

Structural and Dielectric Studies of Fe-Li Substituted Hexagonal Barium Titanate

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ABSTRACT: We have studied the influence of a new lead-free Fe/Li incorporated H-Bt prepared by the solid state reaction method and compared it with pure hexagonal barium titanate. The hexagonal phase was stabilised at room temperature due to substitution with Fe-Li. Lattice constants were refined as $a = 5.720$ A.U., $c = 13.96$ A.U. Both XRD and IR imply that Li enters octahedral as well as Ba sites. Dielectric measurements show an increase from 800 to 10^5 indicating sample to be potential colossal dielectric constant (CDC) material. Abnormal grain growth (AGG) was restricted in the substituted sample and normal grain growth was observed.

KEYWORDS: Barium titanate, hexagonal, colossal dielectric constant, grain growth.

I. INTRODUCTION

In recent years, a number of perovskite ABO_3 -type lead-free materials have been studied for their possible use in environmentally-safe multilayer capacitors, pyroelectric and/or piezoelectric applications. Barium titanate ceramics have been used extensively as capacitor dielectrics in the past few decades [1].

Barium titanate has two structural polymorphs: the cubic perovskite type (CBT) and its hexagonal modification (HBT) with thirty atoms per unit cell. While CBT has been one of the best studied ferroelectric materials for decades [2], work on the structural and dielectric properties of HBT is scarce [3]. The existence of hexagonal barium titanate (HBT) has been known since about the time of discovery of ferroelectricity in tetragonal barium titanate (TBT). The crystal structures of many barium titanates including H-BaTiO₃, Ba₆Ti₁₇O₄₀, Ba₄Ti₁₃O₃₀, Ba₂Ti₉O₂₀ and BaTi₅O₁₁ can be described as hexagonal close packing of Ba and O atoms with partial occupancy of octahedral sites by Ti. (4)

The microwave properties of doped HBT ceramics indicate that all materials are insulators at room temperature with relative dielectric constants between 50 and 80 [5-7]. Oxygen-deficient HBT shows huge dielectric constant also referred to as a colossal dielectric constant (CDC) [8]. La-doped HBT was seen to induce a charge imbalance due to change in the valency from Ti⁴⁺ to Ti³⁺ and subsequent creation of oxygen-deficiencies leading to a retention of the huge dielectric constant [9].

A series of hexagonal Ba (Ti,Fe) O₃ materials where Ti^{IV} was progressively replaced by Fe^{III} and/or Fe^{IV} with oxygen vacancies being formed exclusively in O(1) sites within the H-BaO₃ layers, has been reported [10]. It was first reported in 1960 [11] that certain amounts of Mn are sufficient to stabilize the hexagonal phase of BaTiO₃ at room temperature whereas the hexagonal polymorph of undoped material is stable in air only at temperatures higher than 1703 K [12].

The Jahn-Teller (JTE) distortion was proposed as the common driving force for the transition cubic-hexagonal caused by the Ti³⁺ ions in the case of undoped material or caused by Mn³⁺ in the doped samples.[13]. Investigation of the influence of Cu-doping on the crystal structure and related properties has been made [14]. Besides, Mn³⁺, Cu²⁺ and Cr²⁺ exhibit the strong JTE corresponding to the electron configurations d⁹ and d⁴, respectively. To support this proposal, it is useful to test other 3d-transition elements which exhibit a Jahn-Teller effect (JTE) inside an oxygen octahedron as in the case of BaTiO₃ with respect to their ability to lower the cubic-hexagonal transition temperature and stabilize HBT at room temperature. In the present study, the effects of Fe and Li substitution on the structural, dielectric of the H-BaTiO₃ ceramics are examined.

II. EXPERIMENTAL

Pure Barium titanate and Li-Fe substituted BaTiO₃ (Li_{0.399}Fe_{1.2}Ba_{0.3}Ti_{0.35}O₃) were prepared by the high temperature solid state reaction method. The starting materials, Li₂CO₃, Fe₂O₃, TiO₂ and BaCO₃ (all 99.9 per cent purity – AR grade) were dried in a muffle furnace and mixed in stoichiometric proportion and then ground and calcined in steps of 600°C, 800°C and 1000°C for eight hours each. To obtain homogeneity, these mixtures were pressed into pellets and were finally sintered for 24 hours at 1200°C to ensure a complete reaction. The crystallographic structure was determined at room temperature using the X-ray diffraction patterns of powders obtained by using a highly sophisticated microprocessor based JEOL-JDX8030 diffractometer using a Copper target. The variation in capacitance C and loss factor tanδ with frequency in the range 10kHz-1Mhz at room temperature was recorded on a HP 4277 A LCZ Meter using a two probe method. The same two- probe method system was used to determine dielectric constant in the temperature range 300-773K. The Scanning Electron Microscope (SEM) images were obtained from JEOL, JSM-840A/WDS/EDS analytical scanning microscope along with ion sputter JFC-1100 and grain size was determined by the line intercept method [5].

III. RESULTS AND DISCUSSION

III.1 STRUCTURAL INFORMATION

X-RAY DIFFRACTION STUDIES: The room-temperature x-ray powder diffraction pattern (**Figure 1**) and XRD data (**Table 1**) of the Li_{0.399}Fe_{1.2}Ba_{0.3}Ti_{0.35}O₃ confirm the single phase hexagonal barium titanate structure. This phase must have been stabilized because the Ba to Ti ratio is approximately equal to unity and because of the use of transition element namely Fe. 3d transition elements like Mn, Fe, Ni, Cu are known to decrease the phase transition temperature cubic to hexagonal and stabilize the hexagonal phase at room temperature [14]. All peaks are identified as Hexagonal-BaTiO₃ in space group P63 / mmc [16]. The lattice parameters were refined to a = 5.72 Å, c = 13.96 Å. Reported values of a = 5.738 Å, c = 13.97 Å corresponding to Hexagonal-BaTiO₃ are compared and lithium and iron are seen to reduce the constants 'a' and 'c' and cell volume. (**table 1**). All planes except (110) are observed to be more intense in the substituted sample with respect to the pure reported one [16]. Obviously, Ba²⁺ has been replaced by Li⁺ and Fe³⁺ having lower atomic numbers in (104) and (110) planes. The replacement of Ba²⁺ by an ion smaller ionic radius also explains the decrease in lattice constant. Because of the large differences of the effective ionic radii between Ba²⁺ (161 pm) and Ti⁴⁺ (60.5 pm) the incorporation of Fe²⁺ (63pm) at Ti-sites is more probable [17].

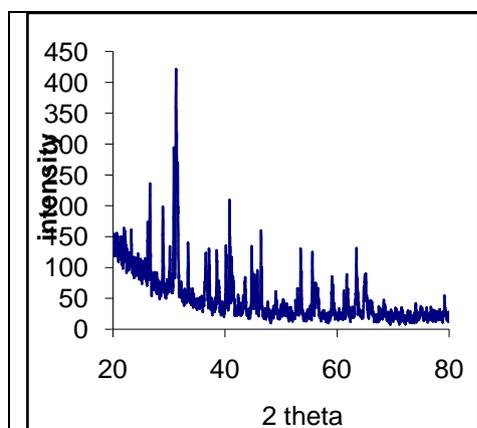


Figure1: X-ray powder diffraction pattern
Li_{0.399}Fe_{1.2}Ba_{0.3}Ti_{0.35}O₃

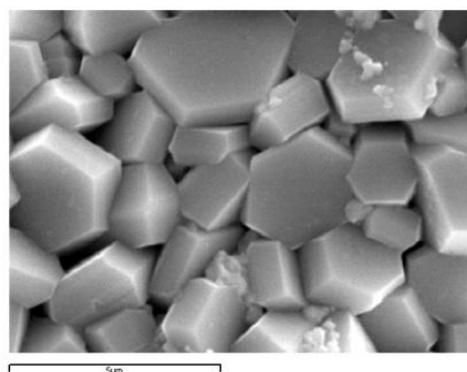


Figure2: SEM image of surface of
Li_{0.399}Fe_{1.2}Ba_{0.3}Ti_{0.35}O₃

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The SEM image of the surface of our sample shows well defined six-sided, plate-like grains with grain size 2.23 μm . (Figure 2). It is well known that grain size depends inversely on Ba/Ti ratio [18, 19]. Ba/Ti < 1 favours growth. Also substitutes like Cr³⁺ cause abnormal grain growth ($\approx 100 \mu\text{m}$) [18]. However, in our sample, the large presence of ion may have curved the grain growth [19].

Table1: Structural Parameters of $\text{Li}_{0.399}\text{Fe}_{1.2}\text{Ba}_{0.3}\text{Ti}_{0.35}\text{O}_3$

	$\text{Li}_{0.399}\text{Fe}_{1.2}\text{Ba}_{0.3}\text{Ti}_{0.35}\text{O}_3$	Hexagonal BaTiO_3
Lattice Const \AA	a = 5.720 & c = 13.96	a = 5.738, c = 13.97
Cell Volume cm^3	457 X 10^{-24}	459 X 10^{-24}

III . 2. DIELECTRIC STUDIES

Figure 3 and table 2 show the dielectric variation in the frequency range 10kHz.-1Mhz. The curves Figure 5.5 are of the Maxwell Wagner type [8] and show relaxation frequency at approximately 12Khz . Table 2 shows that both interfacial polarisation contribution and dipolar polarisation are substantial. The room temp. K' in the present doped sample is almost four times higher at 835 and further rises to an order $\approx 10^5$ when quenched at high temperature. At room temperature, the gradual drop in dielectric const K' and loss factor K'' with increasing frequency indicates the presence of space charge. The dipolar contribution is approximately 30% of that due to space charge.

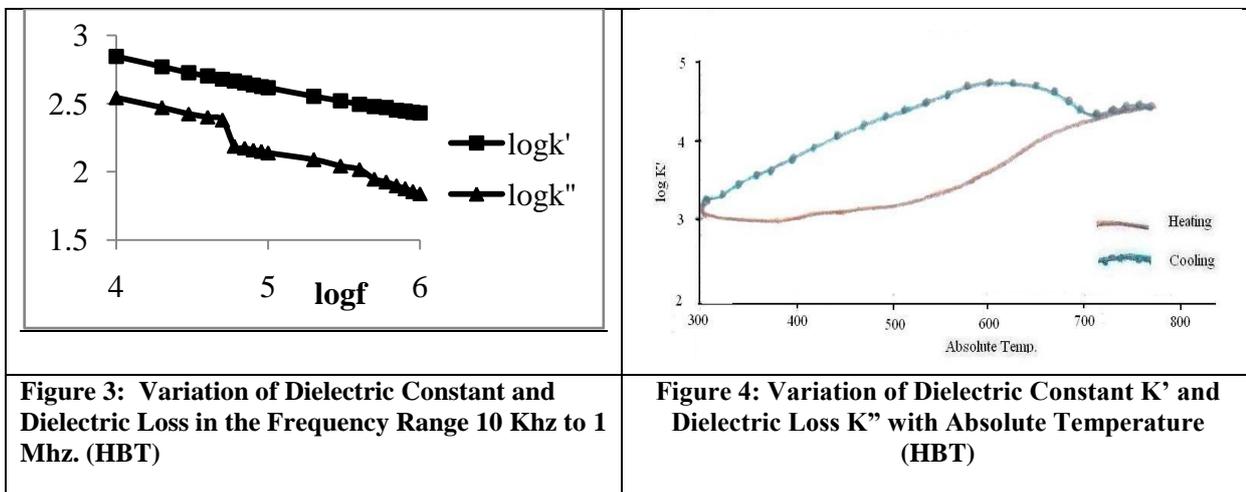


Table 2: K' – Dielectric Constant and K'' – Dielectric Loss (HBT)

K'1 KHz	K''1 KHz	K'10 KHz	K''10 KHz	K'100 KHz	K''100 KHz	K'1 MHz	K''1 MHz	Space Charge
835	245	697	349	411	137	270	69	766

It is interesting to note that the intrinsic K' at room temperature 835. It is worthwhile to note that the dielectric constant can be raised to the order of 10^5 after annealing at 661 K' [18]. We feel that with due heat treatment, our sample can be a potential CDC material. Further it is interesting to note that the curve corresponding to the temperature variation shows a huge hysteresis loop. The dielectric variation with temperature at 1Khz. plotted in Figure 4 shows a relatively high value of dielectric constant of the order $\approx 10^3$ around room temperature, which increases to an order of 10^5 with temperature. The lowered K' value at room temperature is expected as Fe insertion

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weakens dielectric nature [20]. The Oxygen deficient H-bt shows a CDC (Colossal Dielectric Constant) due to Maxwell- Wagner effect contributed by the structural distortion in the material. It has been revealed that an intrinsic permittivity of 200 in the undoped *h*-BaTiO₃ crystal can be increased to 10⁵ by oxygen -deficiency and crystal defects through Maxwell–Wagner relaxation [8]. Therefore, the large dielectric constant in our sample may be due to the presence of Fe²⁺ - Fe³⁺ ion content being very large in our sample. Also, Fe³⁺ occupying Ti⁴⁺ sites would increase polarisation.

This can also be explained by intrinsic and extrinsic effects. The intrinsic effect indicates that the decrease in K' at low temp. reveals the existence of high polarization relaxation or dipolar fluctuation in the domains [21,22]. The giant K' at higher temperature can be interpreted as arising from the Maxwell–Wagner effect contributed by the insulating interfacial barrier layers and the semiconducting bulk crystal. The decrease of K' at room temperature can be explained by the reduction of oxygen vacancies which is one source of the charge. In this connection, it is possible that the lithium occupying the (104) plane holds the charges together giving a net boundary effect.

The high K' may also be dominated by Maxwell–Wagner effects, contributed from grain boundaries in polycrystals, and from twin boundaries in a single crystal [23,24]. If the doping can control the oxygen deficiencies in HBT, the high value of K' can be maintained which is a desirable property. Huge hysteresis loop giving a transition temperature around 753K is observed. It would be interesting to further investigate if this transition temperature coincides with the magnetic curie temperature.

IV. CONCLUSION

We have studied the influence of a new Fe/Li incorporated H-Bt. The hexagonal phase was stabilised using Fe-Li doped BaTiO₃ was stabilised at room temperature thus making the process more ecofriendly. Lattice constants were refined as *a* = 5.720Å, *c* = 13.96 Å. Both XRD and IR imply that Li enters octahedral as well as Ba sites. The SEM pictures showed hexagonal, flat, plate like grains and the EDAX shows significant present of Fe on the grain boundary. Dielectric measurements show an increase from 800 to 10⁵ indicating sample to be potential lead- free CDC material. Abnormal grain growth (AGG) was restricted in the doped sample. Normal grain growth was observed.

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REFERENCES

- 1 Fu C.L., Yang C.R., Chen H.W., Wang Y.X., Hu L.Y., Mat. Sci. Eng. B 119, 185 (2005)
- 2 M.E. Lines and A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials (Clarendon Press, Oxford) (1977).
- 3 M. Yamaguchi, K. Inoue, T. Yagi, and Y. A. Kishige, Phys. Rev. Lett. 74, 2126 (1995);
- 4 E. Tillmanns, W. Hofmeister and W. H. Baur, *J. Solid State Chem.* 58, 14, Paper 9/00957D (1985).
- 5 A. Feteira, K. Sarma, N. M. Alford, I. M. Reaney, and D. C. Sinclair, *J. Am. Ceram. Soc.* 86, 511 (2003).
- 6 G. M. Keith, M. J. Rampling, K. Sarma, N. M. Alford, and D. C. Sinclair, *J. Eur. Ceram. Soc.* 24, 1721 (2004).
- 7 D. C. Sinclair, J. M. S. Skakle, F. D. Morrison, R. I. Smith, and T. P. Beales, *J. Mater. Chem.* 9, 1327 (1999).
- 8 Jianding Yu, Paul-François Paradis, Takehiko Ishikawa, and Shinichi Yoda; applied physics letters volume 85, 14 (2004).
- 9 Natsui, Hidesada; Yu, Jianding Masuno, Atsunobu, Itoh, Mitsuru Odawara, Osamu; Yoda, Shinichi *Ferroelectrics*, Volume 378, Number 1, pp. 195-199(5) (2009).
- 10 I. E. Grey, C. Li, L. M. D. Cranswick, R. S. Roth and T. A. Vanderah, *J. Solid State Chem.*, 135, 312 (1998).
- 11 R. M. Glaister and H. F. Kay, *Proc. Phys. Soc. London* 5, 763 (1960).
- 12 Kirby K W and Wechsler B A *J. Am. Ceram. Soc.* 74 1841 (1991).
- 13 H.T. Langhammer, T. Müller, K.-H. Felgner, H.-P. Abicht, *J. Am. Ceram. Soc.* 83, 605 (2000).
- 14 H.T. Langhammer et al. / *Solid State Sciences* 5, 965–971 (2003).
- 15 K. Inoue, M. Wada, and A. Yamanaka, *J. Kor. Phys. Soc.* 29, S721 (1996).
- 16 Akimoto, J., Gotoh, Y. Oosowa, *Acta Crystallographica Sec. C.*, 50, 160 (1994).
- 17 R B"otcher1, E Erdem1, H T Langhammer2, T M"uller3 and H-P Abicht *J. Phys.: Condens. Matter* 17, 2763– 2774 (2005).
- 18 A. Re'cnik, D. Kolar, *J. Am. Ceram. Soc.* 79, 1015 (1996).
- 19 Lee, Shu-Wei; Lei, Chien-Ming *Ferroelectrics*, Volume 382, Number 1, pp. 36-41(6) (2009).



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- 20 J. Tangsitrakul ; Muangjai Unruan; Piyachon Ketsuwan ; Ferroelectrics, Volume 383, Issue 1, pages 166-173 (2009).
21 A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T.,Vogt, and S. M. Shapiro, Solid State Commun. 15, 17 (2000).
22 C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramirez, Science 293, 673 (2001).
23 D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, Appl. Phys. Lett. 80, 2153 (2002).
24 C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, M. A. Subramanian, and A. P. Ramirez, Phys. Rev. B67, 092106 (2003).