Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 2075–2079
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Influence of manganese substitution into the A-site of perovskite type $Ca_{1-x}Mn_xTiO_3$ ceramic

Weeraphat Pon-On [a,d,*], Siwaporn Meejoo [c], Asiya Mehtar [c], I-Ming Tang [b,d]

[a] Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
[b] ThEP Center, Commission of Higher Education, 328 Si Ayuthaya Rd., Bangkok 10400, Thailand
[c] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Rama 6th Rd., Bangkok 10400, Thailand
[d] Department of Physics, Faculty of Science, Mahidol University, Rama 6th Rd., Bangkok 10400, Thailand

Received 24 February 2010; received in revised form 24 June 2010; accepted 6 October 2010
Available online 20 May 2011

Abstract

$Ca_{1-x}Mn_xTiO_3$ ($x = 0$–1.0) perovskite ceramics were prepared by conventional solid state reaction. XRD was used to confirm the microcrystalline nature of the $Ca_{1-x}Mn_xTiO_3$ crystals. For the $x = 0$ composition, the XRD patterns were those of a single orthorhombic perovskite while for $x = 0.2$–0.8, the XRD spectra were those of two orthorhombic perovskite phases: $CaTiO_3$ and $MnTiO_3$. For $x = 1$, XRD pattern was that of the $MnTiO_3$ phase only. The morphology and particle size of the grains of the different composition were observed using SEM. The size of the particles increased from 0.2 μm to 2–3 μm as x increased from 0 to 0.6. The room temperature dielectric constant at the frequency of 110 kHz for the $x = 0.2$ and $x = 1.0$ ceramics were $\sim 3.41 \times 10^4$ and $\sim 4.99 \times 10^3$, respectively. The ESR linewidth of samples increased with increasing manganese content due to the formation of magnetic cluster. Our ESR studies indicate that the manganese ions are in the Mn^{4+} state.

Keywords: Calcium titanate ceramics; Perovskite structure nanoparticles; Solid state reaction; ESR dielectric constant

1. Introduction

The perovskite structure titanate $ATiO_3$ (A = Ca, Sr, Ba, Pb and K) are of great interest because of their high dielectric constant [1]. Dielectric materials with high permittivity and low loss factors over a wide frequency range are needed for their applications in electronic devices such as high frequency capacitors. Microwave (MW) based low-loss ceramics such as $CaTiO_3$ have been proposed for use in microwave dielectric resonators in MW integrated circuits [2]. This particular titanate, unlike the most of the other titanates does not undergo the structural transition which would lead it to become a ferroelectric. Rupprecht and Bell [1] showed that $CaTiO_3$ is a paraelectric material whose dielectric constant follows a Curie Weiss law with a negative Curie temperature. Renewed interest in the calcium titanates arose when a new ceramic $CaCu_3Ti_4O_{12}$ consisting of one part $CaTiO_3$ and three parts $CuTiO_3$ was created [3,4]. This new ceramic has what is known as a colossal dielectric constant, with ε_0 of order 10^4 [3,5,6].

Calcium titanate $CaTiO_3$ would by itself be a good candidate for a microwave dielectric since it has a high permittivity, $\varepsilon' = 160$ and a Q factor $Q = 8000$ at 1.5 GHz. It however has a large positive temperature coefficient in its resonant frequency [2]. Researchers have sought to improve the performance of this ceramic by doping it with Fe [7] and by mixing it with other titanates [2]. In this paper we are interested in the effects of Mn doping on the dielectric properties of this titanate. The effects of Mn doping on the dielectric properties of barium titanate [8] and strontium titanate [9] and on the colossal dielectric $CaCu_3Ti_4O_{12}$ [10] have been investigated.

In this work, we report on our study of the substitution of Mn into the A-site of $CaTiO_3$. The substitution of Mn ions in place of the Ca ions creates $Ca_{1-x}Mn_xTiO_{3-\delta}$. We have used the usual solid-state reaction technique to fabricate the ceramics. The Mn modified perovskite ceramics exhibit colossal magneto resistance which leads them to be potential materials to be

---

* Corresponding author at: Department of Physics, Faculty of Science, Mahidol University, Rama 6th Rd., Bangkok 10400, Thailand.
Tel.: +66 2 201 5160; fax: +66 2 354 7159.
E-mail address: wponun@yahoo.com (W. Pon-On).

0272-8842/$36.00 © 2011 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2011.05.071

used as solid electrolytes, catalyst, sensors and other novel electronic materials. The evolution of the microstructure of the ceramics as the amount of Mn is increased is investigated. The relationship between the dielectric constant at room temperature (RT) and the amount of Mn in the ceramic is obtained.

2. Materials and methods

$CaCO_3$, MnO_2 and TiO_2 were used to prepare the powdered ceramic samples. All reagents were of high purity (>99.9%) and purchased from Aldrich Chemical (USA). Stoichiometric amounts of the reagents were weighed to yield $Ca_{1-x}Mn_xTiO_{3y}$ with $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0 mol%. Each of the constituent mixtures was mixed together by ball milling in anhydrous ethanol (Merck (Germany)) medium for four hour. After milling, the samples were oven dried (approximately 24 h at 105 °C) before being calcined at 800 °C for 8 h in a furnace (Lenton (England), Model EHF 18/5). The calcined powders were mixed with an appropriate amount of PVA as an organic binder to help in the formation of compacts. The pellets were compressed at 10 tons for 5 s. The pellets of $Ca_{1-x}Mn_xTiO_3$ were sintered at 1100 °C for 12 h under an air atmosphere. The crystal structures of the samples for different manganese contents were determined using a XRD diffractometer (Bruker (Germany), Model D8 Advance) using the Cu Kα radiation and operating at 40 kV with 40 mA current. The crystal structures of the final products were verified by the XRD patterns scanned over the range $2\theta = 20$–$80°$ at a scanning speed of 0.037°/min.

A scanning electron microscope (SEM) (JEOL (Japan) Model JSM-6301F) was used to observe the changes in sizes and the morphology of the different samples. An accelerating voltage of 15 kV was used to obtain the SEM images. The dielectric constants were measured with an Impedance meter (Hewlett-Packard (USA) LCR Meter, Model 4284A) in the frequency range between 100 kHz and 1.1 MHz. The LCR meter was attached to the silver paste which had been applied to the pellets in order to achieve ohmic contact. The spin states of the Mn ions in the structure were determined by an electron spin resonance (ESR) spectrometer (Bruker (Germany), Model e500 ESR) operating in the X-band (9.87 GHz). The spectra were collected at 20.23 mW with modulation amplitude of 2.09 mT.

3. Results and discussion

The crystal phase transitions in the prepared samples were investigated by XRD. The XRD patterns of the $Ca_{1-x}Mn_xTiO_3$ ceramics for all compositions are shown in Fig. 1. All the compositions exhibited orthorhombic perovskite structures. A smaller secondary phase was also observed. The results show that solid phases containing both $CaTiO_3$ and $MnTiO_3$ crystals are obtained at the sintering temperature of 1100 °C. Increasing the concentration of manganese caused the XRD peaks belonging to calcium titanate to decrease in their intensities. The pure $CaTiO_3$ sample ($x = 0$) had only one set of orthorhombic perovskite structure peaks. The XRD patterns for the doped magnetite of composition $x = 0.2$–0.8 showed decreases in the intensities of peaks of the $CaTiO_3$ phase and increases in the intensities of the peaks of the $MnTiO_3$ phase. Only the peaks belonging to $MnTiO_3$ are seen in the XRD pattern of the completely doped ceramic.

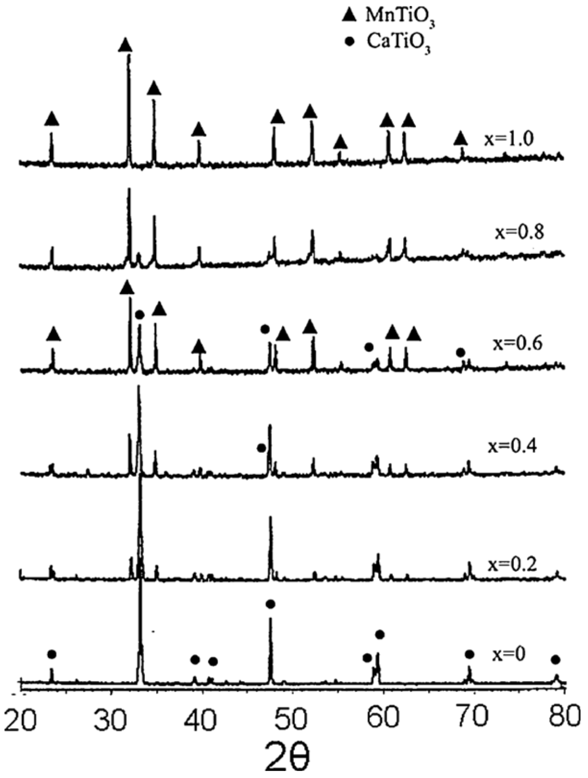

Fig. 1. X-ray diffraction patterns of $Ca_{1-x}Mn_xTiO_3$ powder sintered at 1100 °C for 12 h for composition $x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0 mol%.

The microstructures of $Ca_{1-x}Mn_xTiO_3$ ceramics were observed with a scanning electron microscopy. In Fig. 2, we see the SEM photographs of the sintered samples having the compositions, $x = 0.0$, 0.4 and 0.6. The photographs show that low-density microstructures were obtained. The grain size increased significantly when more Mn was added. This suggests that the substitution of Mn into the perovskite structure lattice promotes grain growth. The powdered form of the Mn-free $CaTiO_3$ had a porous structure. The particle size (diameter) was about 0.5–1 μm. After substituting Mn into the calcium titanate to achieve $Ca_{1-x}Mn_xTiO_3$ (where $x = 0.4$ and 0.6 mol%) the small grains grew to be 1 and 4 μm, respectively.

Fig. 3(a) shows the RT dielectric constant (ε_0) of a pure $CaTiO_3$ ceramic as a function of frequency. The value of dielectric constant is about 61.5 at the frequency of 110 kHz. It remained constant at ~59 in the frequency range between 400 and 1000 kHz. The values of the dielectric constants for the doped ceramics having Mn concentrations in the range between $x = 0.2$ and 1.0 mol%, are shown in Fig. 3(b). The data points indicate that the dielectric constant becomes smaller as the amount of Mn is increased from $x = 0.2$–0.8. It can be seen that the pure $MnTiO_3$ phase has a ε_0 of 4.99×10^3. The highest dielectric constant is possessed by the ceramic doped with 0.2 mol% of Mn. The value of ε_0 for this ceramic is $\sim 3.41 \times 10^4$ at 110 kHz. The changes in the dielectric constant as the Mn impurities are added are due to how the dipole

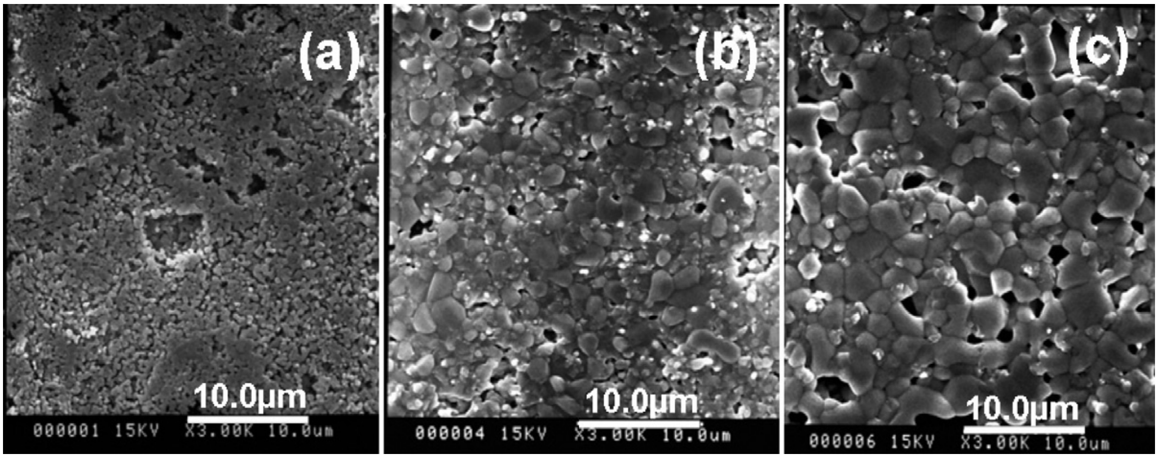

Fig. 2. The SEM photographs of $Ca_{1-x}Mn_xTiO_3$ pellet sintered at 1100 °C/12 h for (a) $x = 0$, (b) $x = 0.4$ and (c) $x = 0.6$.

moment on the Mn ions responds to an external magnetic field. A strong change in the dielectric constant is induced when 0.2 mol% of manganese ions is substituted into $CaTiO_3$. The RT dielectric constant (ε_0) at 1 MHz of $Ca_{1-x}Mn_xTiO_3$ (where $x = 0.2$–1.0 mol%) is plotted in Fig. 3c. There we see that the dielectric constants at 1 MHz decrease as the Mn substitution is raised from 0.2 to 1.0 mol%. The decrease in dielectric constant as Mn is substituted into $CaTiO_3$ is the opposite of what is observed when Mn is substituted in $BaTiO_3$. Wu et al. [8] report that the dielectric constant at 1 kHz increased to 5800 at an optimal doping level of the Mn. They attributed the increase to the reaction

$$Mn^{4+} + 2Ti^{3+} \rightarrow Mn^{2+} + 2Ti^{4+} \qquad (1)$$

This oxidation–reduction reaction in $BaTiO_3$ has been studied by Hahn and Han [11]. They found that Mn doping suppressed the formation of oxygen vacancies at room temperature. Tkach et al. [9] find that the manganese would

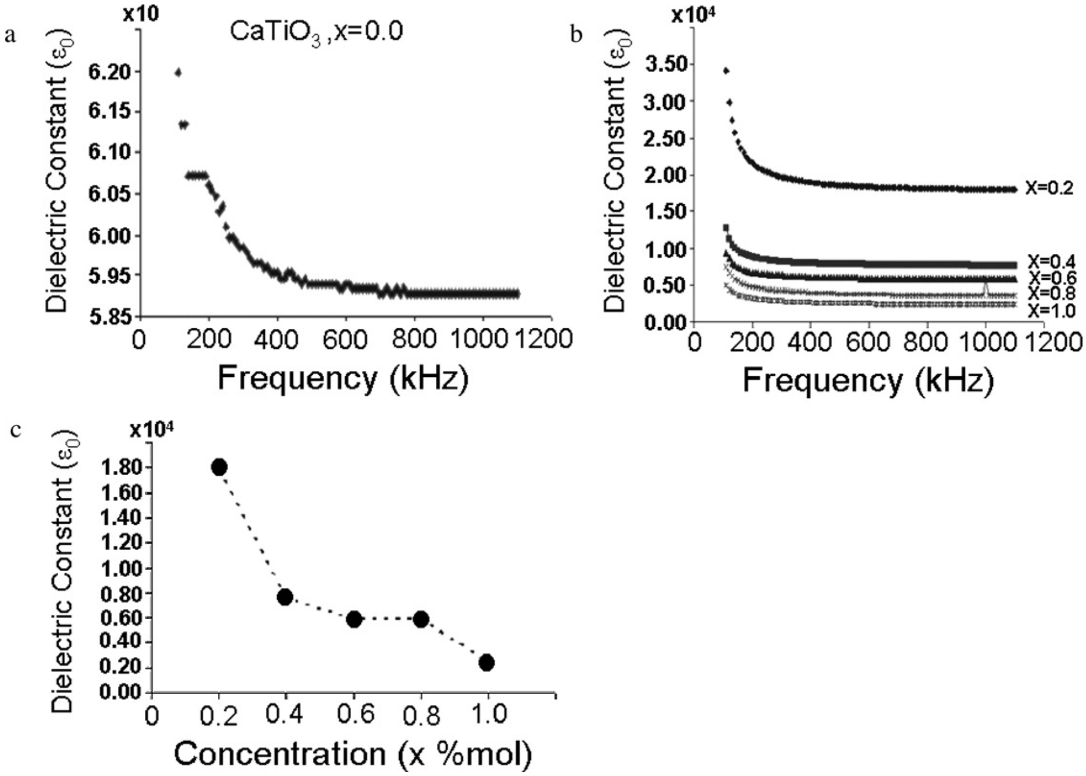

Fig. 3. Frequency dependence of dielectric constant (ε_0) measured at RT of the Mn modified $CaTiO_3$. (a) Dielectric constant (ε_0) of a pure $CaTiO_3$ ceramic, (b) of $Ca_{1-x}Mn_xTiO_3$ where $x = 0.2$–1.0 mol%, and (c) dielectric constant (ε_0) at 1 MHz as a function of concentrations measured at 1 MHz.

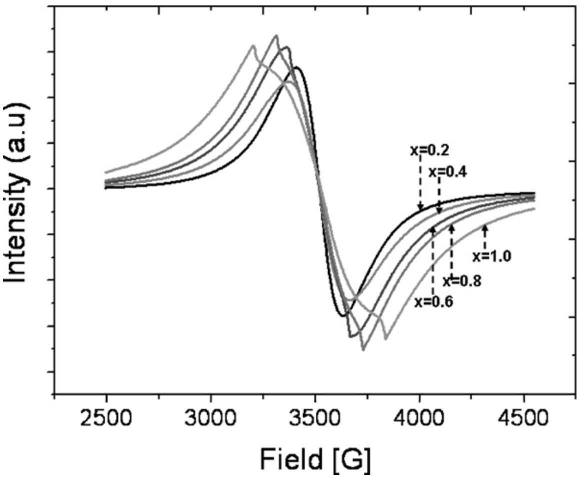

Fig. 4. Room temperature ESR spectra of the samples $Ca_{1-x}Mn_xTiO_3$ with different concentrations $x = 0.2–1.0$ mol% sintered at 1100 °C for 12 h. The sharp spikes at the end and beginning of the resonance peaks in the $x = 1.0$ and 0.8 mol% ESR spectra are due to transition to a ferromagnetic phase.

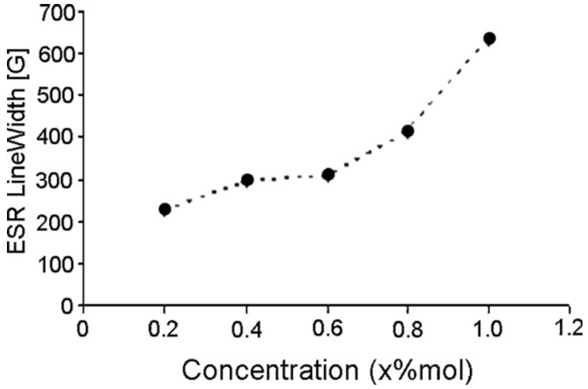

Fig. 5. Concentrations dependent of experiment ESR linewidth of $Ca_{1-x}Mn_xTiO_3$ sintered at 1100 °C 12 h.

substitute in to the A-site as Mn^{2+} when sintered in nitrogen and would substitute as Mn^{4+} in the B site when sintered in oxygen. They proposed that the off-center displacement of the Mn^{2+} ion at the A sites in the strontium titanate ceramic is the source of the observed relaxation behavior seen by them.

Electron spin resonance (ESR) is a useful tool since it can be used to probe the environment surrounding a transition metal ion [12]. Fig. 4 shows the ESR spectra of the $Ca_{1-x}Mn_xTiO_3$ samples measured at RT. As is seen, all the ESR spectra contain a single resonance line having a symmetric line shape which has g factor of 1.99. We wish or point out the extra structures appearing in the shoulder of the ESR peaks for the $x = 0.8$ and 1.0 ceramics. The extra structures are absence in the $x = 0.2$ and 0.4 ceramics and are barely visible in the $x = 0$. We take these structures to be a sign of the paramagnetic phase which are beginning to form in the heavier doped ceramics. The g-factor for Mn^{4+} in an octahedral crystal field is close to 1.994, which is what we see. We cannot however conclude that the Mn is only in the 4+ state. The ESR line for Mn^{3+} would not be observable since the Mn^{3+} ion in an octahedral crystal field has a large zero-field splitting and a short lattice relaxation time.

The line widths of the resonant lines in the ESR as a function of the Mn concentration are plotted in Fig. 5. As we clearly see, the line widths for the lower concentration of Mn ($x = 0.2–0.6$) ceramics are narrow in comparison to the line widths of the higher Mn concentration ($x = 0.8–1.0$ mol%) ceramics. This may mean that the substitution of Mn above a concentration of 0.6 mol% leads to a greater inhomogeneity in the local magnetic fields surrounding the Mn ions or that clustering of magnetic spins occurs when the amount of Mn ions is high. The increase in the line width as the amount of Mn is increased could be a two step process. The first step is reflected in linear increase observed as the Mn concentration is increased from 0.2 to 0.6 mol%. The changes in the line width for these levels of substitution would be due to changes in the crystal structure as lower amounts of Mn were substituted into the ceramics. The second step is reflected in the sharp increase as the Mn content is raised past 0.6 mol%. It is interesting to note that there is a paramagnetic (PM) to ferromagnetic (FM) transition close to $x = 0.6$ mol%. The sudden increase in the line width at $x = 0.6$ mol% might just be the indication that the ferromagnetic domains are being formed. We have conjectured that the structure in the shoulders of the $x = 0.6$, 0.8 and 1.0 mol% is a sign of emergence of the ferromagnetic domain in these ceramics. Thus, the change in the behaviors of the increase in line widths may be an indication that there are two types of phase segregation occurs in $Ca_{1-x}Mn_xTiO_3$ as x increases.

Since we did not see any signature of the Mn^{2+} ions in our ESR spectrums for the Mn doped $CaTiO_3$, we must assume that the oxidation–reduction reaction which occurred in the doping of the other two titanates did not occur in this titanate. We attributed the decreases in the dielectric constant of $Ca_{1-x}Mn_xTiO_3$ when the amount of Mn substitution increased to the change in the relative amounts of two titanates, $CaTiO_3$ and $MnTiO_3$ in the mixed ceramic.

4. Conclusions

The microstructure and dielectric properties of $Ca_{1-x}Mn_xTiO_3$ ceramic materials were investigated as a function of the Mn content. In all the compositions studied, the ceramics contained crystallites which had the orthorhombic perovskite structure. The Mn substitution into the Ca site of the perovskite structure ceramics affected the dielectric constant. When x was increased from 0.2 to 1.0, the RT dielectric constant at 1 MHz decreased from 1.8×10^4 to 2.4×10^3. This result is due to the decrease in the amount of the $CaTiO_3$ phase and the increase in the amount of $MnTiO_3$ phase in the $Ca_{1-x}Mn_xTiO_3$ ceramics. The change in relative amounts of the two pure perovskite ceramics is seen in the XRD patterns of the various doped ceramics. The ESR spectra show that the line widths of the $g = 1.99$ peak increase as the amount of Mn increases. For $x \geq 0.6$, the transition from the paramagnetic state to ferromagnetic state is revealed in ESR spectra. It is suggested that the change in composition in the A-site of perovskite type

$Ca_{1-x}Mn_xTiO_3$ induced by substitution has close correlation with dielectric and magnetic properties.

Acknowledgements

The author would like to acknowledge the financial support from Department of Physics, Faculty of Science, Kasetsart University. Two of the coauthors (WP and IMT) would like to thank the Thailand Center of Excellence in Physics (ThEP), Commission of Higher Education for their financial support during the latter stage of the research. Two of the co-authors (SM and AM) would like to express their gratitude to the Center of Excellence for Innovation in Chemistry (PERCH-CIC) Program, Mahidol University for financial support during the initial stage of this research.

References

[1] G. Rupprecht, R.O. Bell, Dielectric constant in paraelectric perovskites, Phys. Rev. 131 (1964) A748–A751.

[2] A. Pashkin, S. Kamba, M. Berta, J. Petzelt, G.D.C. Csete de Györgyfalva, H. Zheng, H. Bagshaw, I.M. Reany, High frequency dielectric properties of $CaTiO_3$-based microwave ceramics, J. Phys. D: Appl. Phys. 38 (2005) 741–748.

[3] M.A. Subramanian, D. Li, N. Duan, B.A. Reisner, A.W. Sleight, High dielectric constant in $ACu_3Ti_4O_{12}$ and $ACu_3Ti_3FeO_{12}$ phases, J. Solid State Chem. 151 (2000) 323–325.

[4] C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, A.F. Ramirez, Optical response of high-dielectric constant perovskite-related oxide, Science 293 (2001) 673–676.

[5] S.Y. Chung, I.D. Kim, S.J. Kang, Strong nonlinear current–voltage behavior in perovskite derivative calcium ceramics for microwave application, Nat. Mater. 3 (2004) 774–778.

[6] T. Liu, X.Z. Zhao, W. Chen, A/B site modified $CaTiO_3$ dielectric ceramics for microwave application, J. Am. Ceram. Soc. 89 (3) (2006) 1153–1155.

[7] M.A. Ahmed, S.T. Bishay, Effect of annealing time, weight pressure and Fe doping on the electrical and magnetic behavior of calcium titanate, Mater. Chem. Solids 114 (2009) 446–450.

[8] H.S. Wu, S. Wang, L.Y. Chen, X.Y. Wang, Effect of Mn substitutions on dielectric properties of high dielectric constant $BaTiO_3$-based ceramic, J. Mater. Sci. Mater. Electron. 19 (2008) 505–508.

[9] A. Tkach, P.M. Vilarinho, A.L. Kholkin, Dependence of dielectric properties of manganese-dope strontium titanate ceramics on sintering atmosphere, Acta Mater. 54 (2006) 5385–5391.

[10] W. Kobayashi, J. Tersaki, Unusual impurity effects on the dielectric properties of $CaCu_{3-x}Mn_xTi_4O_{12}$, Physica B 329–333 (2001) 771–772.

[11] D.W. Hahn, Y.H. Han, Quantitative analysis of oxidation–reduction behavior of MN-doped $BaTiO_3$, Ceram. Int. 34 (2008) 1341–1344.

[12] M.C. Mozzati, C.B. Azzoni, D. Capsonl, M. Bini, V. Massarotti, Electron paramagnetic resonance investigation of polycrystalline $CaCu_3Ti_4O_{12}$, J. Phys.: Condens. Mater. 15 (2003) 7356–7374.