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$Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films with improved microwave dielectric properties

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Abstract. $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films with different $BaTi_4O_9$ concentrations were deposited on (100) $LaAlO_3$ (LAO) single crystal substrates via a pulsed laser deposition (PLD) using a combined target configuration of $Ba_{0.1}Sr_{0.9}TiO_3$ and $BaTi_4O_9$ ceramics. The $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films showed good crystal growth with *c*-orientation on (100) LAO substrates, which were characterized by X-ray diffraction (XRD). From scanning electron microscopy (SEM) measurements, we could see that the crystal grains of the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films changed from small ordered clusters to big triangle clusters with the increase of $BaTi_4O_9$ concentration. The microwave dielectric properties of the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films under low temperature range from 65 to 120 K were measured at 7.7 Ghz and the results showed that all the thin films were in the paraelectric state. The dielectric constant and loss tangent of the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films were modified by the addition of $BaTi_4O_9$. Specifically, the loss tangent of the composite thin films was greatly decreased from 0.025 for pure $Ba_{0.1}Sr_{0.9}TiO_3$ to 0.020 for the 4.7% $BaTi_4O_9$ doped $Ba_{0.1}Sr_{0.9}TiO_3$, and finally to 0.010 for the 15.9% $BaTi_4O_9$ doped $Ba_{0.1}Sr_{0.9}TiO_3$ sample.

PACS. 84.40.Dc Microwave circuits – 77.55.+f Dielectric thin films – 81.15.Fg Laser deposition – 61.10.-i X-ray diffraction and scattering

1 Introduction

High dielectric tunability and low dielectric loss are the basic requirements for microwave device applications, such as tunable oscillators, phase shifters and varactors [1–4]. Ferroelectric materials, for example, barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$), are known to be the most promising candidates for these applications [3,4]. One of the critical issues for practical device application of ferroelectric materials is to reduce their dielectric losses [5,6].

Recently, many efforts have been made to reduce the dielectric losses of $Ba_xSr_{1-x}TiO_3$. The doping method is one of the most effective and easy operational ways to reduce the loss tangent of $Ba_xSr_{1-x}TiO_3$ materials [5–7]. It has been found that doping of other oxides with low dielectric losses, such as MgO, Al_2O_3 and ZrO_2 et al. into $Ba_xSr_{1-x}TiO_3$ material, could reduce its dielectric losses. Some papers on the dielectric properties of the $Ba_{0.5}Sr_{0.5}TiO_3$ ceramic or thin films doped with MgO or ZrO_2 have been published [5,6,8,9]. It has been found that both dielectric loss and insulating characteristics of the doped $Ba_xSr_{1-x}TiO_3$ thin films were significantly improved compared to that of undoped ones. Unfortunately, the dielectric constant and the tunability of the $Ba_xSr_{1-x}TiO_3$ dramatically decreased as the doped oxide concentration was increased. For instance, the dielectric constant of the doped MgO and Al_2O_3 was much smaller than that of pure $Ba_xSr_{1-x}TiO_3$. In order to solve this problem, new kind of doped materials should be developed.

It is well known that the $BaTi_4O_9$ ceramics (orthorhombic with space group Pmmn) is one of the microwave dielectric materials with low dielectric loss tangent and proper dielectric constant. The microwave dielectric properties have been investigated by Masse et al. [10–13] They reported that $BaTi_4O_9$ had relative dielectric constant of 38, loss tangent of 0.0004, and temperature coefficient of 249 ppm/°C [10–12]. It was also reported by Choy et al. that $BaTi_4O_9$ ceramics prepared via a citrate route had dielectric constant of 36, loss tangent delta of 0.0002 at 10.3 GHz, and temperature coefficient of resonant frequency of 16 ppm/°C [14]. It is well

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known that the microwave devices usually work at 77 K. At the same time, the transition temperature range from ferroelectric to paraelectric state of the $Ba_{0.1}Sr_{0.9}TiO_3$ is near the liquid nitrogen temperature 77 K and it is one of the best candidates to fabricate microwave devices. In the present study, we investigated the low temperature microwave dielectric properties of $Ba_{0.1}Sr_{0.9}TiO_3$ doped with $BaTi_4O_9$ thin films deposited on (100) $LaAlO_3$ single crystal substrate by PLD method tailored to the need of high temperature superconducting tunable devices.

2 Experimental

The $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films were deposited on (100) $LaAlO_3$ single crystal substrates, via a pulsed laser deposition (PLD) system with a KrF excimer laser (Lambda Physik, 248 nm, 30 ns) at 3 Hz repetition frequency, with an energy density of 250 mJ/pulse. The deposition was conducted for 45 minutes, at a substrate temperature of 720 °C and a chamber oxygen pressure of 0.1 mbar. The distance between substrate and target was 50 mm. A $Ba_{0.1}Sr_{0.9}TiO_3$ ceramic target, with a little piece of $BaTi_4O_9$ ceramic sticking on its surface, was used to deposit the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films. The films with different contents of $BaTi_4O_9$ were deposited from the combined targets with different area ratio of $Ba_{0.1}Sr_{0.9}TiO_3$ and $BaTi_4O_9$. Pure $Ba_{0.1}Sr_{0.9}TiO_3$ film was also deposited as a comparison. The thickness of the $Ba_{0.1}Sr_{0.9}TiO_3$ and $BaTi_4O_9$ thin films deposited on LAO was about 500 nm. The $Ba_{0.1}Sr_{0.9}TiO_3$ and $BaTi_4O_9$ targets used in the present experiments were prepared via the conventional ceramic processing, using commercial powders of $BaCO_3$ (MERCK, Germany, 99.9%), $SrCO_3$ (MERCK, Germany, 99.9%), and TiO_2 (MERCK, Germany, 99.9%). The films derived from the targets of pure $Ba_{0.1}Sr_{0.9}TiO_3$ and $Ba_{0.1}Sr_{0.9}TiO_3$ doped with $BaTi_4O_9$ area ratio to the $Ba_{0.1}Sr_{0.9}TiO_3$ target of 10, 20, 30 and 40% were abbreviated as pure S0, S1, S2, S3 and S4, respectively.

Phase composition and crystallization of the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films were characterized by X-ray diffraction (XRD) using Philips PW 1729 type X-ray diffractometer with Cu K_α radiation and the surface morphology was examined by scanning electron microscopy (SEM) using a JEOL JSM-6340F type field emission scanning electronic microscope. Film thickness was determined from cross-sectional SEM images. The element composition was checked by Rutherford backscattering (RBS) analysis in combination with proton induced X-ray emission (PIXE), made by Research Centre for Nuclear Microscopy, National University of Singapore. Microwave dielectric properties of the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films were measured using a home-made nondestructive microstrip dual-resonator method at low temperature ranging from 65 to 120 K and microwave frequency of ~7.7 GHz [15]. The microstrip split resonator, formed by a straight microstrip line with a 36 μm gap in the center, was patterned on a TMM10i microwave substrate. The films were placed on top of the microstrip line, covering the gap. Dielectric constant and loss tangent of the films were derived from the resonant frequency f_1, f_2 and quality factor Q_1, Q_2, of the microstrip dual-resonator. The method was verified by measuring the dielectric properties of $LaAlO_3$ single crystal substrate, with $\varepsilon_r = 21$ and $\tan\delta = 2 \times 10^{-5}$. In the study of the electric field dependence of the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films, a maximum dc voltage of 2.1 kV was applied through two electrode pads on the microstrip circuit board across a gap of about 2.6 mm, corresponding to a maximum electric field of ~8.1 kV/cm.

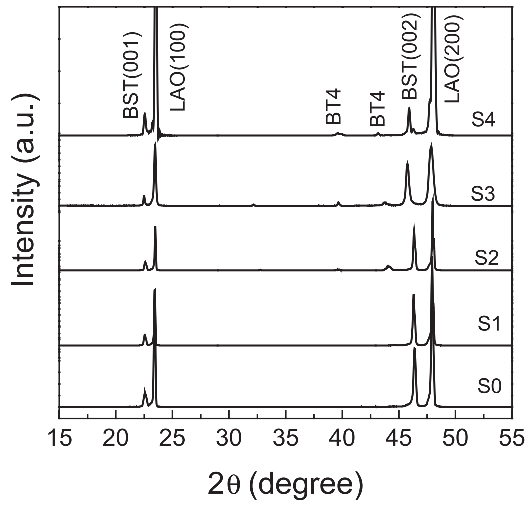

Fig. 1. XRD patterns of pure $Ba_{0.1}Sr_{0.9}TiO_3$ and $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films (S0 to S4) deposited on (100) LAO single crystal substrates.

3 Results and discussion

Figure 1 shows the XRD patterns of the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films. The pure $Ba_{0.1}Sr_{0.9}TiO_3$ (S0) thin film was strongly epitaxial, where only (100) and (200) diffraction peaks can be observed. The 10% target ratio of $BaTi_4O_9$ to $Ba_{0.1}Sr_{0.9}TiO_3$ deposited sample S1 showed a similar XRD pattern compared to the pure $Ba_{0.1}Sr_{0.9}TiO_3$, revealing that the addition of $BaTi_4O_9$ with low concentration does not influence the film structure. As the target ratio of $BaTi_4O_9$ to $Ba_{0.1}Sr_{0.9}TiO_3$ increased to above 20%, the doped $BaTi_4O_9$ phases were detected by the XRD measurement ($2\theta \approx 39.8°$, $44.2°$). With the increase of concentration of $BaTi_4O_9$, the intensity of the peaks corresponding to $BaTi_4O_9$ becomes stronger. The lattice constant c value for the pure $Ba_{0.1}Sr_{0.9}TiO_3$ (S0) and the doped BST (S1 to S4) calculated form the XRD results were 3.911, 3.919, 3.910, 3.921 and 3.918 Å, respectively. The lattice constant c value of the doped BST thin films did not change very much in comparison to that of pure $Ba_{0.1}Sr_{0.9}TiO_3$ thin films, because the lattice constant c value of $BaTi_4O_9$ is 3.797 Å, which is a value very similar to that of pure BST thin films.

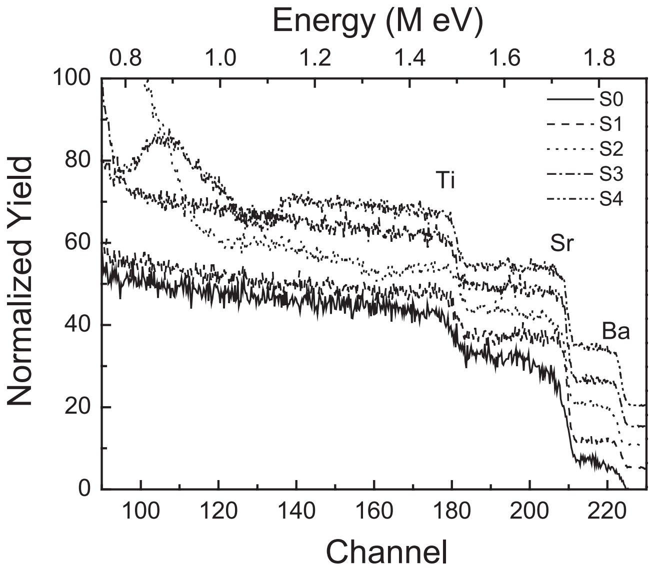

Fig. 2. Representative RBS curves of pure $Ba_{0.1}Sr_{0.9}TiO_3$ and $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films (S0 to S4) deposited on (100) LAO single crystal substrates.

Figure 2 presents the selected RBS curves of the composite films. The composition of the combined thin films calculated from RBS measurements is listed in Table one. The concentration of the $BaTi_4O_9$ in S1 to S4 is about 4.7%, 9.1%, 12.3% and 15.9%, respectively. The doped content of $BaTi_4O_9$ for S1 to S4 increased as the area ratio of $BaTi_4O_9$ to $Ba_{0.1}Sr_{0.9}TiO_3$ targets increased. For the deposition rate of the $BaTi_4O_9$ thin film is not equal to the $Ba_{0.1}Sr_{0.9}TiO_3$ thin film, the doped content value of the combined thin films (S1 to S4) is not as same as the targets area ratio of $BaTi_4O_9$ to $Ba_{0.1}Sr_{0.9}TiO_3$ targets.

The SEM images of the $Ba_{0.1}Sr_{0.9}TiO_3$ and $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films are shown in Figure 3. The pure $Ba_{0.1}Sr_{0.9}TiO_3$ thin films showed smooth surface with small grain size about 80 to 100 nm, as shown in Figure 3a. As the doped $BaTi_4O_9$ content is lower than 4.7% (S1), the crystallization characteristics keeps in same state as the pure $Ba_{0.1}Sr_{0.9}TiO_3$, while its crystal size enlarges. As the content ratio of $BaTi_4O_9$ to $Ba_{0.1}Sr_{0.9}TiO_3$ is larger than 1:0.1 (S2 to S4), the morphology of the combined thin films changes much than the pure $Ba_{0.1}Sr_{0.9}TiO_3$ thin film. The combined thin films have well crystallized property and the crystal grains are in triangle shape and the grain size ranges from 250 to 300 nm. However, the high concentration of $BaTi_4O_9$ led to significant change in the grain size and morphology. The grain size became slightly enlarged and the grain morphology changed to triangular as the $BaTi_4O_9$ content increased. For instance, the grain sizes for the 15.9% $BaTi_4O_9$ doped BST (S4) thin film were about 300 nm and were triangle-shaped.

It is well known that the practical applications require ferroelectric material in paraelectric state since it has relatively lower loss tangent in the paraelectric than in ferroelectric state. As the ferroelectric materials are in ferroelectric state, their dielectric constant increases with the increase of temperature, if their dielectric constant decreases with the increase temperature, it indicates that the ferroelectric materials are in paraelectric state. Figures 4a and b plot the dielectric constant and $\tan\delta$ of the pure $Ba_{0.1}Sr_{0.9}TiO_3$ (S0) and the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films (S1-S4) as a function of temperature ranging from 65 to 120 K, respectively. The dielectric constant of the pure $Ba_{0.1}Sr_{0.9}TiO_3$ and the $BaTi_4O_9$ doped $Ba_{0.1}Sr_{0.9}TiO_3$ thin films all decrease with the increase of temperature, which reveals that the films are all in the paraelectric state in this temperature range. The loss tangent of the pure $Ba_{0.1}Sr_{0.9}TiO_3$ and the $BaTi_4O_9$ doped $Ba_{0.1}Sr_{0.9}TiO_3$ thin films (S0 to S4) almost keep in the same value with a little increase as the temperature increases from 65 to 120 K.

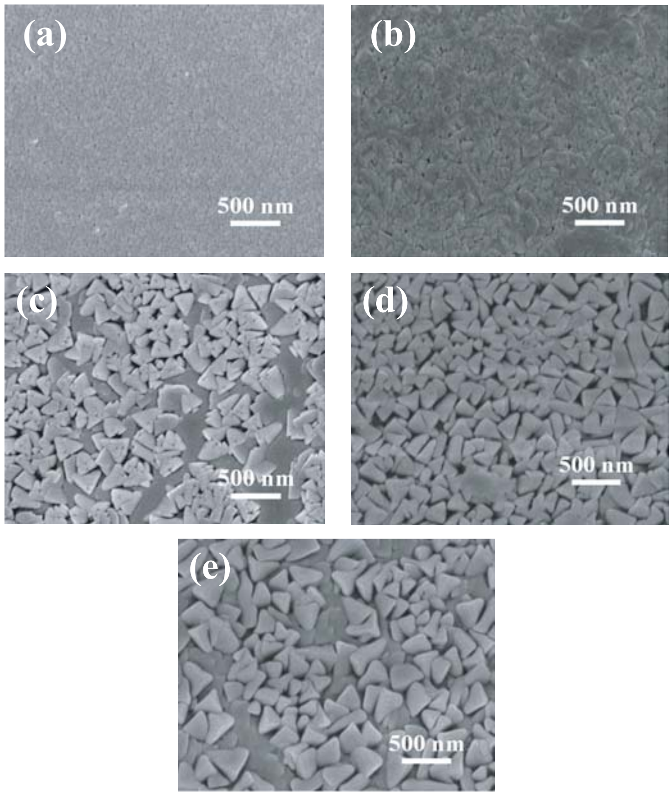

Fig. 3. SEM images of pure $Ba_{0.1}Sr_{0.9}TiO_3$ and $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ composite thin films (S0 to S4): (a) S0, (b) S1, (d) S2, (d) S3 and (e) S4 deposited on (100) LAO single crystal substrates.

Dielectric constant and loss tangent of the pure $Ba_{0.1}Sr_{0.9}TiO_3$ and the $BaTi_4O_9$ doped $Ba_{0.1}Sr_{0.9}TiO_3$ thin films as a function of an external electric field are demonstrated in Figure 5. Both the dielectric constant and loss tangent decrease with increasing electric field. This behavior of ferroelectric materials offers us a good opportunity to fabricate microwave device with device parameters being tunable by a dc bias. In ABO_3 perovskite structure, spontaneous polarization of ferroelectric materials appears due to the presence of the dipole derived from the deviation of B site ion from the center position of octahedral oxygen cage. These dipoles respond to ac electric field but are suppressed by dc field.

Table 1. Dielectric properties of pure $Ba_{0.1}Sr_{0.9}TiO_3$ and $BaTi_4O_9$ doped $Ba_{0.1}Sr_{0.9}TiO_3$ thin films at temperature 77 K.

Sample	$BaTi_4O_9$ Concentration [%]	ε_r	$\tan\delta$	Tunability (%) [at 8.1 kV/cm]	K-factor [at 8.1 kV/cm]
S0	0	932	0.0246	13.95	5.67
S1	4.7	895	0.0198	13.74	6.94
S2	9.1	874	0.0179	13.04	7.28
S3	12.3	836	0.0141	11.00	7.80
S4	15.9	800	0.01	10.5	10.5

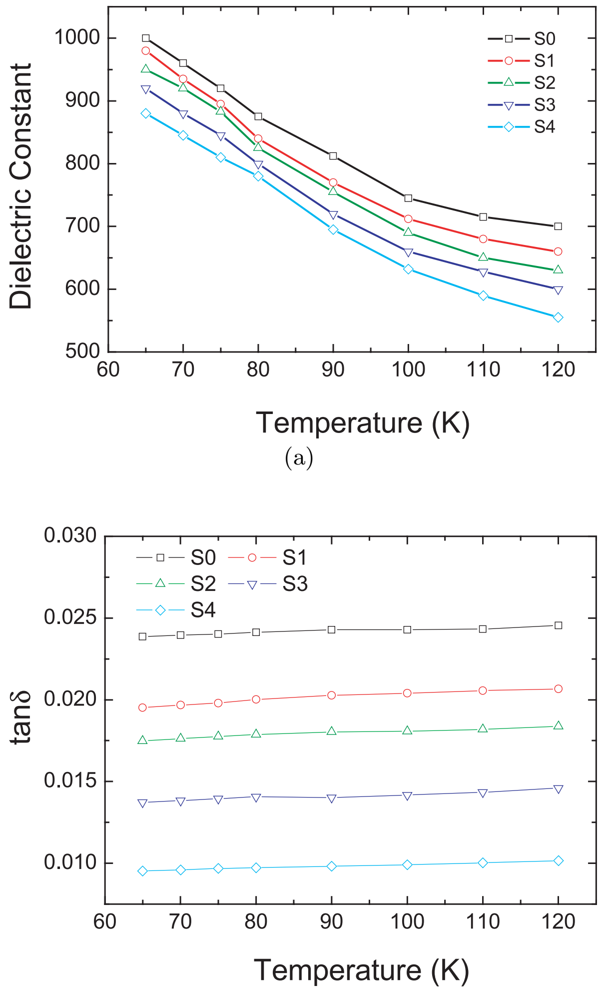

Fig. 4. Microwave dielectric constant (a) and $\tan\delta$ (b) of pure $Ba_{0.1}Sr_{0.9}TiO_3$ and $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ (S0 to S4) thin films deposited on (100) LAO single crystal substrates as a function of temperature ranging from 65 to 120 K at 7.7 GHz measure frequency.

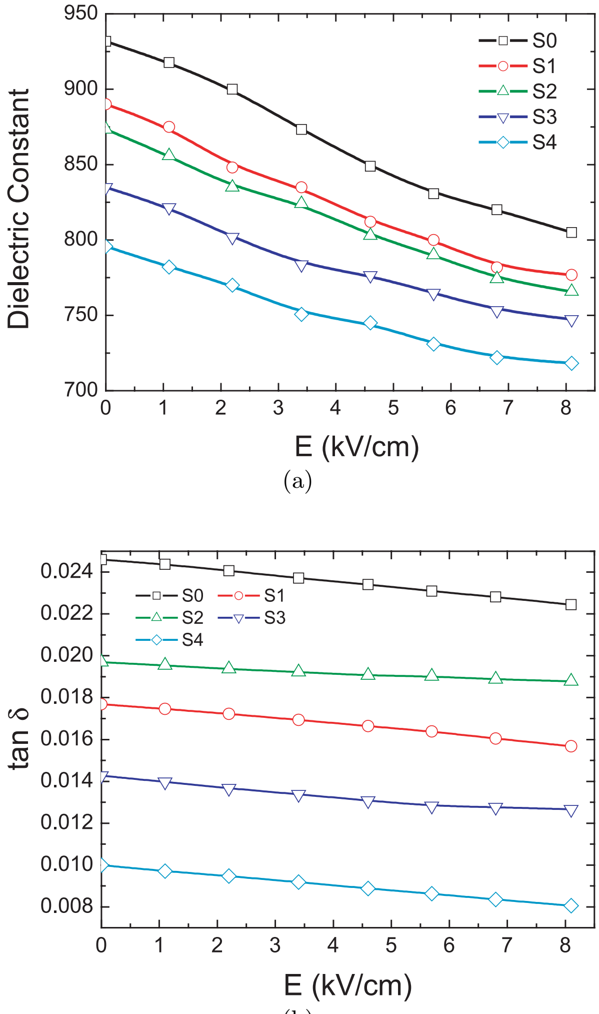

Fig. 5. Dielectric constant (a) and loss tangent (b) of pure $Ba_{0.1}Sr_{0.9}TiO_3$ and $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films (S0 to S4) as a function of applied electric field ranging from 0 to 8.1 kV/cm at the 7.7 GHz measured frequency at 77 K.

The dielectric parameters of the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films are listed in Table 1. It is noted that the pure $Ba_{0.1}Sr_{0.9}TiO_3$ thin film has a dielectric constant of 932 with loss tangent of ~0.025 (both at zero electric field), a tunability of ~14% and a figure of merit of ~5.7 (at 8.1 kV/cm). For the $BaTi_4O_9$ doped $Ba_{0.1}Sr_{0.9}TiO_3$ composite thin films (S1 to S4), dielectric constant, loss tangent and tunability decrease from 895 to 800, 0.02 to 0.01 and 13.7 to 10.5%, respectively, while the figure of merit increases from 6.9 to 10.5.

4 Conclusions

The microwave dielectric properties of $BaTi_4O_9$ doped $Ba_{0.1}Sr_{0.9}TiO_3$ thin films deposited on LAO (100) substrates by PLD have been investigated in the present paper. We found that the pure $Ba_{0.1}Sr_{0.9}TiO_3$ and the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films are all in paraelectric state at the low temperature ranging from 65 to 120 K and their dielectric constant and loss tangent decreased with increasing the concentration of $BaTi_4O_9$. The dielectric properties of the $Ba_{0.1}Sr_{0.9}TiO_3$-$BaTi_4O_9$ thin films are suitable for fabrication of high performance microwave devices working at a low temperature range.

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