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Formation of Perovskite Structure and Microstructure Development of Nb Doped $BaTiO_3$ Based Ceramics

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Abstract

Barium Titanate is a ceramic material having ferroelectric, photorefractive and piezoelectric properties. It is used as dielectric materials in capacitors. In this work, formation and microstructure development of niobium (Nb) doped barium titanate ($BaTiO_3$) was investigated through the mixed oxides route via the process of calcination, starting with based on the formula $BaTi_{1-x}Nb_xO_3$; x=.004, .008, .016. XRD data confirmed the formation of provskite structures when Nb doped $BaTiO_3$ patterns were compared with standard $BaTiO_3$ pattern. Above 90% of theoretical density was achieved for samples having different doping level and different sintering temperature ranged from 1425 to 1475 °C. Consistency in the grain growth behavior was observed when microstructures were studied by scanning electron microscope SEM.

Keywords: *Barium Titanate, Perovskite Structure, Niobium Oxide, X-ray Diffraction, Scanning Electron Microscopy.*

1. Introduction

Barium Titanate is a dominating material in the field of elecroceramics. Many applications of barium titanate in electronic devices come from its diversified properties. It is used extensively as dielectric materials in capacitors especially in MLCCs (Multi Layer Ceramics Capacitor). Moreover, its applications as thermistor, transducer, actuators and ferroelectric random access memory are also remarkable. Ferroelectrocity and piezoelectricity resulted from barium titanate due to its crystal structure and composition. The type of crystal structure that is possessed by barium titanate is termed as perovskite structure formulated by ABX_3 having two cations A, B, and one anion X. Two cations Ba and Ti and O anion are the main constituents of Barium Titanate perovskite where Ti^{4+} is located at the octahedral site of the lattice surrounded by O^{2-} at the octahedral position and Ba^{2+} at the corners of the lattice forming a face-centered cubic structure Fig. 1.

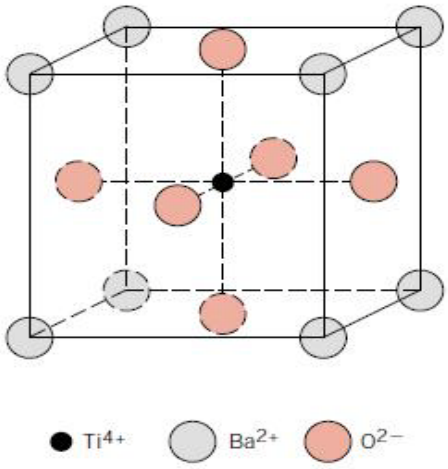


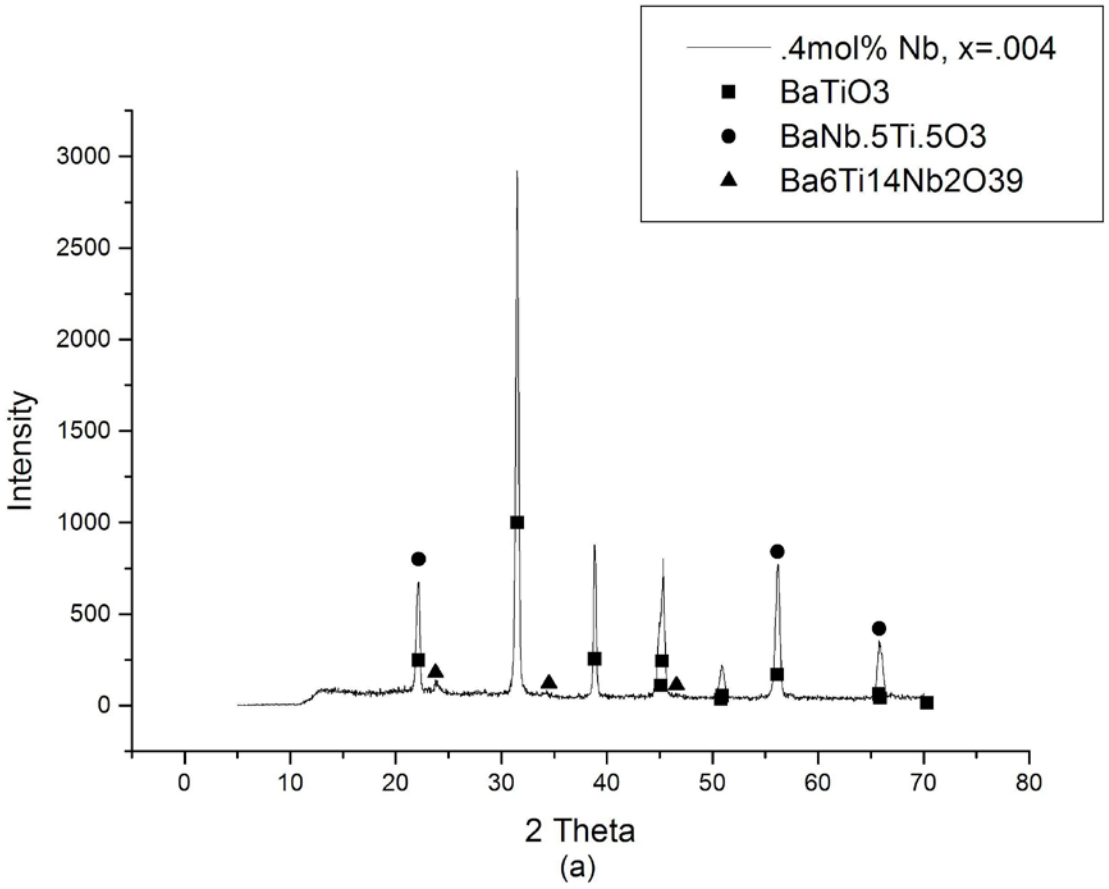
Fig. 1. Crystal structure of barium titanate [1]

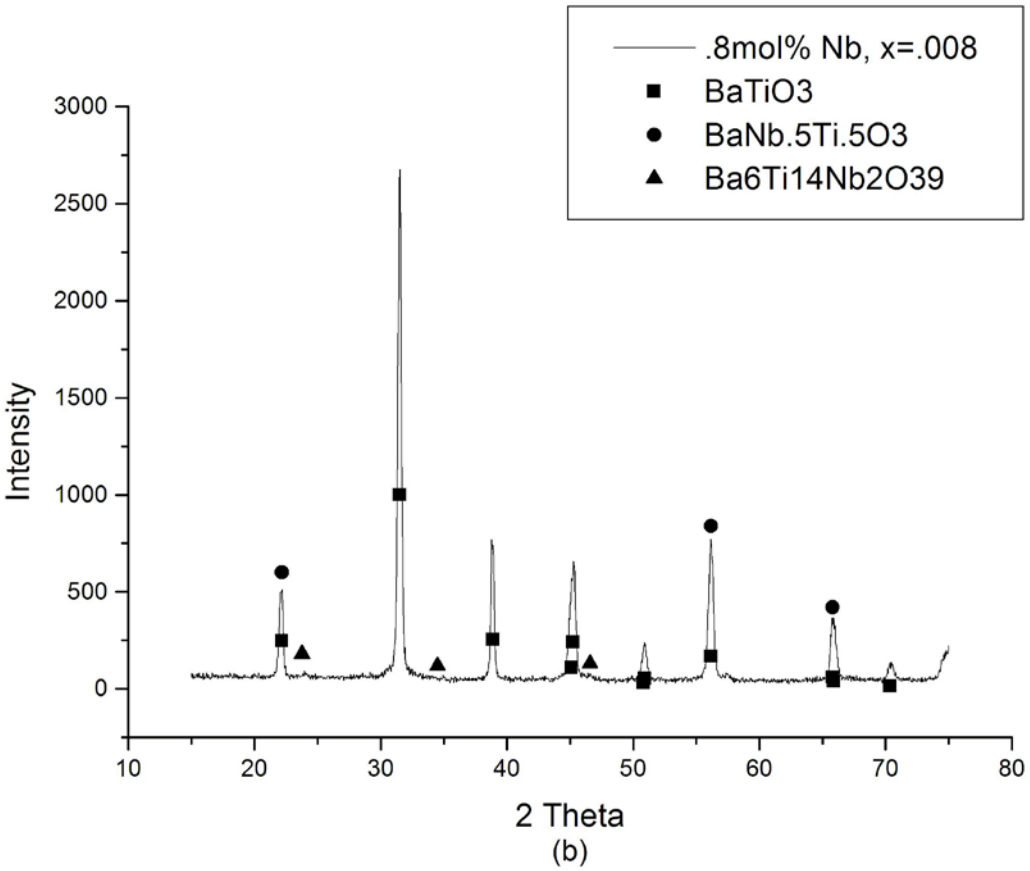
Barium Titanate is large enough compared to the Ti^{4+} ion for its shifting into six possible minimum energy positions around it when an electric field is applied resulting spontaneous polarization and high dielectric constant. Moreover, crystal structure of $BaTiO_3$ changes from cubic to tetragonal below the Curie temperature 120 °C resulting an off-centered position of Ti ion leading to a formation of permanent dipole [2].
Barium titanate is an insulating material and substantial change in properties can be achieved if it is doped with donor dopants such as Nb^{5+}, Ta^{5+} replacing the octahedral Ti ion. However, diffusion of Nb is very sluggish even at high temperature into the octahedral site. That is why an attempt has been made to introduce Nb into the octahedral site by the process of calcination starting with $BaCO_3$, TiO_2 and Nb_2O_5, and simultaneously producing perovskite structure of Nb doped $BaTiO_3$. In addition to that, microstructure development with variable sintering temperature has also been observed.

2. Experimental

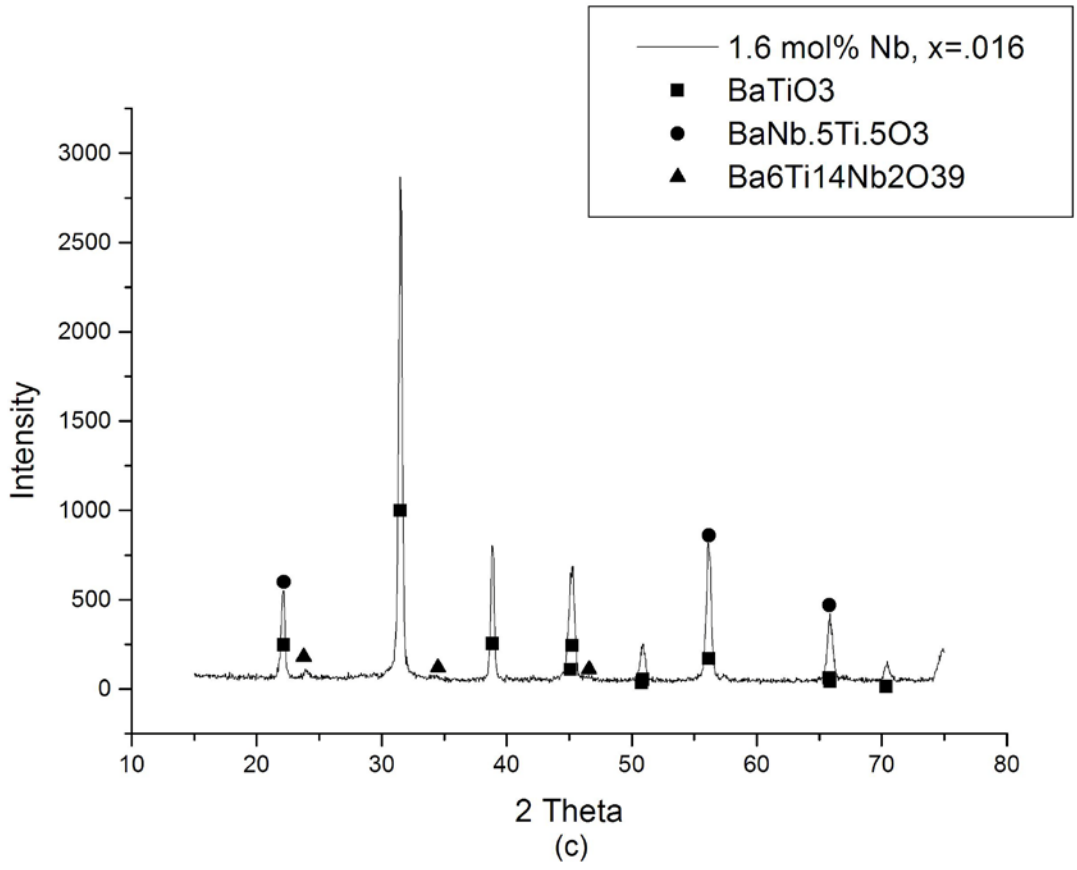
Nb doped $BaTiO_3$ was prepared on the basis of the formula $BaTi_{1-x}Nb_xO_3$, where x=0.004, 0.008 and 0.016 were taken. Nano-sized $BaCO_3$, TiO_2 and Nb_2O_5 were weighed in electronic balance and then were ball milled with yttria stabilized zirconia ball with a milling media of acetone for 18 hours. Milled powders were then dried and calcined at a temperature of 1300 °C for 2 hours in order to form the $BaTi_{1-x}Nb_xO_3$ perovskite. After calcination powders were milled again for 6 hours. Afterwards, mixture was dried and PVA binder was added followed by pressing into pellets. Green pellets were dried prior to sintering and then sintered from 1425 to 1475 °C for 2 hours with an intermediate heating stage at 500 °C in order to remove the binder. Perovkite structure formation was ensured with X-ray diffraction (XRD) patterns analyzed by Bruker D8 Advance diffractometer with $Cu_{k\alpha}$ λ=1.5406 Å radiation. Microstructures of the samples were observed with a Philips Scanning Electron Microscope (SEM). Density was measured with precision electronic balance and slide calipers and was compared with theoretical density in order to obtain the percent theoretical density.

3. Results and Discussion




.8mol% Nb, x=.008
BaTiO3
BaNb.5Ti.5O3
Ba6Ti14Nb2O39
Intensity
2 Theta
0
500
1000
1500
2000
2500
3000
10
20
30
40
50
60
70
80

(b)


1.6 mol% Nb, x=.016
BaTiO3
BaNb.5Ti.5O3
Ba6Ti14Nb2O39
Intensity
2 Theta
0
500
1000
1500
2000
2500
3000
10
20
30
40
50
60
70
80

(c)

Fig. 2. XRD patterns compared with standards (a) .4mol% (b) .8mol% and (c) 1.6 mol% Nb

Initially it was confirmed with the XRF data shown in Table 1, whether calculated and experimental achievement was consistent or not. The formation of Nb doped $BaTiO_3$ or $BaTi_{1-x}Nb_xO_3$ perovskite in the case of different doping level x=.004, .008 and .016 was ensured with XRD data as shown in Fig. 2. Formation of perovskite structure was ensured as the position of the standard $BaTiO_3$ having perovskite structure indicated by solid square marks in figure 2 nearly superimposed on the peaks generated from the samples. The existence of double square on the peak corresponding to the 2θ value of 45^o resulted due to the presence of twin peak in standard perovskite $BaTiO_3$ (Fig. 2). In addition, pattern positions indicated by solid circle correspond to the pattern of $BaNb_{.5}Ti_{.5}O_3$ [3] from which it can be realized that substitution of Ti ion by Nb ion has been occurred in the octahedral sites. Formation of new phase has also been identified, indicated by solid triangle in figure 2 in the form of $Ba_6Ti_{14}Nb_2O_{39}$ [4]. Since Nb content is very low, the peak height of secondary phase is too low to observe.

Table 1. XRF data of sample of .4mol% Nb sintered at 1475°C

Calculated Weight Percent Initially Added	Weight Percent After Sintering by XRF
$BaCO_3$ 55.276	BaO 61.9858
TiO_2 28.679	TiO_2 36.874
Nb_2O_5 .19166	NbO 0.2576

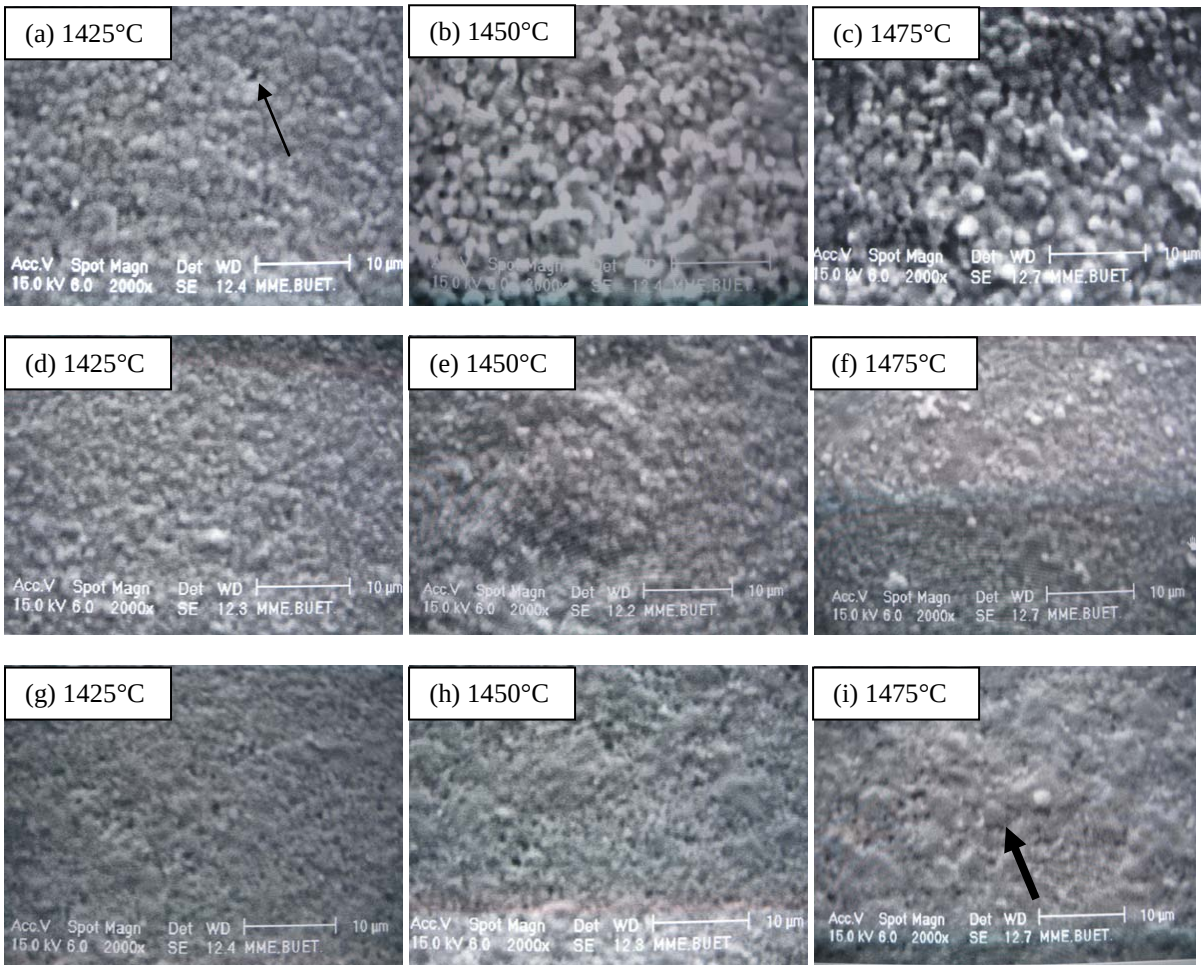


Fig. 3. SEM micrograph of $BaTi_{1-x}Nb_xO_3$ samples with different sintering temperature and doping level (a, b, c) .4mol% Nb, (d, e, f) .8mol% Nb and (g, h, i) 1.6 mol% Nb

Table 2. Density data of Nb doped $BaTiO_3$

Nb mol%	Sintering Temperature °C	Density gm/cc	% Theoretical Density Achieved
.4	1475	5.83±0.06	96.63±1.01
.8	1475	5.95±0.01	98.49±0.17
1.6	1475	5.83±0.11	96.19±1.87
.4	1450	5.91±0.12	97.97±1.78
.8	1450	5.67±0.06	93.94±0.98
1.6	1450	5.73±0.06	94.57±0.99
.4	1425	5.95±0.06	98.72±1.03
.8	1425	5.99±0.02	99.15±0.25
1.6	1425	5.51±0.04	90.91±0.66

In Table 2 the density data of the samples is shown. For all the samples percent theoretical density that has been achieved is more than 90%. High density material is with finer grain size is always required for achieving better dielectric properties.

In Fig. 3 micrographs of the samples are shown, where Fig. 3-a,b and c corresponds to the samples containing .4mol% Nb; d,e and f corresponds to the samples containing .8mol% Nb and g, h and i representing 1.6 mol% Nb. Sintering temperatures of the samples are indicated on micrographs.
From Fig. 3, existence of porosity has been observed in the microstructure indicated by arrow for sample (a) sintered at 1425°C doped with 0.4mol% Nb. Minimum porosity was found for figs. 3(d-f) compared with other microstructures. Distinct and developed grain formation with few porosities was observed for samples doped with 0.4 mol% Nb, Figs. 3(a-c). An increase in holding time may be required to remove the remaining porosities.
In figs. 3 (d–f), finer grains with low porosity are evident. In figs. 3 (g–i), structure with some coarse grains (indicated by arrow in Fig. 3-i) and porosities can be found which is thought to be not the optimum microstructure required for better dielectric properties. It is therefore essential that more energy is required to remove the pores in terms of holding time or sintering temperature. In this scenario, the issue of fine grain microstructure may need to be compromised. Second stage sintering can be a solution in this situation so that shorter holding at higher temperature and longer holding at lower temperature can restrict the grain growth with minimum porosity.
There are six transport mechanisms that may occur during sintering: surface diffusion, volume diffusion, evaporation-condensation, grain boundary diffusion, volume diffusion and plastic flow [5]. Transport of material is required into the pores in order to reduce the same. It is the dominating mechanism or combination of mechanisms corresponding to the sintering parameter and doping agent that decide the amount and size of pore. On the other hand, driving force for densification that acts during sintering is the reduction of excess surface free energy of the particles and it may be reduced by reducing the total surface area with increasing average size of the particle thus grain coarsening [6]. The dominant phenomena between these matter transport and grain coarsening decides the final microstructure of ceramics.

As the sintering temperature range is narrow, only 50 °C starting from 1425 to 1475 °C, the effect of sintering temperature on grain size is not so significant for 0.4 and 0.8 mol% Nb concentration, but for 1.6 mol% Nb, increasing number of coarse grains have been observed with increasing sintering temperatures which has been indicated by arrow in Fig. 3-i. Higher temperature and higher Nb content may be responsible for the grain growth of the samples. Grain growth due to higher Nb content has also been reported earlier [3].

4. Conclusion

Successful formation of Nb doped $BaTi_{1-x}Nb_xO_3$ perovskite was observed for doping levels of 0.4, 0.8 and 1.6 mol% Nb after calcianing at 1300 °C with the presence of secondary phases. Over 90% of the theoritical density was achieved for these compositions. In addition, fine-grain microstructure was obtained with less porosity for samples containing 0.8 mol% Nb and with some porosity for 0.4 mol% Nb. Coarse grains along with some fine grains were observed for samples containing 1.6mol%. Nb.

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