



Synthesis and Investigation of the Structural Properties of the $\text{BaTi}_{0.92}\text{Ga}_{0.08}\text{O}_{3-\delta}$ Perovskite by X-ray Diffraction

Shahzad H.^{1*}, M. Abdul Jalil^{2*}, Shafinaz A. Lopa², S. M. H. Rahman³, S. Eriksson³, S. Norberg³, S. M. Yunus¹, I. Kamal¹, A. K. M. Zakaria¹, T. K. Datta¹, A. K. Das¹

ABSTRACT

The polycrystalline samples of $\text{BaTi}_{0.92}\text{Ga}_{0.08}\text{O}_{3-\delta}$ perovskite was prepared in the conventional solid state ceramic method in O_2 gas environment at 1400°C for 6 hrs with heating/cooling rate of $5^\circ\text{C}/\text{min}$. The X-ray diffraction patterns showed sharp Bragg peaks indicating the formation of single phased cubic structure and the data showed that oxygen vacancies occur only in the close packed layers between the face-sharing Ti_2O_9 dimers. Exaggerated grain growth ($\leq 100\ \mu\text{m}$) occurs for ceramic processed at $\geq 1400^\circ\text{C}$ and or for sintering period ≥ 6 hours.

INTRODUCTION

As good dielectric materials and are commonplace in the electroceramics market barium titanate have long been recognized. For example, tetragonal BaTiO_3 (t- BaTiO_3) is a ferroelectric material that can exhibit exceptionally large permittivity value, ca. 10,000-20,000 making it an important dielectric material for ceramic capacitors. Other phases which are not ferroelectric, such as BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ have permittivity value of ~ 40 , low dielectric loss ($\tan \delta = 1/Q$) in the GHz range and have been used as microwave dielectric materials. In all cases, the desirable permittivity characteristics result from the high polarisability of Ti^{+IV} ions in TiO_6 octahedra within the crystal structure. With the constant demand for improved performance and miniaturisation of dielectric based devices, the search continues for new or modified materials with higher permittivities and lower dielectric losses compared to existing materials. BaTiO_3 has various polymorphs, all of them are based on the perovskite structure ABO_3 ; however due to high permittivity, ferroelectric t- BaTiO_3 based materials have received the most attention. Surprisingly, very little is known about the electrical properties and defect chemistry of the high temperature hexagonal (6H) polymorph, h- BaTiO_3 , which is stable above 1430°C in undoped BaTiO_3 [1].

The crystal structures of many barium titanates including h- BaTiO_3 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ can be described as closed packing of Ba and O atoms with partial occupancy of octahedral sites by Ti^{+IV} [2]. Stoichiometric h- BaTiO_3 crystallizes in the space group (SG) $\text{P6}_3/\text{mmc}$ [3] and can

¹Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission
G.P.O. Box: 3787, Dhaka-1000

²Department of Electrical & Computer Engineering, Presidency University, Bangladesh.

³Department of Chemical & Biological Engineering, Environmental Inorganic Chemistry, Chalmers University of Technology, Gothenburg, Sweden.

*Corresponding author: Email: shahzad_baec@yahoo.com (Shahzad H.);
jalil_a@presidency.edu.bd (M. Abdul Jalil)

be described as close packed BaO₃ layers, with a [cch]₂ sequence where c and h refer to cubic and hexagonal stacking, respectively.

The hexagonal polymorph of BaTiO₃ has been stabilized at room temperature by partial reduction of Ti^{+IV} to Ti^{+III} in t-BaTiO₃ [4] and by partial substitution of Ti by various d-block cations, for example Mn, Co, Ru, Rh, Ir and Pt [5]. In both cases, it is commonly accepted that oxygen non-stoichiometry plays a central role in stabilizing the hexagonal polymorph.

In an attempt to prepare electrically insulating, h-BaTiO₃ based materials with high permittivities we have investigated Ti-site doping with p-block element such as Mg, Al, Ga and In. Here we report on the synthesis and characterization of the Ga-series where single phase, cubic BaTiO₃ type materials can be obtained at room temperature.

EXPERIMENTAL

The samples of ~5 grams were prepared according to the formula BaTi_{1-x}Ga_xO_{3-δ} (x = 0.08) via a mixed oxide route using BaCO₃, TiO₂ and Ga₂O₃. Initially the chemicals were mixed together and ball milled with 99.5% ethanol in Zirconium crucible for 40×20 minutes at 400 rpm. The sample was calcined at 1000⁰ C in a muffle furnace for 24 hours in Pt crucible. The sample was then grinding with acetone, dried in 100⁰ C on a magnetic heater, grinding and then given at 1300⁰ C for calcinations again for 24 hrs in a Pt crucible and have done XRD for 15 min (cubic structure with some impurities of Ga₂O₃). Then the pellets were pressed to 5-6 tons in a 13 mm dia stainless steel die and were sintered at 1400⁰ C for 03 hrs in O₂ gas environment with heating and cooling rate of 5⁰ C/min and have done XRD and showed cubic pattern with tiny impurity of Ga₂O₃. Finally the pellets (13 mm dia with pressure 5-6 tons) were sintered at 1400⁰ C for 06 hrs in flowing O₂ gas with the same rate. Pellets densities were compared to the theoretical X-ray density using the dimensions and mass of the sintered ceramics. The phase purity of calcined and sintered pellets was established by a combination of X-ray diffraction (XRD).

RESULTS AND DISCUSSION

XRD patterns of the sample calcined at 1300⁰ C showed that single-phase materials of the cubic polymorph were obtained for x = 0.08. It should be noted that the solid solution limits are dependent on the calcinations temperature. For example, for powders calcined at 1350⁰ C the lower limit of x~0.04.

Fig. 1 shows the X-ray diffraction patterns of as-prepared BaTi_{0.92}Ga_{0.08}O_{3-δ} sample. The diffraction patterns indicate that the sample was crystalline and no impurity peaks were detected at the higher temperature one.

Fig. 2 shows the X-ray diffraction patterns of BaTi_{0.92}Ga_{0.08}O_{3-δ} sample at three different temperatures which clearly indicated that the middle one is the best

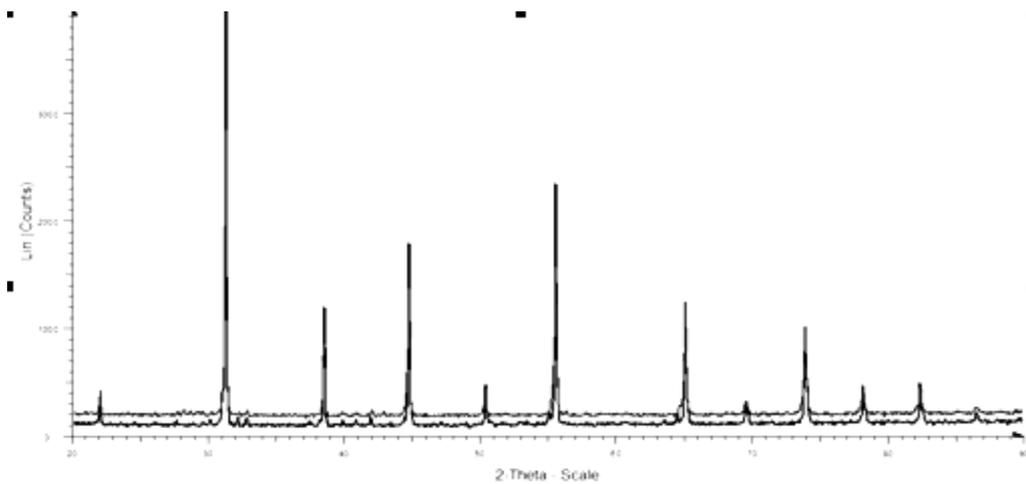


Fig.1: XRD- pattern for the sample at 1300⁰ C_24h (below) and 1400⁰ C_3h (upper).

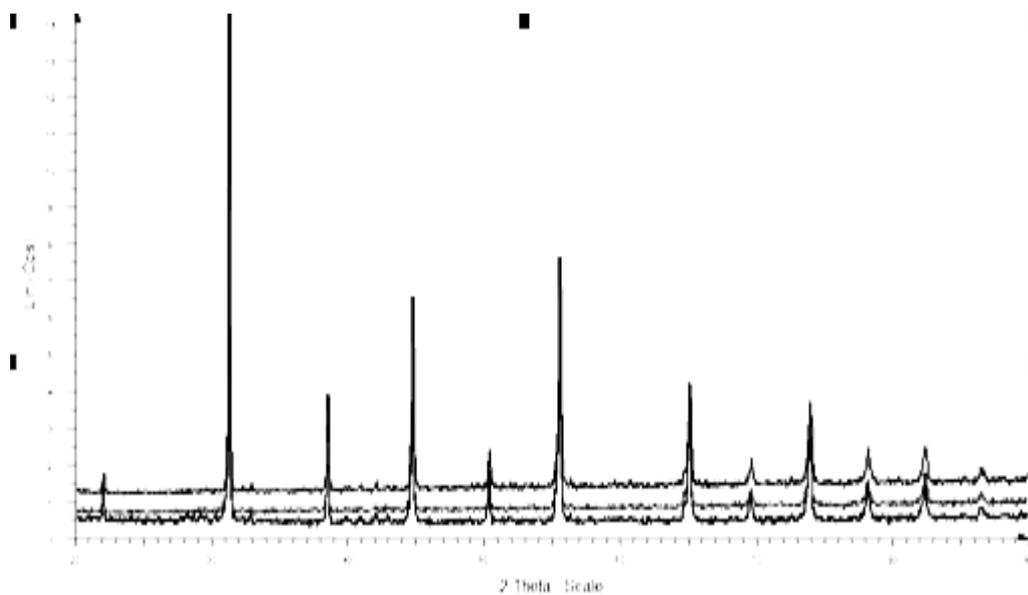


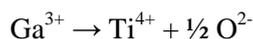
Fig.2: XRD- pattern for the sample at 1400⁰ C_3h (below), 1400⁰ C_6h (middle) and 1450⁰ C_3h (upper) .

The result for $x = 0.8$ is in good agreement with existing literature on oxygen-deficient cubic BaTiO_3 type perovskites and related materials. For example, we have shown that oxygen vacancies form exclusively in O (1) sites within the h- BaO_3 layers in oxygen deficient h- BaTiO_3 [6]. Grey et al [7] have shown the same result for h- $\text{Ba}(\text{Ti,Fe})\text{O}_{3-\delta}$ and

Jacobson [8] has demonstrated an unequal distribution of oxygen vacancies between h-BaO(1)₃ and c-BaO(2)₃ layers in 6H BaFeO_{2.79} with most vacancies located in the hexagonal layers. In general pellet density increased with sintering temperature from ~91-93% (1350⁰ C) to ~95-97% (1450⁰ C).

CONCLUSION

This research has shown that it is possible to stabilize the cubic polymorph of BaTiO₃ at room temperature by partial replacement of Ti with Ga, according to the substitution mechanism,



The oxygen vacancies created are located in the c-BaO₃ layers which results in repulsion between the cations in the face sharing. Dense ceramics (>95%) of the theoretical X-ray density) can be prepared by sintering at >1400⁰ C.

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