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Preparation, properties and characterization of $CaTiO_3$-modified $Pb(Fe_{1/2}Nb_{1/2})O_3$ dielectrics

X. Hu, X.M. Chen*, S.Y. Wu

Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

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Abstract

$CaTiO_3$ modified $Pb(Fe_{1/2}Nb_{1/2})O_3$ dielectrics were prepared by a solid-state reaction process and the structure analysis was performed together with the dielectric characterization. The cubic perovskite structures were identified by X-ray diffraction for all compositions in the present system. The short-range order in the dielectrics was revealed by the Raman spectroscopy as the complementarities of XRD. The Raman spectra showed structure transition with the $CaTiO_3$ content increasing to 0.9. The effects of incorporating $CaTiO_3$ on the dielectric properties of $Pb(Fe_{1/2}Nb_{1/2})O_3$ dielectrics were connected to the shifting curie temperature to the low temperature side and the structure transition. Low loss dielectrics with reduced temperature coefficient and high dielectric constant were obtained in the present system, and good microwave dielectric properties ($\varepsilon = 164$, $Qf = 6\,180$GHz, $\tau_f = +583$ppm/°C) were obtained in the present modified dielectrics.

Keywords: Dielectric ceramics; Microwave dielectric properties; Perovskites; $Pb(Fe,Nb)O_3$; Raman spectra

1. Introduction

In the past decade, there has been an increasing interest in the research of relaxor ferroelectrics. In relaxors, the lead-based complex perovskites $Pb(B'_{1-x}B''_x)O_3$ have attracted much attention for their characteristic dielectric nature, i.e. high dielectric constant and good temperature stability around the broad diffuse phase transition.[1] There are many evidences on firming that structural disorder upon certain crystallographic sites is responsible for the diffuse phase transition in the complex perovskites.[2] According to the different degrees of order in the B-ion sublattice, the perovskites with different phase transitions exhibit a great variety of physical properties.[3]

For the behavior of some characteristic features such as the anomaly of the dielectric constant with a relatively small temperature coefficient in lead complex perovskite relaxors, many investigations have been carried out on restraining frequency-dispersion in relaxors for their microwave applications. Recently, Kato et al.[4] previously modified the lead-based complex perovskites by Ca^{2+} substitution for Pb^{2+}. Chen et al modified lead-based complex perovskites by introducing the paraelectric perovskite titanate.[5,6] By their means, the dielectric losses and temperature coefficients of lead complex perovskites were significantly reduced, and some compositions indicated good microwave dielectric properties. But in the previous work, nanoscale structural phase transition and the order degree in modified complex lead perovskites had not been discussed.

Lead iron niobate is one of the family of lead-based complex perovskites which is of interest as a component in commercial electronic ceramic materials for its high relative permittivity and low sintering temperature.[7] Many investigations have been carried out on the microwave dielectric properties of modified lead iron niobate perovskites by A-site or B-site substitution.[8–10] In the present study, the low-loss phase $CaTiO_3$($\epsilon = 170$, $Qf = 3600$GHz, $\tau_f = +800$ppm/°C)[11] was incorporated into the $Pb(Fe_{1/2}Nb_{1/2})O_3$ matrix, and the polycrystalline materials of such modified dielectrics were prepared by a solid-state reaction method. The microstructures are characterized together with the dielectric properties.

2. Experimental procedure

$CaTiO_3$ modified $Pb(Fe_{1/2}Nb_{1/2})O_3$ dielectrics were prepared by a solid-state reaction process with the columbite precursor method, where the raw powders all

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* Corresponding author. Tel./fax: +86-571-8795-2112.
E-mail address: xmchen@cmsce.zju.edu.cn (X.M. Chen).

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had high purity (more than 99%). $FeNbO_4$ powders were first synthesized at 1100 °C in air for 3 h from Fe_2O_3 and Nb_2O_5, then the $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ powders were synthesized by the mixtures of $FeNbO_4$, PbO, $CaCO_3$, and TiO_2 sintered at 850–1000 °C for 3h. The synthesized powders were pressed into compacts of 12 mm in diameter under 98 MPa, and then sintered at 1050 °C to 1250 °C in air for 3 h.

X-ray diffraction using Ni-filtered CuK_α radiation was carried out for phase identification. Raman scattering measurements were conducted using a Raman scope (Thermo Nicolet ALMEGA Dispersive Raman) and the excitation light source was a diode pump solid-state frequency doubled YAG laser (532 nm) with 30 mW of power.

Measurements of the dielectric constant and dielectric loss were conducted from 10 kHz to 1 MHz at room temperature by an HP4284A LCR meter, and the temperature coefficient of the dielectric constant τ_ϵ was measured at 1 MHz in the range from room temperature to 85 °C. A silver paste was used for the electrode. The microwave dielectric characterization was evaluated by the Hakki and Coleman's dielectric resonator method[12] at the frequency of 1.4–2.8 GHz.

3. Results and discussion

The densification of $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ can be performed by sintering at 1100-1200 °C in air for 3 h. As shown in Fig. 1, a single-phase structure is obtained for all compositions. The lattice parameters of the perovskite (in Fig. 2) are submitted to linear relationship with the content of $CaTiO_3$. Despite that the symmetries of the phases of PFN are still open to debate,[13–15] the PFN ceramics we have prepared are considered as cubic phase because the X-ray diffraction pattern in Fig. 1 shows that all peaks are assigned to cubic perovskite structure. When x equals to 0.9, the only one additional peak indicates the minor oxide orthorhombic distortion in the cubic perovskite phase. XRD patterns of the present ceramics do not reveal the existence of the order because superlattice reflection lines have not been observed.

For an ideal cubic perovskite $ABO_3(O_h^1)$ structure, no first-order Raman lines are allowed.[16–18] On the Raman spectrum (in Fig. 3), the strong lines can correspond to local structures that are quite different from the structure expected for the average Pm3m space group which is characterized through XRD analysis. This work

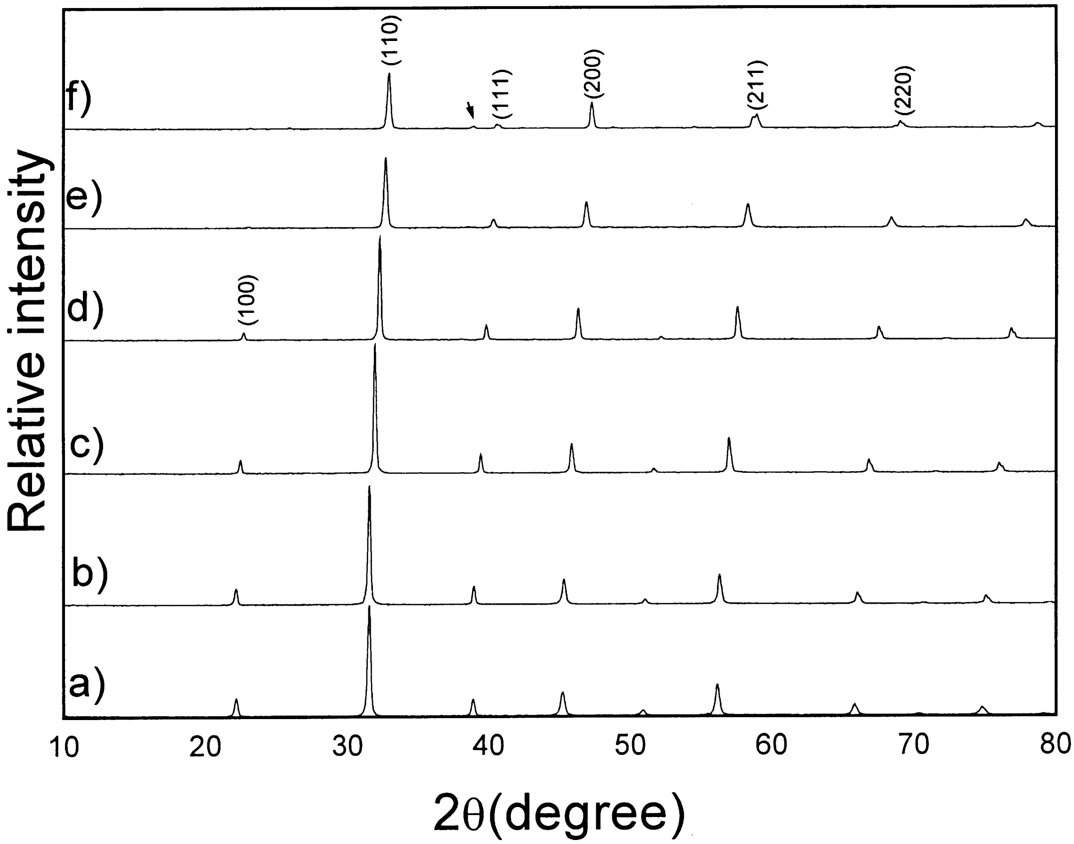

Fig. 1. XRD patterns of $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ dielectrics with various compositions: (a) $x=0$; (b) $x=0.1$; (c) $x=0.3$; (d) $x=0.5$; (e) $x=0.7$; (f) $x=0.9$.

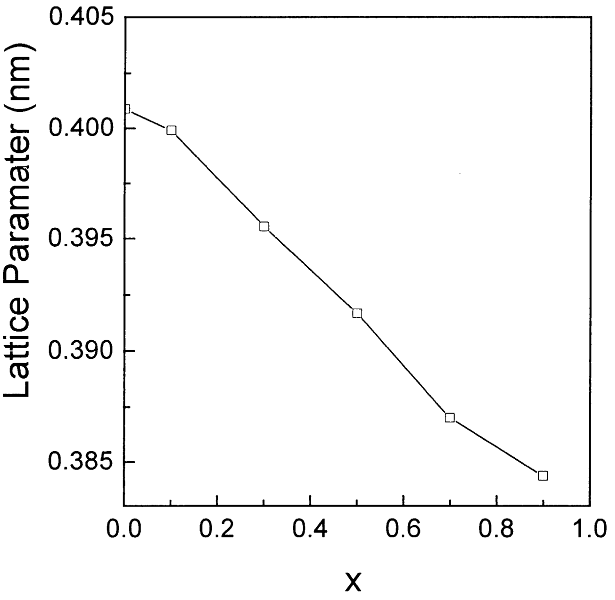

Fig. 2. Lattice parameter of cubic perovskite phase as function of x in $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ dielectrics.

demonstrates the complementarities of the Raman spectroscopy (sensitive to short-range order) to X-ray diffraction (long-range order) in the determination of the microstructure of the present dielectrics. Though disorder in PFN had been reported before,[3] the Raman spectra imply that the existence of 1:1 ordered clusters taking on Fm3m space symmetry at least in nanoscale regions. The analogous lines at 265, 430, 510, 570 and 785 cm^{-1} had been found in short-range order PMN.[17] Fig. 3 shows that the ordered clusters do not disappear with the addition of $CaTiO_3$ because of the existence of the near 800 cm^{-1} peak in all compositions. The lines in $x=0.9$ spectrum appear at 181, 238, 276, 462 and 639 cm^{-1} and similarly lines in $CaTiO_3$[19] appear at 180, 247, 286, 471, 639 cm^{-1}. It can be concluded that there are structural changes when x equals to 0.9.

The dielectric properties of $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3$–$xCaTiO_3$ at 1 MHz are shown in Figs. 4–6. Dielectric constant increases firstly when x equals to 0.1, then decreases with further addition of $CaTiO_3$. When x equals to 0.1, the high dielectric constant ($\epsilon = 14{,}400$

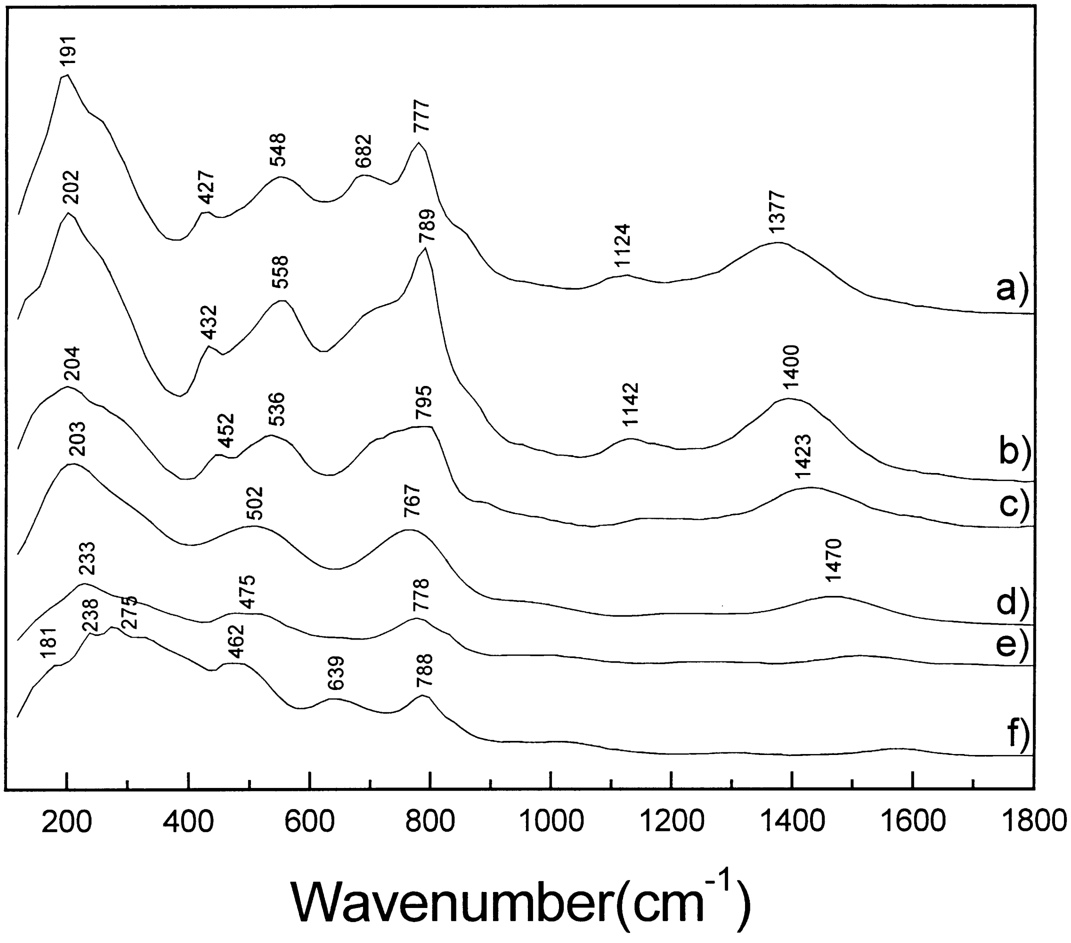

Fig. 3. Raman spectra of $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ dielectrics with various compositions: (a) $x=0$; (b) $x=0.1$; (c) $x=0.3$; (d) $x=0.5$; (e) $x=0.7$; (f) $x=0.9$.

measured at 100 kHz at 20 °C) is attributed to the shifting of $T_{\max}$ to near room temperature as shown in Fig. 7. Meanwhile, the dielectric loss can keep the 10^{-3} order at relatively wide temperature range. And no $T_{\max}$ is observed at the temperature above −50 °C, when x is more than 0.1. As shown in Fig. 5, the dielectric loss is suppressed significantly with increase in the content of $CaTiO_3$. Though the temperature coefficient of dielectric constant shows a non-linear relationship whith $CaTiO_3$ content, the remarkably reduced temperature coefficient of dielectric constant is obtained in the present modified ceramics, which takes the minimum at $x = 0.7$.

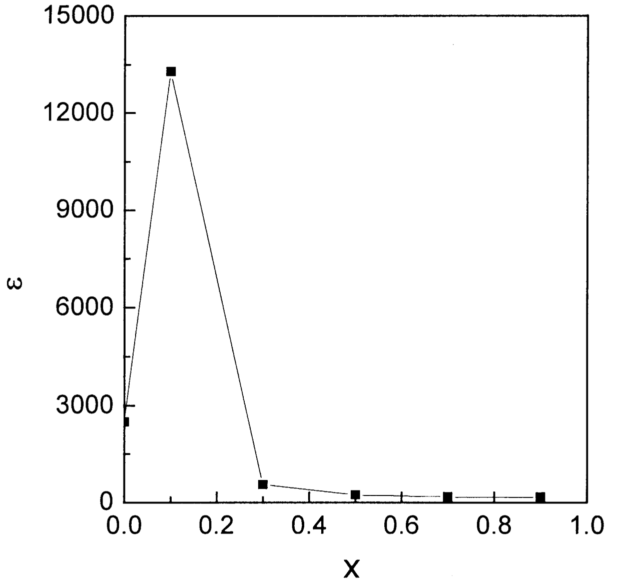

Fig. 4. Dielectric constant (at 1 MHz) of $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ dielectrics as function of composition measured at 20 °C.

In the present system, the dielectric properties do not exhibit similar behavior in many solid solutions for the ferroelectricity of end member. In many solid-solutions, the polarizability of any intermediate composition x can be calculated as a linear mixture of the polarizabilities of the end compounds and the oxide additivity rule is closely obeyed resulting in a near-linear compositional dependence of the τ_ϵ and ϵ.[20–22] As shown in Fig. 4, however, the dielectric constant of the present modified dielectrics with $x = 0.9$ is smaller than those for both end members $CaTiO_3$ and $Pb(Fe_{1/2}Nb_{1/2})O_3$. Also, there is a minimum for the absolute value of the temperature coefficient of dielectric constant with varying the composition in the present system (see Fig. 6). It is similarity to PMN–$CaTiO_3$ solution where ϵ equals to 140 and τ_ϵ equals to −560 when $x = 0.8$.[5] These phenomena may owe to the following reasons. With the addition of $CaTiO_3$, the reduced $T_{\max}$ primarily contributes to the reduction of dielectric constant and τ_ϵ. But the structure change also affects the temperature coefficient of dielectric constant, and therefore the temperature coefficient of dielectric constant turns to increase when x equals 0.9.

In the present system, low loss dielectrics ($\sim 10^{-4}$ at 1 MHz) with high dielectric constant (165–250) and reduced temperature coefficient ($\tau_\epsilon \sim -800$ to −1200ppm/°C) are obtained. The above results suggest that the present materials are the promising candidates for high-frequency capacitors and temperature-compensated capacitors. As shown in Table 1, the improved microwave dielectric properties are obtained in the present ceramics, and a good combination of dielectric constant, Qf value and τ_f is observed for $x = 0.9$: $\epsilon = 164$, $Qf = 6{,}180$ GHz, $\tau_f = +583$ ppm/°C. The present modified ceramics have great potential as high-ϵ microwave

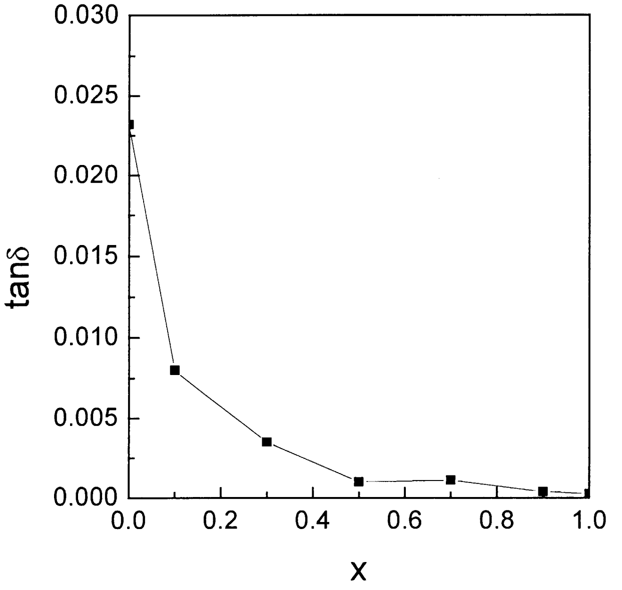

Fig. 5. Dielectric loss (at 1 MHz) of $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ dielectrics as function of composition.

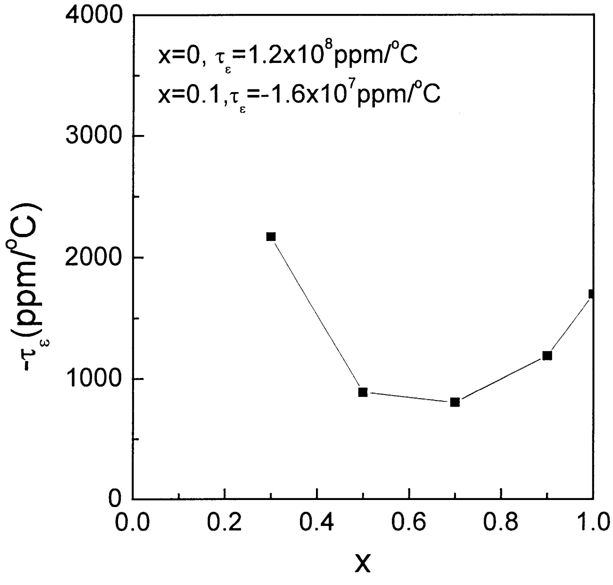

Fig. 6. Temperature coefficient of dielectric constant of $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ dielectrics as function of composition.

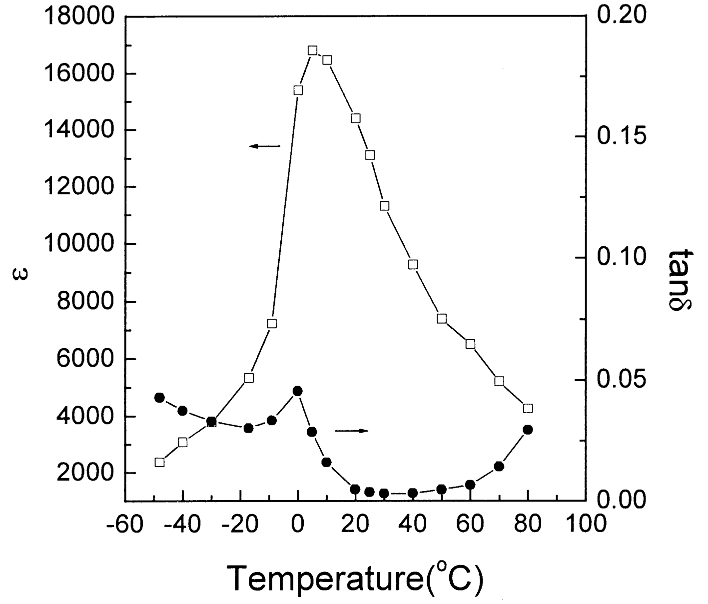

Fig. 7. Temperature dependence of dielectric constant and dielectric loss in $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ dielectrics ($x=0.1$) at 100 KHz.

Table 1
Microwave dielectric properties of $(1-x)Pb(Fe_{1/2}Nb_{1/2})O_3/xCaTiO_3$ dielectrics

x	Sintering condition	f_o (GHz)	ϵ	tanδ	Qf (GHz)	τ_f (ppm/°C)
0.3	1150 °C/3 h	1.42	565.9	0.012	120	1075
0.5	1200 °C/3 h	2.35	232.1	0.0027	870	433
0.7	1200 °C/3 h	2.66	172.7	0.0033	810	392
0.9	1200 °C/3 h	2.78	164.2	0.00045	6180	583

materials if the temperature coefficient can be suppressed further.

4. Conclusions

The low-loss dielectrics with high dielectric constant and reduced temperature coefficient were prepared by incorporating low-loss phase $CaTiO_3$ into $Pb(Fe_{1/2}Nb_{1/2})O_3$, where ceramics all took cubic perovskite structure according to X-ray diffraction. The Raman spectra, however, were consistent with the Fm3m space symmetry which implies the existence of similar 1:1 ordered clusters at least in nanoscale regions, except for $x=0.9$. The variation tendency of the dielectric constant and the temperature coefficient of dielectric constant much differed from the linear mixture rule, and these phenomena were connected to the shifting T_{max} to the low temperature side and the structural transition. Good microwave dielectric properties were obtained for $x=0.9$:$\epsilon=164$, $Qf=6{,}180$GHz, $\tau_f=+583$ ppm/°C. It would be the primary issue to further reduce the temperature coefficient in the future work.

Acknowledgements

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