.* **1983**, 18, 3041.
DOI: [10.1007/BF00700786](https://doi.org/10.1007/BF00700786)
- Li, Z.; Fan, H. *J Phys. D: Appl. Phys.* **2009**, 42, 075415.
DOI: [10.1088/0022-3727/42/7/075415](https://doi.org/10.1088/0022-3727/42/7/075415)
- Kongtaweelert, S.; Sinclair, D.C.; Panichphant, S. *Curre. Appl. Phys.* **2006**, 6, 474.
DOI: [10.1016/j.cap.2005.11.043](https://doi.org/10.1016/j.cap.2005.11.043)
- Roeder RK, Slamovich EB. *J. Am. Ceram. Soc.* **1999**, 82, 1665.
DOI: [10.1111/j.1151-2916.1999.tb01984.x](https://doi.org/10.1111/j.1151-2916.1999.tb01984.x)
- Jeon, J.H. *J. Eur. Ceram. Soc.* 2004, 24, 1045.
DOI: [10.1016/S0955-2219\(03\)00385-6](https://doi.org/10.1016/S0955-2219(03)00385-6)
- Hung, K.M.; Yang, W.D.; Huang, C. *J. Eur. Ceram. Soc.* **2003**, 23, 1901.
DOI: [10.1016/S0955-2219\(02\)00431-4](https://doi.org/10.1016/S0955-2219(02)00431-4)
- Sharma, K.P.; Varadan, V.V.; Varadan, V. K. *J. Euro. Ceram. Soc.* **2003**, 23, 659.
DOI: [10.1016/S0955-2219\(02\)00191-7](https://doi.org/10.1016/S0955-2219(02)00191-7)
- Razak, K.A.; Asadov, A.; Yoo, J.; Haemmerle, E.; Gao, W. *J. Alloys Compd.* **2008**, 449, 19.
DOI: [10.1016/j.jallcom.2006.02.093](https://doi.org/10.1016/j.jallcom.2006.02.093)
- Brankovic, G.; Brankovic, Z.; Goes, M.S.; Paiva, C.O.; Cilense, M.; Varela, J.A.; Longo, E. *Mater. Sci. Eng. B* **2005**, 122, 140.
DOI: [10.1016/j.mseb.2005.05.016](https://doi.org/10.1016/j.mseb.2005.05.016)
- Pazik, R.; Hreniak, D.; Strek, W. *Mater. Res. Bull.* **2007**, 42, 1188.
DOI: [10.1016/j.materresbull.2006.10.021](https://doi.org/10.1016/j.materresbull.2006.10.021)
- Khollam, Y.B.; Deshpande, S.B.; Potdar, H.S.; Bhoraskar, S.V.; Sainkar, S.R.; Date, S.K. *Mater. Charact.* **2005**, 54, 63.
DOI: [10.1016/j.matchar.2004.11.00](https://doi.org/10.1016/j.matchar.2004.11.00)
- Gleiter, H.; Weissmuller, J.; Wollersheim, O.; Wurschum, R. *Acta Mater.* **2001**, 49, 737.
DOI: [10.1016/S1359-6454\(00\)00221-4](https://doi.org/10.1016/S1359-6454(00)00221-4)
- Chen, J.F.; Shen, Z.G.; Liu, F.T.; Liu, X.L.; Yun, J. *Script. Mater.* **2003**, 49, 509.
DOI: [10.1016/S1359-6462\(03\)00361-0](https://doi.org/10.1016/S1359-6462(03)00361-0)
- Phule, P.P.; Risbud, S.H. *J. Mater. Sci.* **1990**, 25, 1169.
DOI: [10.1007/BF00585422](https://doi.org/10.1007/BF00585422)
- Dus, W.; Lisinska, Z.; Adamczyk, O.; Osinska, K.; Kozielski, L.; Czeka, D. *Mate. Sci. Poland* **2007**, 25, 791.
http://materialscience.pwr.wroc.pl/bi/vol25no3/articles/ms_22wode.pdf
- Huiquing, Z.F. *J Phys D: Appl. Phys.* **2009**, 42, 75415.

25. Mao, C.; Dong, X.; Zeng, T.; Chen, Y.H.; Cao, F. *Ceramics International* **2008**, *34*, 45.
DOI: [10.1016/j.ceramint.2006.08.002](https://doi.org/10.1016/j.ceramint.2006.08.002)
26. Chen, J.; Zhang, Y.; Deng, C.; Dai, X. *Mater. Chem. Phys.* **2010**, *121*, 109.
DOI: [10.1016/j.matchemphys.2010.01.015](https://doi.org/10.1016/j.matchemphys.2010.01.015)
27. Somani, V.; Kalita, S.J. *J. Electroceram* **2007**, *18*, 57.
DOI: [10.1007/s10832-007-9008-7](https://doi.org/10.1007/s10832-007-9008-7)
28. Kelsall, R.; Hamley, I.; Geoghegan, M. *Nanoscale Science and Technology* Wiley, Chichester, England, **2005**.
29. Majumder, S.B.; Jain, M.; Martinez, A.; Katiyar, R.S.; VanKeuls, F.W.; Miranda, F.A. *J. Appl. Phys.* **2001**, *90*(2), 896.
DOI: [10.1063/1.1378811](https://doi.org/10.1063/1.1378811)
30. Shen, C.; Li, Q.F.; Liu Q. *Mater. Lett.* **2004**, *58*, 2302.
DOI: [10.1016/j.matlet.2004.02.009](https://doi.org/10.1016/j.matlet.2004.02.009)
31. Durán, P.; Capel, F.; Gutierrez, D.; Tartaj, J.; Banares, A.; Moure, C. *J. Mater. Chem.* **2001**, *11*, 1828.
DOI: [10.1039/B010172I](https://doi.org/10.1039/B010172I)
32. Zuo, X.H.; Deng, X.Y.; Chen, Y.; Ruan, M.; Li, W.; Liu, B.; Qua, Y.; Xuc, B. *Mater. Lett.* **2010**, *64*, 1150.
DOI: [10.1016/j.matlet.2010.02.034](https://doi.org/10.1016/j.matlet.2010.02.034)
33. Mao, C.; Dong, X.; Zeng, T. *Mater. Lett.* **2007**, *61*, 1633.
DOI: [10.1016/j.matlet.2006.07.089](https://doi.org/10.1016/j.matlet.2006.07.089)
34. Macdonald, J.R. *Impedance Spectroscopy*, Wiley Publication, NY, **1987**.
35. Shockley, W.; Read, W.T. *Physical Review* **1952**, *87*, 835.
DOI: [10.1103/PhysRev.87.835](https://doi.org/10.1103/PhysRev.87.835)
36. Jonscher, A.K. *Nature* **1977**, *267*, 673.
DOI: [10.1038/267673a0](https://doi.org/10.1038/267673a0)
37. Almond, A.P.; West, A.R.; Grant, J.R. *Solid State Commun.* **1982**, *44*, 1277.
DOI: [10.1016/0038-1098\(82\)91103-6](https://doi.org/10.1016/0038-1098(82)91103-6)
38. Jonscher, A.K. *Dielectric Relaxation in Solids* Chelsea Dielectric, London, **1983**.
39. Jain, H.; Mundy, J.N. *J. Non-Cryst. Solids* **1987**, *91*, 315.
DOI: [10.1016/S0022-3093\(87\)80342-3](https://doi.org/10.1016/S0022-3093(87)80342-3)
40. Funke, K. *Prog. Solid State Chem.* **1993**, *22*, 111.
DOI: [10.1016/0079-6786\(93\)90002-9](https://doi.org/10.1016/0079-6786(93)90002-9)
41. Elliott, S.R. *Solid State Ionics* **1994**, *70*, 27.
DOI: [10.1016/0167-2738\(94\)90284-4](https://doi.org/10.1016/0167-2738(94)90284-4)
42. Burfoot, J.C.; Taylor, G.W. *Polar dielectric and their applications*, Macmillan Press, London, **1979**.
43. Buchanan, R.C. *Ceramics materials for electronics* Marcel Dekker, New York, **1986**.

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