

Dielectric Properties of Barium Zirconate Titanate Ceramics Prepared using Hydrothermal Method



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Received: 16 Aug. 2014, Revised: 26 Sep. 2014, Accepted: 16 October 2014

Published online: 30 November 2014

Abstract

Barium titanate (BT) with different content of Zr (0.001 and 0.008) is prepared using hydrothermal method at 150°C for 2h. It is found that with increased of Zr content, the lattice constant a increases while the lattice constant c decreases. It is observed also that the curie temperature peak shift to lower temperature and be broadened. The lattice constants have the same value at Zr content equal to 0.027. For BT samples sintered at 1000°C, the dielectric constant below Curie temperature is about 2000 and becomes 6000 at Curie temperature. With the increased of sintered temperature (1200°C), the dielectric constant is about 4000 and becomes 9600 at Curie temperature (T_c). At Curie temperature the dispersion in BZT1 ($x=0.001$) is distinct than that of pure BT. At near T1 (temperature at phase transition from tetragonal to orthorhombic) the little broadening is observed of BZT1 in comparing with BT. The dispersion of BZT2 ($x=0.008$) is more distinct than that of BZT1 ($x=0.001$) and BT. After adding gradual increasing of Zr, both T1 (tetragonal to orthorhombic phase transition) and T_c are shifting to each other.

Keywords: Hydrothermal method, Dielectric constant, BT & BZT

Introduction

Due to high dielectric constant and low dielectric loss, tetragonal BaTiO₃ is one of the attractive candidate ferroelectric material for manufacturing thermistors, ceramic capacitor and especially multi-layer ceramic capacitors (MLCCs) [1].

The solid state reaction for preparing of BT involves repeated milling and calcinations (>1200°C) of BaCO₃ and TiO₂ powders. According to this method, the formation of secondary phases are formed, such as Ba₂TiO₄, BaTi₂O₅ and BaTi₄O₉, which often lead to a compositional inhomogeneity[2]. Recently, wet chemical technologies such as the sol-gel method [1], oxalate method [3, 4] and hydrothermal method [5-8] have replaced the

classical solid state reaction for the synthesis of BT.

The most research workers who prepared BT hydrothermally have done on structural properties only [9-14]. Very little work is concerned with the dielectric properties of this material using hydrothermal method [15, 16]. The dielectric constant in the latter was low compared with the solid state reaction. It can be thought that the reason is the existence of defects ingrained inside the BT lattice during the hydrothermal process. These defects need to higher annealing temperature to release them[15].

The BT ceramic shows normal ferroelectric behavior and dielectric anomalies corresponding to cubic to tetragonal (T_c), tetragonal to orthorhombic (T1) and

orthorhombic to rhombohedral (T2) phase transition [17]. One of the desired properties in BT is that the variation of dielectric constant as a function of temperature should not be sharp near Curie temperature (T_c). To get rid of this problem, many researchers [18-20] suggest the adding of zirconium (Zr) to the structure of BT which leads to broadening of the curve near that region.

Substitution of Ti^{4+} (atomic weight of 49.9, ionic radius of 0.068 nm) with Zr^{4+} (atomic weight of 91.2, ionic radius of 0.087 nm) exhibits several interesting features in the dielectric behavior for BT ceramic[2]. This lead free relaxor material (BZT) presents a great interest both for applications in the field of environmental protection and for fundamental studies[21]. In solid state method, the adding of a small amount of Zr can barely create the desired broadening. The BT exhibits the highest dielectric constant at Curie temperature. Below T_c , the lattice of BT has non-central symmetry. This gives rise to a spontaneous polarization. When the active Ti^{4+} ions are partially replaced by the non-active Zr^{4+} , some of unit cells exhibited centrosymmetry. This leads to the polarization becomes irregular and T_c is lowered[22].

However in the present work, using hydrothermal method, the effect of adding of small amount of Zr on electrical properties has been studied.

Experimental

Appropriate amounts of $Ba(OH)_2 \cdot 8H_2O$ (98%), $TiCl_4$ (99%) and $ZrOCl_2$ were weighted and used as precursor. A 6.3 g of $Ba(OH)_2 \cdot 8H_2O$ was weighted and dissolved into 50 ml distilled water. The $Ba(OH)_2$ solution was heated at $80^\circ C$ until $Ba(OH)_2$ resolved completely. The dilution procedure consists of adding the concentration $TiCl_4$

slowly to the distilled water, which is kept close to freezing temperature ($\sim 5^\circ C$) by water bath, under the constant stirring conditions same as ref. [2]. The result is $TiOCl_2$ which mixed with $ZrOCl_2$ solution. Reactive gels were precipitated by the dropping of aqueous ammonia solution to $TiOCl_2$ and $ZrOCl_2$ solution. The gels were washed from free of chloride ions and mixed with 0.6M $Ba(OH)_2$ solution with vigorous stirrer. The molar ratio of $Ba/(Ti+Zr)$ and pH are kept at 1.6 and 13 respectively.

The hydrothermal reaction was carried out in Teflon-lined stainless steel autoclave and the degree of fill was 80 %. The sealed vessel was heated to $150^\circ C$ for 2h. After cooling down to room temperature, the resultant precipitated was washed with distilled water for several times and finally dried at $60^\circ C$ for 24h. After drying and grinding, the powder then pressed into pellets with the dimension of 10 mm in diameter and 1.5 mm in thickness, and then all samples were sintered at $1200^\circ C$ for 2 h. Silver slurry was pasted on the two main sides of as fired compact for further electrical measurements.

Crystal structure of the produced particles was analyzed at room temperature using XRD (D/Max-RB Model). The dielectric constant and loss of the samples were measured at different temperatures and different frequencies using a HP 4192A LF Impedance Analyzer.

Result and Discussion

Fig. 1 XRD pattern of $BaTiO_3$ with different content of Zr (0, 0.001 and 0.008) prepared hydrothermal method treated at $150^\circ C$ for 2 h Fig. 1 shows the XRD pattern of BT, BZT1 and BZT2 using hydrothermal method at $150^\circ C$ for 2h. The XRD pattern is fitted well with the peak positions of standard cubic BT, BZT1 and

BZT2 with lattice constant 4.0189, 4.021 and 4.0225Å^o respectively. The *d* spacing according to Bragg's law of diffraction is given by:

$$d = n\lambda/\sin\theta \dots\dots\dots(1)$$

where *n* is a numerical integer, λ is the wavelength and θ is the Bragg angle. The expression for the ratio of *d* spacing of the *c* axis to that of the *a* axis is given by[23]:

$$c/a = d_{(002)} / d_{(200)} = \sin\theta_{(200)} / \sin\theta_{(002)} \dots\dots(2)$$

Bragg's law can be used to obtain the lattice constant for cubic phase through the following relation:

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}} \dots\dots\dots(3)$$

It indicates that the addition of Zr is forming a stable solid solution with BT lattice. Because of larger radius of Zr than that of Ti, the increasing of lattice constant with increase of Zr content is shown. To discuss the expanding of lattice constants for BT and BZT, it is important to study the reasons of suppression of tetragonal phase.

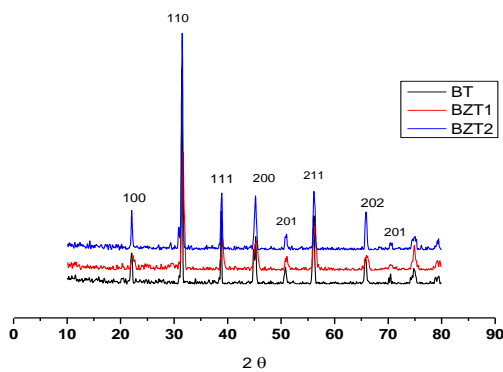


Fig. 1 XRD pattern of BaTiO₃ with different content of Zr (0, 0.001 and 0.008) prepared hydrothermal method treated at 150°C for 2 h.

Fig. 2 shows the behavior of two lattice constants as a function of Zr content. The lattice constants were calculated from XRD results. BT has maximum value of lattice constant (*c*=4.015Å^o) and minimum value of (*a*

=3.988Å^o). After adding Zr atoms in BT, the lattice constant *a* increases while lattice constant *c* decreases. We have experimentally observed, that the two lattice constants have the same value at 0.027 using extrapolation method.

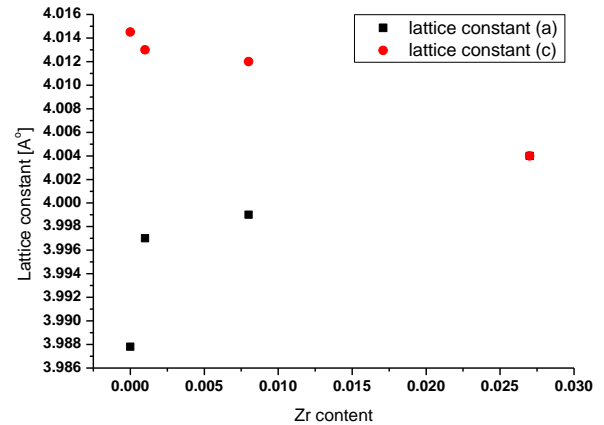


Fig. 2 Lattice constants of BT and BZT (*a* and *c*) with different Zr content.

Fig. 3 Dielectric constant as a function of temperature for BT prepared using hydrothermal method at 10 kHz. At 17°C, the BT changes from orthorhombic to tetragonal phase and at 127°C it changes from tetragonal to cubic phase for samples calcined at 1000 (BT1) and 1200°C (BT2). There is a different value between *T*₁ (17°C) and *T*_c (127°C) at present work with previous work which can be ascribed to varying prepared method[24]. The hydrothermal method results a nano BT, while solid state reaction results a micro BT[2]. There is no effect of calcined temperature on transition and Curie temperature for BT prepared using hydrothermal method. The dielectric constant is higher for sample calcined at 1200°C than those calcined at 1000°C. From zero to 120 degree the dielectric constant is about 2000 and 4000 while at Curie

temperature (127°C) it becomes about 6000 and 9600 for BT1 and BT2 respectively.

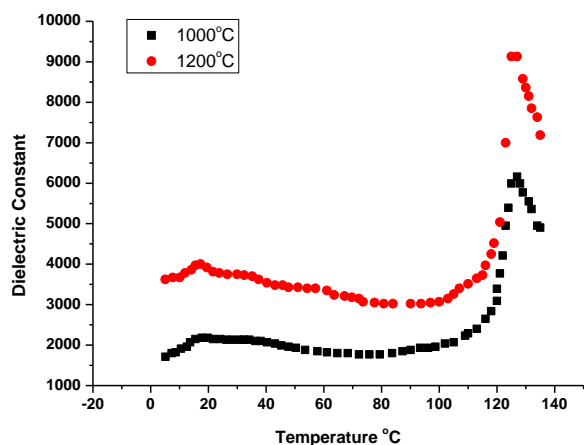


Fig. 3 Temperature dependence of the dielectric constant of BT with different sintered temperature at 10 kHz.

Fig. 4 shows the variation of the dielectric constant as a function of temperature for BT sintered to 1200°C at 1, 10, and 100 kHz. There are two important regions lay in near T_1 (~18°C) and T_c (~127°C), where the dispersion (the curves are separated with different frequencies) is clear. However, beyond the Curie temperature the dielectric constant tend to merge. It can be seen also, the dielectric constant decreases with increases frequency especially at phase transition. At T_1 , the dielectric constant is 4650, 3950, and 3800 for BT ceramics while, at T_c the dielectric constant becomes 9400, 9550, and 10500 for 1, 10, and 100 kHz respectively.

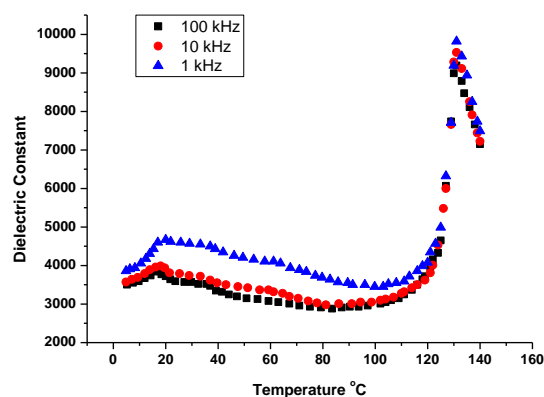


Fig. 4 Temperature dependence of the dielectric constant of BT with diefferent frequencies.

Fig. 5 shows the variation of the dielectric constant as a function of temperature for BZT1 at 1, 10, and 100 kHz. A shifting of T_1 toward high temperature was observed, while the shifting of T_c toward low temperatures. All curves are distinct and no merge within the curves. The dispersion in this case at Curie temperature is wider than pure BT. Although, the broadening near T_c is very little in comparing with BT, the broadening is at the expense of the values of dielectric constant.

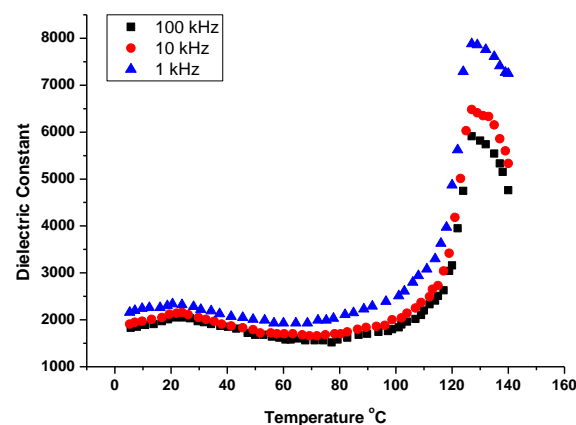


Fig. 5 Temperature dependence of the dielectric constant of $BaTi_{0.999}Zr_{0.001}O_3$ with diefferent frequencies.

Fig. 6 demonstrates the behavior of dielectric constant as a function of temperature for BZT2 in various frequencies (1, 10, and 100 kHz). It is clear that the dispersion is more distinct than that of BZT1. As Zr content increases, the shift of the curie peak to lower temperature was observed and be broadened. The T₁ were about 18, 24, and 50°C while and T_c were about 127, 125, and 120 for BT, BZT1, and BZT2 respectively. We observe that both T₁ and T_c are shifting to each other and after adding gradual increasing of Zr, the two peaks at T₁ and T_c maybe to become one peak.

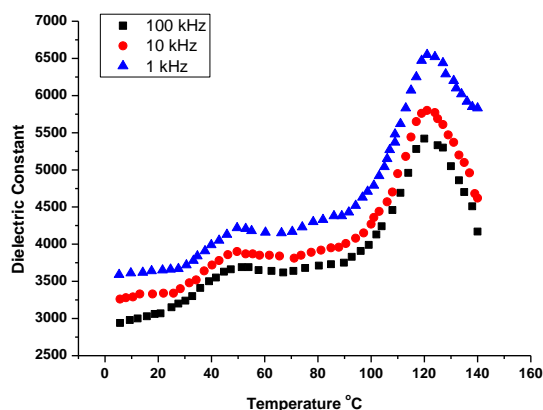


Fig. 6 Temperature dependence of the dielectric constant of $BaTa_{0.992}Zr_{0.008}O_3$ with diefferent frequencies.

Fig. 7 shows the dielectric loss as a function of temperature for BT, BZT1, and BZT2 at 10 kHz. The dielectric loss changes with the increase in Zr content. The dielectric loss increases clearly near transition temperatures (T₁, T_c) only, other regions decrease for BT and BZT1. As Zr content increases, the dielectric loss has increased so that BZT2 has more dielectric loss than others (BT, BZT1). It is also showed that the dielectric loss of BZT2 decreases with

increasing temperature for all ranged, while in BT and BZT1 it increases near the T_c.

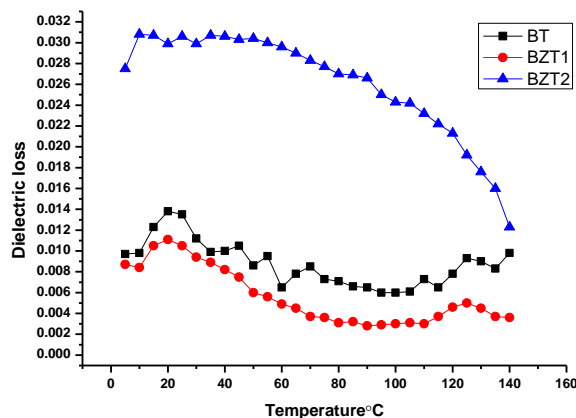


Fig. 7 Dielectric losses with diefferent Zr content at 10 kHz.

Conclusion

The influence of adding Zr on structure of BaTiO₃ and dielectric properties was investigated using hydrothermal method. A perovskite phase was found by X-Ray diffraction and the increased of Zr content caused a decreased in tetragonality and shifted of Curie peak to lower temperature. The dielectric constant decreases with increases frequency especially at phase transition for all samples. The broadening near T_c is very little of BZT1 and increasing with increased Zr content in comparing with BT, the broadening is at the expense of the values of dielectric constant. The dispersion at Curie temperature of BZT1 and BZT2 is wider than pure BT but the broadening is at the expense of the values of dielectric constant and dielectric loss.

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