

Effect of Sr Substitution on Structure and Thermal Diffusivity of $Ba_{1-x}Sr_xTiO_3$ Ceramic

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Abstract: Problem statement: The aim of this research was to study the effect of Sr substitution on structure and thermal diffusivity of $Ba_{1-x}Sr_xTiO_3$ ceramic at room temperature. **Approach:** Structural and thermal diffusivity of $Ba_{1-x}Sr_xTiO_3$ were studied by performing X-ray diffraction and photoflash measurements. The effects of Sr substitution on the structure and on the thermal diffusivity of $Ba_{1-x}Sr_xTiO_3$ ($0 \leq x \leq 1$) were investigated. All samples were prepared by standard solid state reaction technique. **Results:** The results showed that by substituting of Ba^{2+} ion with the Sr^{2+} the crystallite size decreased. The effect made the thermal diffusivity of $Ba_{1-x}Sr_xTiO_3$ decreased from $11.30 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$ (for $BaTiO_3$) to $6.467 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$ (for $SrTiO_3$) as x varied from 0-1. **Conclusion:** This study showed a significant effect of structure on thermo-physical property of materials.

Key words: Perovskites, lattice parameter, photoflash, X-ray analysis, thermal diffusivity

INTRODUCTION

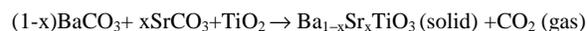
Perovskite materials with the chemical formula ABO_3 are the subject of extensive investigations because of their technical importance and the fundamental interest in physical properties and phase transition phenomena. $BaTiO_3$ is a tetragonal crystal at the room temperature. The cubic modification occurred at temperature higher than 120°C . This modification can be described as a distortion of the tetragonal structure. This distortion occurred when the titanium atom within the oxygen octahedron is shifted respectively from the octahedral corner toward the center. By doping with foreign cations the phase change Temperature (T_c) can be varied. Barium titanate, perovskite structure, is widely used in many applications. When Ba^{2+} ions in $BaTiO_3$ are partially replaced by Sr^{2+} , the electronic and optical properties of solid solution $Ba_{1-x}Sr_xTiO_3$ (BST) can be tailored over a broad range with a molar ratio $0 \leq x \leq 1$ ^[1,2].

By varying the value of x , it is possible to obtain a specific property that can be used in various electroceramic applications, such as electronic, piezoelectric transducer, pyroelectric detector, thermal application and some electro-optical devices^[2]. In order to understand these properties of the material, the thermo-physical properties of a material must be studied. The most important thermo-physical properties of a material are thermal conductivity, thermal diffusivity and specific heat. They are needed in any

heat transfer calculations. Thermal conductivity is the property that determines the working temperature levels of a materials and it is an important parameter in problems involving steady state heat transfer. However, measuring the rapidity of the heat propagation through the material is known by thermal diffusivity. It becomes important when it involves with non-steady state heat conduction^[3,4]. The photoflash method has been widely used for measuring thermal diffusivity of materials. In the present study, the photoflash technique was used to measure the thermal diffusivity of $Ba_{1-x}Sr_xTiO_3$ at room temperature. The aim of this study is to report the effect of Sr substitution on structure and thermal diffusivity of $Ba_{1-x}Sr_xTiO_3$ ceramic measured at room temperature.

MATERIALS AND METHODS

The $Ba_{1-x}Sr_xTiO_3$ ceramic samples were prepared from raw materials of $BaCO_3$ (99.8% in purity), $SrCO_3$ (99% in purity) and TiO_2 (97% in purity), via solid state reaction method. The $BaCO_3$, TiO_2 and $SrCO_3$ powders were mixed together and graining for 2 h. The solid state reaction can be described by the general reaction as:



The $Ba_{1-x}Sr_xTiO_3$ powder was calcined in double tube furnace at 900°C for 12 h similar to the procedure reported earlier^[5,6]. After calcinations, the ceramic

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powder was mixed with Polyvinyl Alcohol (PVA) and the powder was pressed into pellets of 13 mm diameter and 3.5 mm thickness using a hydraulic pressing machine (Carver No.4350). The pellet was sintered at 1200°C for 24 h and cooled to room temperature at a rate of 117°C h⁻¹[7]. For structure study, the sintered pellets were grounded to a fine powder and examined by X-ray diffraction machine (Philips, PW1710 with Cu-Kα radiation). The x-ray data was analyzed using XPERT HIGH SCORE software in which the lattice constants and unit cell volume were determined[8]. The interlayer spacing (d) and crystallite size were calculated using Bragg and Scherrer equations. In this study the density of sample was measured using Archimedes' principle. Distilled water was used as the immersion liquid where the density at 20°C was taken to be 0.9982 g cm⁻³[9].

The thermal diffusivity was measured using photoflash technique. The photoflash experimental set up is shown in Fig. 1. A K-type thermocouple was used to measure the temperature profile at the rear sample surface. The thermal diffusivity α was calculated by measuring the half rise time, t_{1/2} of temperature profile of the sample thus for sample thickness, L the thermal diffusivity was given as:

$$\alpha = \frac{0.1388L^2}{t_{1/2}} \quad (1)$$

Thermal diffusivity, α is related to thermal conductivity, λ by a simple well-known relationship given as:

$$\alpha = \frac{\lambda}{\rho C_p} \quad (2)$$

Where:

ρ = The sample density

C_p = The specific heat capacity

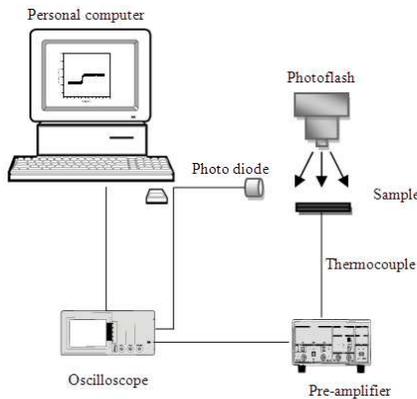


Fig. 1: Experimental setup of photoflash technique

RESULTS

Figure 2 shows the XRD patterns of Ba_{1-x}Sr_xTiO₃ (0 ≤ x ≤ 1) obtained from powder form of the sample. It can be observed that the increasing of Sr content causes systematic shift of peaks towards higher 2θ angles due to the substitution of Ba²⁺ [R (Ba²⁺) = 1.0325268 Å] by Sr²⁺ [R (Sr²⁺) = 0.7640699 Å] thus decreases the d spacing of the structure^[10]. For BaTiO₃, the phase transformation from tetragonal to cubic structure occurs at 120~130°C^[11]. However, in the case of the BST samples investigated in this study, increasing of Sr content decreases the temperature of phase transformation. Figure 3 shows the lattice parameters and the cell volume of the tetragonal and cubic phases in the BST system at room temperature. The cell volume decreases by increasing of Sr concentration. Lattice parameters and the cell volume calculated from x-ray diffraction data are presented in Table 1.

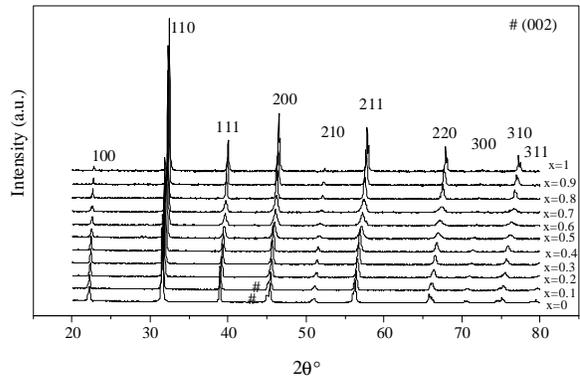


Fig. 2: XRD pattern of Ba_{1-x}Sr_xTiO₃ (0 ≤ x ≤ 1) powder sintered at 1200°C for 24 h

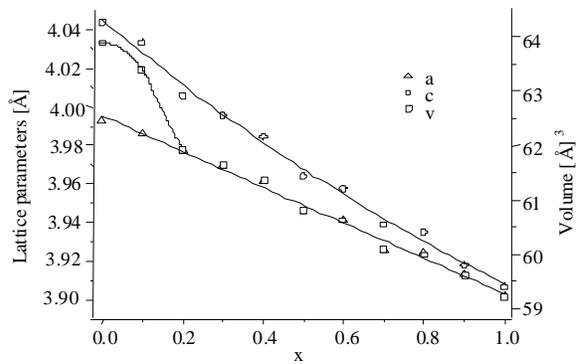


Fig. 3: Lattice parameters and unit cell volume as a function of x value of Ba_{1-x}Sr_xTiO₃

Table 1: Lattice parameters, volume and crystallite size of Ba_{1-x}Sr_xTiO₃ obtained from the structural refinement of X-ray data measured at room temperature

x	Lattice parameter [Å]		Tetragonality (c/a ratio)	Volume [Å] ³	Crystallite size [Å]
	a	c			
0.0	3.9926	4.0328	1.010	64.3	757
0.1	3.9867	4.0195	1.008	63.9	649
0.2	3.9773	3.9773	1.000	62.9	585
0.3	3.9697	3.9697	1.000	62.6	572
0.4	3.9614	3.9614	1.000	62.2	558
0.5	3.9459	3.9459	1.000	61.4	455
0.6	3.9412	3.9412	1.000	61.2	426
0.7	3.9268	3.9268	1.000	60.6	356
0.8	3.9237	3.9237	1.000	60.4	312
0.9	3.9125	3.9125	1.000	59.8	284
1.0	3.9018	3.9018	1.000	59.4	263

Table 2: Density and thermal diffusivity for Ba_{1-x}Sr_xTiO₃

x	Density (gm cm ⁻³)	Thermal diffusivity ×10 ⁻³ (cm ² sec ⁻¹)
0.0	6.080	11.302
0.1	5.996	9.622
0.2	5.952	9.237
0.3	5.872	8.204
0.4	5.862	7.623
0.5	5.812	7.494
0.6	5.743	7.081
0.7	5.697	6.868
0.8	5.681	6.805
0.9	5.597	6.559
1.0	5.545	6.467

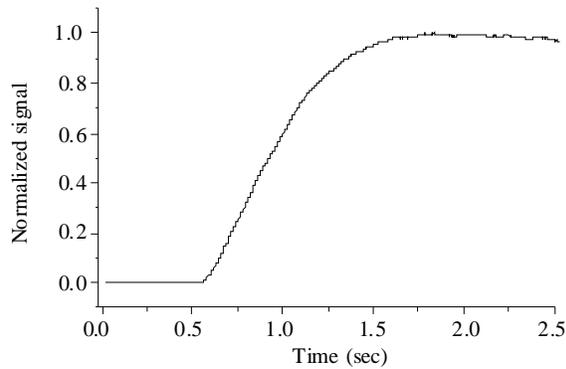


Fig. 4: Thermogram obtained for pure BaTiO₃ (Thickness, L = 0.25 cm)

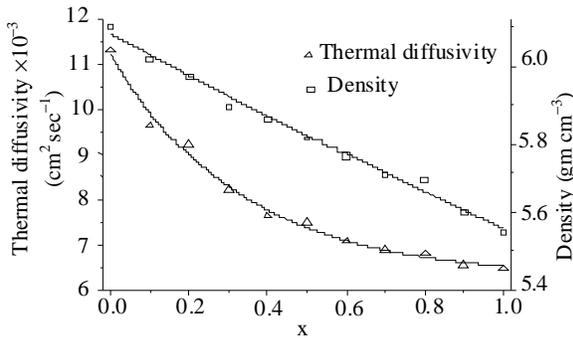


Fig. 5: Thermal diffusivity and density as a function of x value of Ba_{1-x}Sr_xTiO₃

Using Archimedes' principle, the average density of the present Ba_{1-x}Sr_xTiO₃ (0 ≤ x ≤ 1) samples was determined. The values were obtained using two set of samples with different thicknesses and each measurement was repeated several times. The difference in density can be attributed by the effect of different doping ratio in the specimens.

Figure 4 shows the temperature profile obtained from photoflash measurement. The thermal diffusivity was calculated using Eq. 1 where the half-rise time was determined from temperature profile curve. Variation of the thermal diffusivity and density of Ba_{1-x}Sr_xTiO₃ with Sr concentrations are shown in Fig. 5. The density and thermal diffusivity values are listed in Table 2.

DISCUSSION

From Figure 2 it is observed that all of the samples were crystallized into single-phase solid solutions of Perovskite structure. The (002) and (200) peaks at 2θ = 44.918 and 45.395° were merged into (200) peak and increase its intensity as consequence of phase transition from tetragonal to cubic structure. It can be seen that the intensity of the peaks (100), (210) and (300) decreases as the concentration of Sr increases. Similarly, the peak (311) decreases with decreasing of Sr content but the peak position is shifted to the higher 2θ value. Other peaks, such as (211) and (310) increases with the increasing of Sr concentration due to the phase transition. However, other phases appeared are due to the impurity presents in the samples. The XRD patterns confirmed that BST sample has cubic structure at room temperature, as we expected. The decreasing of the lattice parameter with increasing of Sr content in BST solid solution was confirmed after refinement. Tetragonality (c/a ratio) decreases with the increasing of Sr concentration and approaches 1 of the cubic phase for composition x ≥ 0.2 as reported in literature^[12]. It was found that the change of order and the diffuseness of the phase transition in BST could be attributed to the cell volume effect^[9].

Figure 5 shows that the thermal diffusivity drops rapidly from 11.30 × 10⁻³ (pure BaTiO₃) - 6.467 × 10⁻³ cm² sec⁻¹ (SrTiO₃). However, the sample density decreases linearly with the increasing of Sr ion. The thermal diffusivity value for pure BaTiO₃ is in good agreement

(within the experimental error~4%) with the values reported in the literature ($11.8 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$)^[9].

These results indicate that the Sr substitution gives a significant effect on the thermal properties of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ^[4]. This behavior can be explained by the relation between the crystallite size and the thermal conductivity (λ). Dybe equation state that the thermal conductivity increasing with the increase of mean free path of phonon^[13]. The increasing of crystallite size made the mean free path increase, thus the thermal conductivity as well as the thermal diffusivity increases. It is well known that for some materials, the thermal conductivity increase almost linearly with the crystal size. Increase in crystallite size raises the mean-free path and reduces phonon-phonon scattering. This explains the thermal diffusivity behavior of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ in the present study.

CONCLUSION

The phase transition and thermal diffusivity of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics with $0 \leq x \leq 1$ have been successfully studied using x-ray diffraction and photoflash measurements. The results show that by substituting of Ba^{2+} ion with the Sr^{2+} the phase transition occurred from tetragonal to cubic structure. This effect makes the thermal diffusivity of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ decreases from 11.30×10^{-3} (for BaTiO_3)- $6.467 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$ (for SrTiO_3) for x varied from 0-1. This study shows a significant effect of structure on thermo-physical property of materials.

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REFERENCES

1. Xiao, C.J., C.Q. Jin and X.H. Wang, 2008. Crystal structure of dense nanocrystalline BaTiO_3 ceramics. *Mater. Chem. Phys.*, 111: 209-212. DOI: 10.1016/J.MATCHEMPHYS.2008.01.020
2. Liqin, Z., P.M. Vilarinho and J.L. Baptista, 2001. Dielectric properties of bismuth doped $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics. *J. Eur. Ceramic Soc.*, 21: 531-534. DoI: 10.1016/S0955-2219(00)00239-9
3. Seog, K.K. and J.K. Yong, 2008. Determination of apparent thickness of graphite coating in flash method. *Thermochim. Acta*, 468: 6-9. DOI: 10.1016/j.tca.2007.11.012
4. Ebrahimi, J., 1970. Thermal diffusivity measurement of small silicon chips. *J. Phys. D. Applied Phys.*, 3: 236-239. DOI: 10.1088/0022-3727/3/2/422
5. Teoh, W.T., Z.A. Ahmad and A.F.M. Noor, 2006. Dielectric properties and microstructure of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ derived from mechanically activated $\text{BaCO}_3\text{-SrCO}_3\text{-TiO}_2$. *J. Mater. Online*, 2: 1-10. DOI: 10.2240/azojomo0228
6. Yuan, X.W., 2005. First-principles study on the structure instability and electronic structure of cubic $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$. *Solid State Commun.*, 135: 290-293. DOI: 10.1016/J.SSC.2005.05.012
7. Helmi, A., H. khemakhem, G. Vélú, J.C. Carru and R.V.D. Mühl, 2005. Dielectric properties and ferroelectric phase transitions in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ solid solution. *J. Alloys Compound*, 399: 1-6. DOI: 10.1016/j.jallcom.2005.03.007
8. Da, J., P. Hing and C.Q. Sun, 2000. Growth dynamics and electric properties of $\text{PbT}_{0.1}\text{iZr}_{0.9}\text{O}_3$ ceramics doped with cerium oxide. *J. Applied Phys.*, 33: 744-752. DOI: 10.1088/0022-3727/33/6/324
9. Yi, H., 2004. Heat capacity, thermal conductivity and thermal expansion of barium titanate-based ceramics. *Thermochim.ica Acta*, 419: 135-141. DOI: 10.1016/J.TCA.2004.02.008
10. Dulal, C.G. and R. Biswas, 2003. Theoretical Calculation of Absolute Radii of Atoms and Ions. Part 2: The ionic radii. *Int. J. Mol. Sci.*, 4: 379-407. DOI: 10.3390/i4060379
11. Dang-Hyok, Y. and B.I. Lee, 2002. BaTiO_3 properties and powder characteristics for ceramic capacitors. *J. Ceramic Process. Res.*, 3: 41-47. DOI: 10.1016/j.ceramint.2008.04.030
12. Markovic, S., M. Mitric, N. Cvjticanin and D. Uskokovic, 2006. Preparation and properties of $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ multilayered ceramics. *J. Eur. Ceramic Soc.*, 27: 505-509. DOI: 10.1016/J.JEURCERAMSOC.2006.04.066
13. Qian-ming, G., Z. Li, B. Xiao-dong, D. Li, Y. Zhao and J. Liang, 2004. Thermal properties of aligned carbon nanotube/carbon nanocomposites. *Mater. Sci. Eng. A.*, 384: 209-214. DOI: 10.1016/J.MSEA.2004.06.006