

DIFFUSE PHASE TRANSITION AND DIELECTRIC PROPERTIES OF Mn^{4+} -DOPED $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Sn}_{0.06}\text{Ti}_{0.94}\text{O}_3$ PEROVSKITE CERAMICS

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Received: May 10, 2024; Revised: September 05, 2024; Accepted: October 25, 2024

Abstract

In this work, a conventional solid-state reaction technique was used to successfully fabricate lead-free $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Sn}_{0.06}\text{Ti}_{0.94-x}\text{Mn}_x\text{O}_3$ (BCSTM) perovskite ceramics, where $x = 0.00, 0.03, 0.06$, and 0.09 . The effect of Mn^{4+} doping on structure, dielectric properties, and phase transition was investigated. The dielectric constant (ϵ) of Mn^{4+} -doped BCST ceramics was enhanced by Mn^{4+} incorporation, as measured by LCR meter at room temperature. The dielectric constant (ϵ) of 4963 and the low dielectric loss ($\tan\delta$) of 0.0241 were obtained at the composition of $x = 0.06$ at room temperature, with a frequency of 1 kHz. The dielectric property investigation indicated that the degree of the diffuse phase transition behavior increased with Mn^{4+} substitution. The phase transition from tetragonal to cubic symmetry was significantly dependent on the amount of Mn^{4+} added. It also was found that the diffuseness of the phase transition behavior of BCST ceramics was enhanced, while the phase transition temperature (T_C) of these ceramic samples decreased with an increase in the content of Mn^{4+} . In addition, the diffuseness of the phase transition behavior was enhanced with an increase in the content of Mn^{4+} . The replacement of Mn^{4+} at the Ti^{4+} site led to diffuseness and a rapid decrease in the phase transition temperature (T_C or T_m).

Keywords: Dielectric Properties; Diffuse Phase Transition; Lead-Free Ceramic

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DOI: <https://doi.org/10.55766/sujst9017>

Suranaree J. Sci. Technol. 32(1):030254(1-7)

Introduction

As the need for environmental conservation grows, extensive research on diverse lead-free piezoelectric ceramics is being conducted to meet the demand for environmentally friendly applications. Currently, extensive research has been conducted on the diffuse phase transition and dielectric behavior of various perovskite ferroelectric ceramics, which have applications in numerous micro- and nano-electronic devices, such as micro-actuators and multilayer capacitors (Kantha *et al.*, 2014; Kantha *et al.*, 2017; Chitra *et al.*, 2022; Kornphom *et al.*, 2023; Pattanakasem *et al.*, 2023; Wang *et al.*, 2023; Wannasut *et al.*, 2023). Modified barium titanate compositions are extensively utilized in multilayer ceramic capacitors (MLCCs) owing to their high dielectric constant and low dielectric loss. However, the temperature range for their application is influenced by the phase transition (Li *et al.*, 2012; Chen *et al.*, 2013; Kantha *et al.*, 2017). The substitution of both isovalent and aliovalent cations in the perovskite lattice plays a crucial role in enhancing the electrical properties and phase transition of the materials (Kuang *et al.*, 2009; Li *et al.*, 2012; Jaiban *et al.*, 2017; Kantha *et al.*, 2017; Jaiban *et al.*, 2019; Iriani *et al.*, 2024; Rui *et al.*, 2024). Recently, Chen *et al.* reported that the $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Sn}_{0.06}\text{Ti}_{0.9}\text{O}_3$ ceramics showed high piezoelectric and dielectric properties of $d_{33} = 405$ pC/N and $\epsilon \sim 4000$ at room temperature (Chen *et al.*, 2013). In addition, doping Mn in ceramics can improve the piezoelectric properties and dielectric properties (Li *et al.*, 2013; Liu *et al.*, 2014). The investigation of Mn^{4+} -substituted BaTiO_3 ceramics has garnered attention due to several interesting features in the dielectric behavior of the materials. In this work, $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Sn}_{0.06}\text{Ti}_{0.94-x}\text{Mn}_x\text{O}_3$ (BCSTM) ceramics with $x = 0.00, 0.03, 0.06$, and 0.09 were prepared by a conventional solid-state reaction technique. The BCST ceramics were investigated by XRD analysis. Finally, the diffuse phase transition and dielectric properties of BCSTM ceramics were studied as a function of frequency and temperature to establish structure-property relationships.

Experimental Details

Lead-free $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Sn}_{0.06}\text{Ti}_{0.94-x}\text{Mn}_x\text{O}_3$ (BCSTM) perovskite ceramics with varying Mn^{4+} contents ($x = 0.00, 0.03, 0.06$, and 0.09) were meticulously synthesized using conventional solid-state reaction technique. High-purity raw materials, including BaCO_3 (99.0%), CaCO_3 (99.0%), MnO_2 (99.0%), SnO_2 (99.0%), and TiO_2 (99.5%), were subjected to

ball milling with ethanol, followed by drying and calcination at 1300°C for 4 hours. Subsequently, the finely calcined powders underwent uniaxial pressing to form 10 mm-diameter pellets, which were then sintered at temperatures ranging from 1400 to 1500°C for 4 hours in an ambient air.

The crystal structure and phase identification of the resulting ceramics were comprehensively analyzed using an X-ray diffractometer equipped with $\text{Cu K}\alpha$ radiation. The dielectric constant (ϵ) and dielectric loss ($\tan\delta$) of all ceramic samples were systematically measured across various temperatures spanning from -40°C to 100°C , employing a heating/cooling rate of $5^\circ\text{C}/\text{min}$, and assessed using an LCZ meter (Model 4276A, Hewlett Packard). The piezoelectric constant value (d_{33}) was measured by piezoelectric- d_{33} -meter.

Results and Discussion

The XRD patterns of BCSTM ceramics with $x = 0.00, 0.03, 0.06$, and 0.09 are shown in Figure 1. The diffraction patterns suggested that all ceramics were of single-phase perovskite structure without a second phase except for the composition of $x = 0.09$. All of the ceramics possessed a tetragonal structure (corresponding to the JCPDS file No. 83-1880), seen in the splitting of (002)/(200) peaks between 2θ of 44 – 47° in Figure 1.

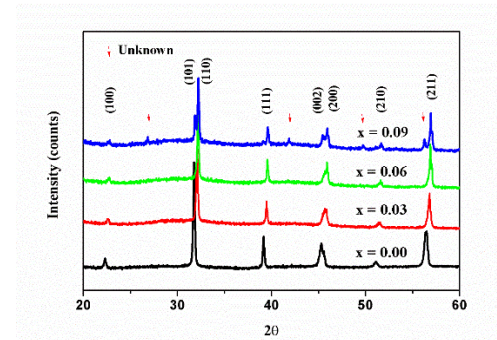


Figure 1. X-ray diffraction patterns of the BCSTM ceramics

The tolerance factor (t) is a measure introduced by Goldschmidt to assess the stability and distortion of crystal structure, and it is calculated using the following formula (Kongputhon *et al.*, 2023):

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (1)$$

where R_A and R_B are the ionic radii of the ions occupying the A-site (CN = 12) and B-site (CN = 6),

respectively. R_O is the ionic radius of oxygen (CN = 6). The average ionic radii of A-site and B-site ions in the $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ ceramics can be calculated by the following equations:

$$R_A = 0.9r_{Ba^{2+}} + 0.1r_{Ca^{2+}} \quad (2)$$

$$R_B = 0.06r_{Sn^{4+}} + (0.94 - x)r_{Ti^{4+}} + xr_{Mn^{4+}} \quad (3)$$

The calculation of t values is displayed in Table 1. Based on the reported ionic radii, Pisitpipathsin *et al.* (2013) of A-site ions such as Ba^{2+} (1.61 Å) and Ca^{2+} (1.34 Å) as well as those of B-site ions including Mn^{4+} (0.53 Å), Sn^{4+} (0.69 Å) and Ti^{4+} (0.605 Å), the t -factors of Mn^{4+} modified BCST were calculated and found to increase from 1.049 to 1.053 with increasing Mn^{4+} content from 0 to 0.09. Overall, the stability of the perovskite structure was observed within the range of 0.880 to 1.090, with greater symmetry observed as the value of t approaches 1 (Shannon, 1976; Lee *et al.*, 2009; Kongputhon *et al.*, 2023;). Additionally, the t value indicates the maximum distance that atoms can deviate from their ideal stacking positions within the perovskite structure without compromising its integrity. It reflects structural modifications to the octahedra, including deformation, rotation, and tilt (Bhalla *et al.*, 2000). These structural factors consequently affect the electrical properties of the perovskite materials.

Table 1. The average ionic radius of A-site and B-site ions and the tolerance factor of $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ ceramics

Composition (x)	Ionic radii (Å)		Tolerance factor (t)
	A-site	B-site	
0.00	1.583	0.610	1.049
0.03	1.583	0.608	1.051
0.06	1.583	0.606	1.052
0.09	1.583	0.603	1.053

The Mn^{4+} (0.530 Å (Shannon, 1976) for 6 coordinates) ions that occupied Ti^{4+} -site ions were smaller than those occupying Ti^{4+} ions. It can be seen that the average ionic radius of B-site ions reduced with increasing Mn^{4+} content. Therefore, it is reasonable to assume that the substitution of Mn^{4+} for Ti^{4+} led to the obvious shifting and evolution of the peaks between 2θ of 44-47° in Figure 1 as the Mn^{4+} contents increased. Furthermore, the excess of Mn^{4+} doping at $x = 0.09$ induced lattice distortion and the formation of a second phase in $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ ceramics.

The dielectric constant of lead-free $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ (BCSTM) perovskite ceramics at room temperature, where $x = 0.00, 0.03,$

0.06, and 0.09, was measured and shown in Figure 2. A function of Mn^{4+} content was plotted with various frequencies at room temperature. It was found that the addition of Mn^{4+} enhanced the dielectric constant of BCSTM ceramics while also reducing their dielectric loss at room temperature. At 1 kHz, the ϵ_r for pure BCST ($x = 0.00$) was approximately 3449, which increased up to 4943 at $x = 0.06$. The considerable initial increase in ϵ values may have been mainly due to the reduction of Curie temperature as shown in Figure 3. This trend was observed at all frequencies.

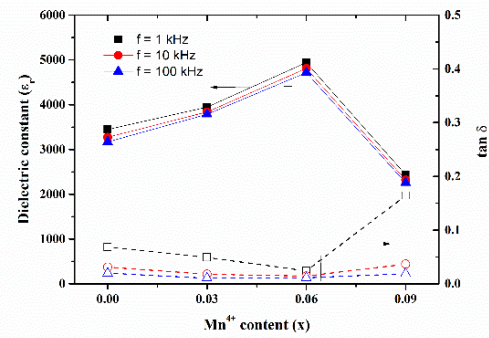


Figure 2. Dielectric constant (ϵ) and loss ($\tan\delta$) of BCSTM ceramics as a function of Mn^{4+} content at 1-100 kHz at room temperature

The dielectric constant of lead-free $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ (BCSTM) perovskite ceramics at room temperature, where $x = 0.00, 0.03, 0.06,$ and 0.09 , was measured and shown in Figure 2. A function of Mn^{4+} content was plotted with various frequencies at room temperature. It was found that the addition of Mn^{4+} enhanced the dielectric constant of BCSTM ceramics while also reducing their dielectric loss at room temperature. At 1 kHz, the ϵ_r for pure BCST ($x = 0.00$) was approximately 3449, which increased up to 4943 at $x = 0.06$. The considerable initial increase in ϵ values may have been mainly due to the reduction of Curie temperature, as shown in Figure 3. This trend was observed at all frequencies.

The temperature-dependent dielectric constants (ϵ) and $\tan\delta$ of BCSTM ceramics at $f = 1-100$ kHz as a function of Mn^{4+} content are shown in Figure 3, which demonstrates two obvious polymorphic phase transitions at T_C and T_{O-T} . The first phase transition occurred at the T_{O-T} , corresponding to the ferroelectric-ferroelectric (FE-FE) transition (Orthorhombic structure to tetragonal structure). The second occurred near the T_C or T_m (tetragonal structure to cubic structure), corresponding to the ferroelectric-paraelectric (FE-PE) transition.

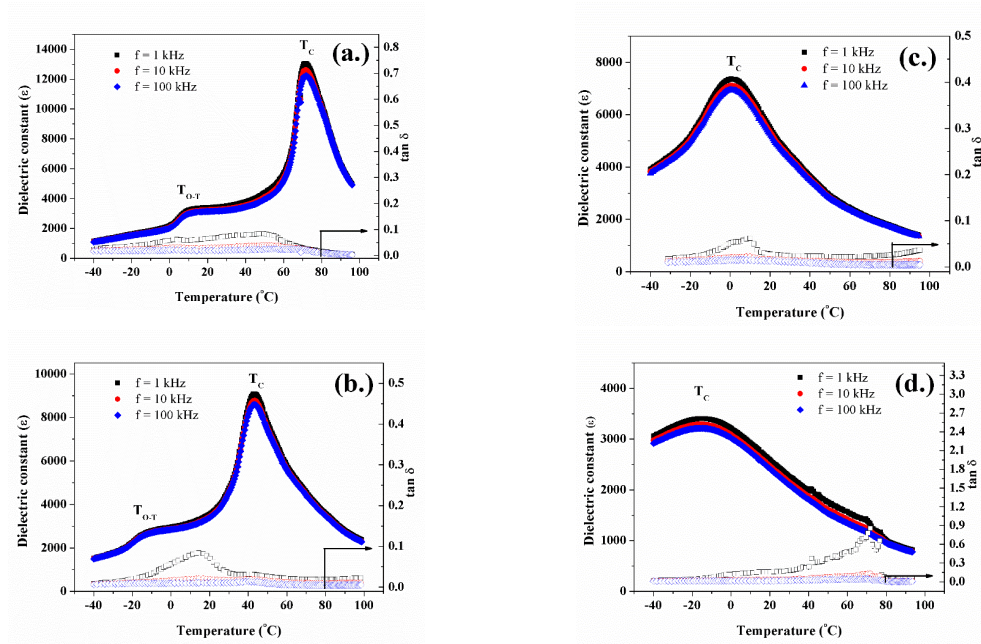


Figure 3. The temperature-dependent dielectric constants (ϵ) and $\tan\delta$ of BCSTM ceramics at $f = 1$ -100 kHz as a function of Mn^{4+} content, where (a) $x = 0.00$, (b) $x = 0.03$, (c) $x = 0.06$ and (d) $x = 0.09$

Table 2. Electrical properties of $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Sn}_{0.06}\text{Ti}_{0.94-x}\text{Mn}_x\text{O}_3$ ceramics

Mn^{4+} content (x mole)	T_C or T_m ($^{\circ}\text{C}$) (1 kHz)	T_C or T_m ($^{\circ}\text{C}$) (100 kHz)	ΔT_m ($^{\circ}\text{C}$)	T_{O-T} ($^{\circ}\text{C}$) (1 kHz)	ϵ_{max} (1 kHz)	$\tan\delta$ (1 kHz at T_m)
0.00	71.84	71.84	0	12.29	13,060	0.0266
0.03	43.20	43.20	0	10.12	9,087	0.0308
0.06	0.52	0.52	0	-	7,362	0.0582
0.09	-14.60	-14.60	0	-	3,404	0.0534

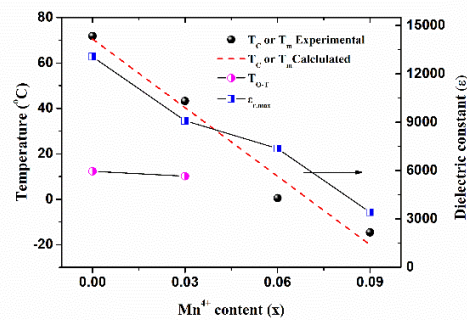


Figure 4. The experimental and calculated values of $\epsilon_{r,\text{max}}$, T_{O-T} , T_C or T_m for BCSTM ceramics as a function of Mn^{4+} content

The T_C and T_{O-T} transition peaks shifted toward lower temperatures with Mn^{4+} addition (see in Figure 3 and Table 2). However, while this shift is not clear at present, Mn^{4+} addition might also influence the chemical effect. The irregularity of T_m as a function of doping content in the BCSTZ system was also reported (Liu *et al.*, 2014; Li *et al.*,

2013). In this work, the BCSTM ceramics for $0.03 \leq x$ showed two obvious polymorphic phase transitions corresponding to the orthorhombic to tetragonal (T_{O-T}) and tetragonal to cubic (T_C) phases. Furthermore, only the T_C phase transition was found for the BCSTM ceramics for $0.06 \leq x \leq 0.09$. Additionally, it was clearly observed that the maximum dielectric constant ($\epsilon_{r,\text{max}}$) reduced with the addition of Mn^{4+} . The T_C and T_{O-T} as a function of Mn^{4+} content are shown in Figure 4. It was found that the T_{O-T} transition peaks slightly shifted toward lower temperatures with Mn^{4+} addition.

The T_C and maximum dielectric constant ($\epsilon_{r,\text{max}}$) as a function of Mn^{4+} content are shown in Figure 4. It was found that the T_C of the ceramic sample decreased with increasing content of Mn^{4+} . The T_C of BCSTM ceramics decreases with increasing Mn^{4+} content, which can be used to obtain an empirical estimation of the T_C reduction via equation (4).

$$T_C = -1006.67x + 70.54 \quad (4)$$

Where T_C is the ferroelectric-paraelectric (FE-PE) phase transition of the ceramics and x is the Mn^{4+} content of $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ ceramics.

Observably, an increase in frequency led to a downward shift in T_C or T_m . This observation is indicative of typical frequency dispersion. To explore the empirical relaxation strength and describe the frequency dispersion of T_m , the parameter ΔT_m was introduced, as defined in equation 1 (Kantha and Pisitpipathsin, 2018).

$$\Delta T_m = T_m (100 \text{ kHz}) - T_m (1 \text{ kHz}) \quad (5)$$

where ΔT_m is derived from the dielectric measurements of $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ ceramics. The values of ΔT_m for all the studied samples are shown in Table 2. These data further confirm that $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ ceramics exhibit second-order or diffuse phase transition behavior.

In order to study the effect of Mn^{4+} on the diffuse phase transition (in contrast to sharp phase transition), the diffuseness parameter (δ_γ) was determined using the following expression (Pilgrim *et al.*, 1990; Tawichai *et al.*, 2010):

$$\frac{\varepsilon_{r,max}}{\varepsilon_r} = \exp \left[\frac{(T-T_m)^2}{2\delta_\gamma^2} \right] \quad (6)$$

where $\varepsilon_{r,max}$ is the maximum value of the relative dielectric constant at $T \geq T_m$, ε_r is the dielectric constant, and δ_γ is the diffuseness parameter of the transition. The value of δ_γ can be determined from the $\ln(\varepsilon_{r,max}/\varepsilon_r)$ versus $(T-T_m)^2$ curve. This value is valid for $\varepsilon_{r,max}/\varepsilon_r < 1.5$, as clarified by Pilgrim *et al.* (1990). The values of parameter δ_γ at various Mn^{4+} contents are exhibited in Figures 5 and 6. The δ_γ of BCSTM ceramics increases with increasing Mn^{4+} content, which can

be used to obtain an empirical estimation of the increase in δ_γ via equation (7).

$$\delta_\gamma = \exp (2.81237 + 3.23.94x + 81.7997x^2) \quad (7)$$

where δ_γ is the diffuseness parameter of the ceramics and x is the Mn^{4+} content of $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ ceramics.

It was also found that the δ_γ values increased as Mn^{4+} content increased, from 15.81 to 43.60, confirming that the addition of Mn^{4+} promoted the diffuse phase transition of the BCSTM ceramics.

Table 3 illustrates the piezoelectric coefficient (d_{33}) values for $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ ceramics. The maximum d_{33} value of 267 pC/N was achieved when $x = 0.03$, signifying that the Mn^{4+} content enhanced piezoelectric performance., However, d_{33} values subsequently declined as the Mn^{4+} concentration increased further. For instance, the $x = 0.09$ sample exhibited a notably reduced d_{33} value of 28 pC/N. This decrease in the piezoelectric property may be attributed to the concurrent reduction in the Curie temperature (T_C).

Table 3. Physical and electrical properties of $Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO_3$ ceramics

Mn content (x mole)	Density (g/cm ³)	d_{33} (pC/N) (in this work)	g_{33} (VmN ⁻¹) (in this work)
0.00	4.64	251	8.1×10^{-3}
0.03	4.70	267	7.6×10^{-3}
0.06	4.61	31	0.7×10^{-3}
0.09	4.68	28	1.3×10^{-3}

To further assess the piezoelectric characteristics, the permittivity and d_{33} values are employed in calculating the piezoelectric voltage coefficient ($g_{33} = d_{33}/\varepsilon_0\varepsilon_r$) (Pisitpipathsin and Kantha 2018; Kongputhon *et al.*, 2023). Here, ε_0 represents the permittivity of free space, and ε_r is the relative

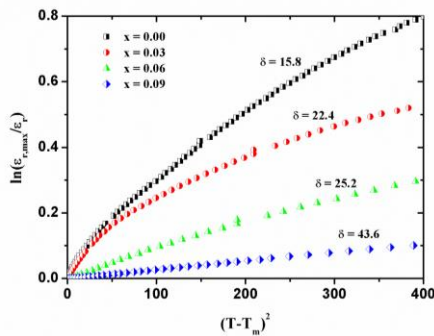


Figure 5. Quadratic dependence of temperature on logarithmic dielectric constant of the BCSTM ceramics

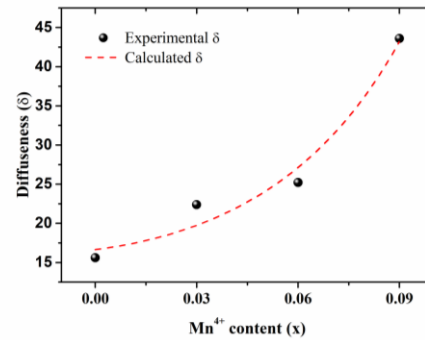


Figure 6. Plots of diffuseness parameter (δ_γ) of BCSTM ceramics as a function of Mn content

permittivity of BCSTM ceramics. Consequently, at room temperature, the g_{33} coefficients for BCSTM ceramics in the $x = 0 - 0.09$ range were 8.1×10^{-3} , 7.6×10^{-3} , 0.7×10^{-3} , and 1.3×10^{-3} VmN⁻¹, respectively.

Conclusion

The dielectric properties and diffuse phase transition of Mn⁴⁺-doped Ba_{0.9}Ca_{0.1}Sn_{0.06}Ti_{0.94-x}Mn_xO₃ ceramics were investigated. It was found that various Mn⁴⁺ contents had a strong effect on the dielectric properties and phase transition temperature of BCSTM ceramics. The dielectric properties at room temperature were improved when the Mn⁴⁺ concentration was increased to $x = 0.06$, which yielded the maximum dielectric constant of 4943 and tan δ of 0.0241. In addition, the diffuseness of the phase transition behavior was enhanced with an increase in the Mn⁴⁺ content. The replacement of Mn⁴⁺ at the Ti⁴⁺ site led to diffuseness and a rapid decrease of the phase transition temperature (T_C or T_m). The phase transition of T_{O-T} was observed at composition $x = 0.00-0.03$. Furthermore, the optimum composition for lead-free piezoelectric ceramic was found at $x = 0.03$ due to its good piezoelectric properties with a high value of $d_{33} = 267$ pC/N and the voltage coefficient (g_{33}) = 7.6×10^{-3} Vm/N.

Acknowledgements

This research project is supported by Science Research and Innovation Fund. Contract No. FF66-P1-044.

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