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The effect of manganese doping on the grain size and transition temperature of barium titanate ceramics

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The structural and electrical properties of pure and manganese doped barium titanate ($BaTiO_3$) with a general formula $BaMn_xTi_{1-x}O_3$ (where x=0.00, 0.01, 0.02, 0.03, and 0.04) were investigated. For the observation of the surface morphology and estimation of grain sizes scanning electron microscopy (SEM) was employed. The grain size of $BaTiO_3$ increased with an increase of the Mn doping. The Curie temperature (T_c) which indicates the tetragonal-to-cubic transition, of each sample was found from the resistivity versus temperature curve, and T_c of $BaTiO_3$ increased linearly with an increase of the Mn doping. The T_c of un-doped $BaTiO_3$ was lower than that of the doped samples. The T_c value of pure $BaTiO_3$ was found to be 120 °C. It was found that the dielectric constant versus temperature curve also shows a similar type of T_c. The dielectric constant of $BaMn_xTi_{1-x}O_3$ was found to decrease with an increase of Mn doping and the T_c of $BaTiO_3$ increases with the addition of Mn.

Key words: Surface morphology, Grain size, Transition temperature, DC resistivity, Dielectric constant.

Introduction

Ferroelectricity is a phenomenon discovered in 1921 and a high dielectric constant was first discovered in the United States in 1942 [1-4]. In 1946 it was discovered that barium titanate ($BaTiO_3$) had a dielectric constant 100 times larger than that of other insulators [5]. It allows the manufacture of capacitors, which are smaller in size but have a larger capacity than other materials, thus improving electronic circuits and developing a new use for ceramic materials. The $BaTiO_3$ perovskite family includes many titanates used in various electroceramic applications, for examples, in electronics, in electro-optical devices, and in the electromechanical applications of ceramics. $BaTiO_3$ based compounds are commonly and frequently used in the electrical and electronic industries for their unique dielectric, ferroelectric and piezoelectric properties. In addition, because of its simple crystal structure, $BaTiO_3$ can easily form solid solutions with other oxides. For this reason $BaTiO_3$ is most widely used in various fields of electrical applications and widely utilized to manufacture electronic components such as multilayer capacitors (MLCs), positive temperature coefficient (PTC) thermistors, piezoelectric transducers, and a variety of electro-optic devices [6]. The high dielectric constant of $BaTiO_3$ makes it an especially desirable material as its electrical properties can be controlled within a wide range by means of mixed crystal formation and doping. Because of the demand people, research on the dielectric (essentially non-conducting) characteristics of ceramic materials is increasing rapidly. At the same time people are attempting to reduce the size of all communication devices to be as small and as light as possible. Due to this trend, high dielectric constant materials such as barium titanate have become more and more important ceramics materials. $BaTiO_3$ powder is usually mixed with various types of additives in order to obtain a better performances and a good control over the grain size and electrical characteristics of the ceramic. It has been found that the dielectric properties of polycrystalline $BaTiO_3$ depend to a great extent on the grain growth during sintering and on the additive type and concentration [7, 8]. Additives which change the microstructure can also modify the dielectric properties of $BaTiO_3$ ceramics. Studies on the effect of a MnO_2 addition to $BaTiO_3$ found that a Mn addition shifted the Curie point and depressed the dielectric peak. Mn^{4+} can substitute for Ti^{4+} ions as an isovalent dopant. Addition of manganese particles into barium titanate can also form a core-shell structure. The desired temperature-stability in dielectric properties is achieved by the formation of core-shell grains [9]. In this study, the effects of MnO_2 doping on the microstructural development, electrical and dielectric properties of $BaTiO_3$ ceramics have been investigated.

Experimental Procedure

Barium carbonate ($BaCO_3$), titanium Dioxide (TiO_2) and manganese dioxide (MnO_2) were used for the

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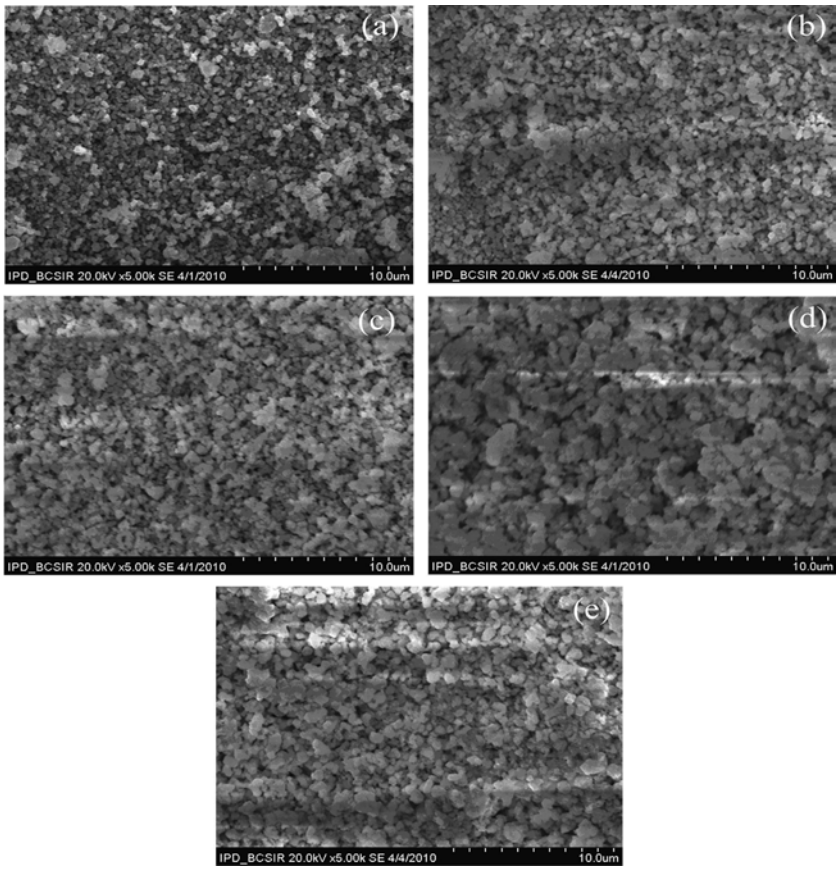

Fig. 1. SEM images of $Ba(Mn_xTi_{1-x})O_3$ samples sintered at 1200 ^oC (a) x=0.0, (b) x=0.01, (c) x=0.02, (d) x=0.03, and (e) x=0.04.

preparation of [$Ba(Mn_xTi_{1-x})O_3$] samples (where x=0.00, 0.01, 0.02, 0.03 and 0.04) and the raw oxides were collected from the local market. The samples were prepared by a solid state reaction method where $BaCO_3$ and TiO_2 were used as the parent materials and MnO_2 was used as an additive. An appropriate amount of the starting materials was thoroughly mixed, dried and ball milled in a polyethylene jar for 12 hours in a wet medium and then calcined at 900 ^oC for one hour. The calcined powders were re-milled for 12 hours and pellets were formed by manually pressurizing the mixture. The pellets were then sintered at 1200 ^oC for four hours. A Hitachi S-3400N scanning electron microscope (SEM) was employed for the observation of the surface morphology and an estimation of grain sizes with increasing MnO_2 content. These pellets were used for the measurement of the temperature-dependent resistivity and dielectric constant. For the electrical measurements both sides of the samples were coated with highly-conducting silver paste (Demetron, Leipzigerstr. 10, Germany) after polishing. A two-probe method was used for the measurement of the resistance and capacitance of the samples.

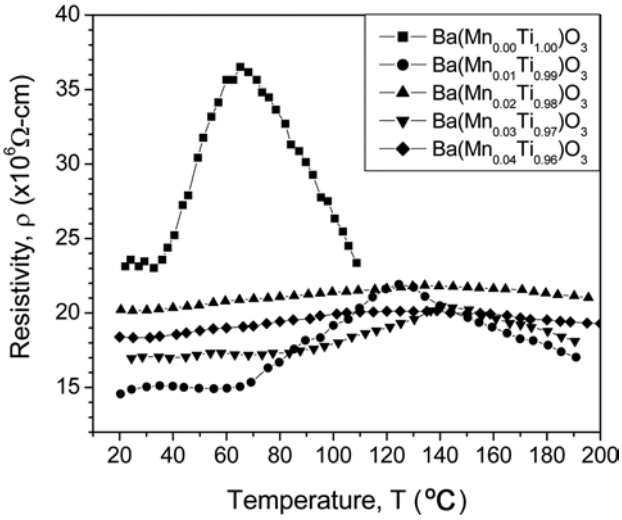

Fig. 2. Plot of resistivity versus temperature for the samples.

Results and Discussion

Surface morphology

The effects of MnO_2 additions to $BaTiO_3$ are compared in the SEM micrographs shown in Fig. 1. The microstructure of $BaTiO_3$ ceramics doped with MnO_2 at different concentrations exhibits homogeneous grain distributions. A dense microstructure with smaller grains (average grain size~340.4 nm) was observed for pure $BaTiO_3$. The grain size increased linearly with an increase of MnO_2 doping in $BaTiO_3$.

Table 1. Effect of Mn doping on different parameter of $BaTiO_3$.

Sample composition	Average Grain size, D (nm)	Resistivity at room temperature (Ω-cm)	Transitiontemperature, T_c (°C)	Resistivity at T_c (Ω-cm)
$Ba(Mn_{0.00}Ti_{1.00})O_3$	340.40	16.8×10^6	120	36.6×10^6
$Ba(Mn_{0.01}Ti_{0.99})O_3$	415.37	14.5×10^6	130	21.9×10^6
$Ba(Mn_{0.02}Ti_{0.98})O_3$	456.87	20.210^6	135	21.9×10^6
$Ba(Mn_{0.03}Ti_{0.97})O_3$	526.00	16.3×10^6	145	20.4×10^6
$Ba(Mn_{0.04}Ti_{0.96})O_3$	552.00	20.2×10^6	140	20.2×10^6

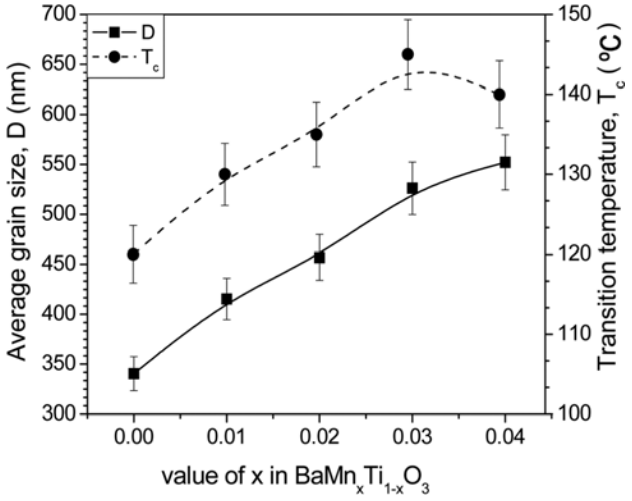

Fig. 3. Change of transition temperature (T_c) and grain size (D) due to Mn doping in $BaMn_xTi_{1-x}O_3$.

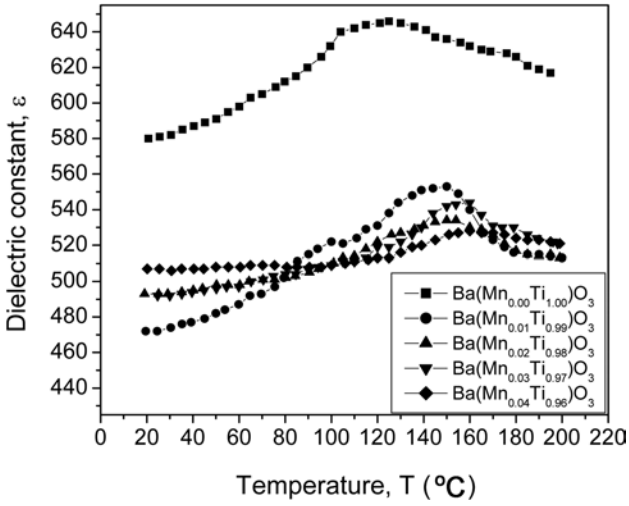

Fig. 4. Dielectric Constant as a function temperature of $Ba(Mn_xTi_{1-x})O_3$ samples.

Temperature dependence of electrical resistivity

The effect of appropriate MnO_2 on the electrical behavior of doped $BaTiO_3$ can be analyzed through resistivity versus temperature curves as shown in Fig. 2. The direct current (DC) resistivity of $BaTiO_3$ was measured as a function of temperature and showed that the resistivity increased with temperature up to 120 °C and then decreased. This indicates a transition from tetragonal to cubic in the $BaTiO_3$ structure [10, 11]. The resistivity of $BaTiO_3$ at this transition temperature was found to be about 36.6×10^6 Ω-cm. The resistivities of the samples of MnO_2 doped $BaMn_xTi_{1-x}O_3$ show the same characteristics but the value of resistivity decreases with an increase of the doping concentration which is represented in Table 1. The transition temperature increases linearly with an increase in Mn doping in $BaMn_xTi_{1-x}O_3$ as shown in Fig. 3.

In Fig. 2 the resistivity showed an increase up to the transition temperature (tetragonal to cubic transition), passed through a maximum value and began to decrease. The resistivity showed a maximum value of about 36.6×10^6 Ω-cm when the sample was pure and the grain size was around 340.4 nm. With Mn doping in the first step the resistivity decreases significantly but with further doping, the resistivity decreases slowly. As the resistivity of $BaTiO_3$ strongly depends on the grain size, so with an increase of the grain size of the samples the resistivity decreases and the T_c increases with an increase of the grain size as shown in Fig. 3. It is observed that $BaTiO_3$ has the lowest transition temperature, while when Mn is added to $BaMn_xTi_{1-x}O_3$, the T_c increased and the highest transition was found to be 145 °C for x=0.03. In contrast, with an increase of the value of x in $BaMn_xTi_{1-x}O_3$ at x=0.04 the T_c decreased to 140 °C as listed in Table 1. The shift of the transition temperature for x=0.04 may be due to some structural disorder.

Temperature dependence of dielectric constant

The observed microstructural features together with the type of additive have a direct influence on the dielectric properties of doped $BaTiO_3$. Figure 4 shows the variation of the dielectric constant of the compounds with temperature for different concentrations of Mn in $BaMn_xTi_{1-x}O_3$. It was found to follow the general trend of ferroelectrics i.e., the dielectric constant increases with a rise in temperature up to a maximum value at the Curie temperature (T_c) where it undergoes a phase transition from a ferroelectric to a para-electric phase. It is observed in Fig. 4 that for un-doped $BaTiO_2$, the

Table 2. Change in dielectric constant, e at T_c.

Sample composition	Average Grain size (nm)	Transition temperature, T_c (°C)	Dielectric Constant, ε at T_c
$Ba(Mn_{0.00}Ti_{1.00})O_3$	340.40	125	646.11
$Ba(Mn_{0.01}Ti_{0.99})O_3$	415.37	150	552.96
$Ba(Mn_{0.02}Ti_{0.98})O_3$	456.87	155	534.13
$Ba(Mn_{0.03}Ti_{0.97})O_3$	526.00	160	530.97
$Ba(Mn_{0.04}Ti_{0.96})O_3$	552.00	160	528.04

dielectric constant reaches a maximum value of about 646 at temperature 125 °C and above this temperature it decreases. Dielectric properties have been found to be dependent on the grain size [12,13]. With an increase of MnO_2 the dielectric constant of the samples at T_c decreases to a value of about 528 for sample 5. Thus it is seen that the grain size increases as the MnO_2 content increases in $BaTiO_3$ thereby decreasing the dielectric constant at the T_c as shown in Table 2.

It was found that when Mn was doped the transition temperature of $BaMn_xTi_{1-x}O_3$ increases with an increase of the value of x as well as grain size. When the grain size was about 415 nm, the transition temperature increased rapidly and then increased slowly with an increase of the grain size.

Conclusions

The DC electrical resistivity, dielectric and microstructural properties of $BaTiO_3$ ceramics was influenced significantly by small additions of MnO_2. It is found that with an increase of Mn in $BaMn_xTi_{1-x}O_3$ (where x=0.00, 0.01, 0.02, 0.03 and 0.04), the grain size of the samples increases. The un-doped $BaTiO_3$ sample exhibited the highest resistivity among the experimental samples. This increases with temperature up to a maximum value at a temperature which is termed the Curie temperature or the transition temperature (T_c) and then the resistivity decreases. The T_c rises with an increase of the value of x in $BaMn_xTi_{1-x}O_3$ as well as the grain size. The dielectric constant of the pure $BaTiO_3$ sample was largest and was found to decrease with an increase of the Mn addition and it also decreases with an increase of the grain size.

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