

# Effect of ferroelectric material activity on dielectric properties of ferroelectric-dielectric composite ceramics

Jingjing Jin (✉ [1461032691@qq.com](mailto:1461032691@qq.com))

Shandong University of Technology

Le Xin

Zibo Normal College

Shiting Shen

Shandong University of Technology

Zhengxin Li

Shandong University of Technology

Yuze Xue

Shandong University of Technology

Luchao Ren

Shandong University of Technology

Xue Guo

Shandong University of Technology

Long Chen

Shandong University of Technology

Jiwei Zhai

Tongji University

Mingwei Zhang

Shandong University of Technology

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## Research Article

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# Abstract

$Ba_{0.6}Sr_{0.4}TiO_3$  ceramic doped with MgO was prepared by a conventional solid state reaction method. The effects of  $Ba_{0.6}Sr_{0.4}TiO_3$  pre-sintering at different temperatures on the phase composition, microstructure and microwave dielectric properties of composite ceramics were studied. The effect of different pre-sintering temperatures on composite ceramics is mainly reflected in different ion diffusion degree. The results show that the different pre-sintered ceramics have two crystal phases of perovskite structure  $Ba_{0.6}Sr_{0.4}TiO_3$  and cubic phase MgO. As the pre-sintering temperature increases, the dielectric permittivity of the composite ceramic decreases, and the grain size decreases obviously. When the pre-sintering temperature rises above  $1200^{\circ}C$ , the Curie peak of composite ceramic was strongly suppressed and broadened. The tunability at room temperature increases with the increase of the pre-sintering temperature of  $Ba_{0.6}Sr_{0.4}TiO_3$ , which is due to the lower ion diffusion weakens  $T_c$  movement to low temperature. In addition, the loss tangent of the samples at room temperature was kept at a low level. When the pre-sintering temperature of  $Ba_{0.6}Sr_{0.4}TiO_3$  is  $1250^{\circ}C$ , the tunability is up to 29% (at 30 kV/cm), and the best Q value 132 (at 1.37GHz) was generated which is the most obvious improvement in dielectric properties compared to other pre-sintering temperature. This indicates that with the decrease of ion diffusivity, the properties of the ferroelectric-dielectric composite ceramics were significantly improved.

## Relevance Summary

- 1.The effect of pre-sintering temperature on material activity makes the degree of ion diffusion between the ferroelectric-dielectric phases different.
- 2.The ferroelectric-dielectric material exhibits compound effect at a higher pre-sintering temperature, which reduces the decrease in dielectric properties caused by the doping effect.
- 3.Studying the phenomenon of ion diffusion is beneficial to improve the dielectric properties of BST to meet the application requirements of electronic equipment.

## 1. Introduction

Barium strontium titanate (abbreviated as BST) is an infinite solid solution of strontium titanate and barium titanate with the characteristics of low loss tangent and high tunability. It is widely used in tuning microwave devices, such as ferroelectric phase shifters, resonators, filters and phased array radars[1–3]. However, it is difficult to achieve impedance matching for the pure barium strontium titanate because of the excessive dielectric permittivity[4, 5]. The most effective method to solve this problem is to composite and/or dope BST with some special materials with low dielectric permittivity and high Q value, such as non-ferroelectric oxides, rare earth oxides or transition metal oxides[6–8].

Summarizing the existing research results, it is found that although the ferroelectric-dielectric composite ceramics solved the problem of high dielectric permittivity of BST, it also deteriorates its Q value significantly[9, 10]. When implementing the pure composite effect, the Q value of ferroelectric-dielectric composite ceramic should be between BST and dielectric material. But the reality is that the Q value of the sample is even smaller than that of BST, which is quite different from the original idea. Therefore, it considers that this is attributed to the effect of ion diffusion on the harmonic vibration of Ti ions at the B site in the BST[11–13].

A lot of research work confirmed that MgO doped BST has a good modification effect compared with other oxides or dielectric[6, 7, 14–16]. BST with different activity was obtained at different pre-sintered temperatures. In this paper, we attempted to composite the BST pre-sintered at different temperatures and MgO, then study the influence on the properties of composite ceramics according to the different ion diffusion effects exhibited when BST and MgO are combined with different activities. The relationships among phase structure, microstructure, dielectric properties and ion diffusion were systematically analyzed.

## 2. Experimental

Composite ceramic 92.5wt%Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub>-7.5wt%MgO was prepared by solid-state sintering process. Used high-purity BaTiO<sub>3</sub> (99.9%), SrTiO<sub>3</sub> (99.9%) and MgO(99%) as raw materials. The pre-sintered temperatures of barium strontium titanate were 1100°C, 1150°C, 1200°C, 1250°C, respectively. Mixed Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> and MgO with zirconia ball in ethanol at a stoichiometric ratio for 12h and consequently dried at 110°C. Then add 8% polyvinyl alcohol (PVA) to the powder to make granules and press them into a disk-shaped pallets. The sample was debonded at 550°C for 240 minutes and then sintered at 1400°C for 4 hours.

Using X-ray diffraction (XRD) analyzed the phase structure of the material (Bruker AXS D8 Advance, Germany). The microstructure and element distribution of the sample was tested by Backscattered Electron Image (BEI) (Quanta 250 USA) and Energy disperse spectroscopy (EDS). The density of the sample that we tested and calculated on the basis of Archimedes' law using the weighing method. LCR (Tonghui 2827C, China) was used to measure the relationship between the low-frequency dielectric properties and the temperature of the sample. A high-voltage source (Keithley 2410, USA) was used to interconnect the LCR meter (TH2816A, China) to measure the dielectric permittivity at room temperature and 10khz DC bias voltage. Using the vector network analyzer (Keysight E5071C, USA) to test the microwave dielectric properties of ceramic samples.

## 3. Results And Discussion

Figure 1 is the XRD pattern of the sintered samples, it is obvious that only the cubic MgO and perovskite BST can be observed. Without any other impurity phases. It can be seen that when the pre-sintering temperature is 1100°C, the diffraction peak intensity of the sample is significantly lower than other

temperatures. This may be due to the low pre-sintering temperature affecting the crystallinity of the composite ceramic[17, 18]. Compared with pure BST, the diffraction peaks shifted to low angle after doping with MgO. The movement of the diffraction peak is due to the ion diffusion caused by the doping effect, and  $Mg^{2+}$  (0.067nm) is larger than  $Ti^{4+}$  (0.0607nm) in the ionic radius. Therefore,  $Mg^{2+}$  replaces  $Ti^{4+}$  at the B site into  $ABO_3$  perovskite structure, reducing the crystal parameters and causing the diffraction peak to move to the low angle. The inset in Fig. 1 shows an enlarged view from  $45.0^\circ$  to  $46.8^\circ$ . As the temperature of BST increases, the diffraction peak shifts slightly to the high angle. This is mainly because the high pre-sintering temperature reduces the activity of BST, obstructs the ion diffusion during the sintering process, and reduces the driving force to move to a low angle, which is getting closer to the diffraction peak of pure BST. As the pre-sintering temperature reaches  $1250^\circ C$ , the degree of ion diffusion is suppressed to the limit, so the diffraction peak no longer moves to a high angle. On the other hand, this change may be attributed to the increase in stress caused by the reduction of grain size[19]. Both of these factors cause the shrinkage of BST crystal lattice, which is the reason for the deviation of perovskite diffraction peak to the high angle.

Figure 2 presents the BEI image of the sample. It can be observed that with the increase of pre-sintering temperature, the grain size decreases and the uniformity of the crystal particles tends to be reduced. As a grain growth retardant, MgO has the effect of grain refinement. This indicates that the ion diffusion weakens when the pre-sintering temperature is higher, which more reflects the composite effect between the ferroelectric-dielectric phase. In addition, the chemical compositions of the crystal grains in different colors were detected using EDS, which were displayed in Fig. 3. The results showed that the main element of the black particles (area 1) were Mg and O proving the existed MgO grains, and a small amount of Ba and Ti were detected. The light color particles, which were determined to be BST particles according to the EDS results, and the appearance of few Mg elements in area 2 meant a complex ion diffusion occurred between BST and MgO. When the BST's pre-sintering temperature from  $1150^\circ C$  increased to  $1200^\circ C$ , the composite effect of this two phase are dominant, and the effect of MgO on inhibiting grain growth has gradually emerged, which has significantly reduced the grain size. However, as the pre-sintering temperature from  $1200^\circ C$  increased to  $1250^\circ C$ , the BST grains sizes were kept small because the reduced powders activity at high pre-sintering temperature weakened, the sintering driving force to limit the growth of the crystal.

Figure 4 shows the density of the sintered samples. It can be seen that as the BST pre-sintering temperature increases, the density of the material decreases. According to the sintering mass transfer theory of electronic ceramics, under the same sintering conditions the higher the activity of the powder, the faster the grain grow [20]. When the pre-sintering temperature is lowered, the powder activity is high and the growth rate will be big, so the grain size of the sample is large. The pores are gradually eliminated along with the movement of the grain boundary, forming a densified ceramic with a larger bulk density. With the pre-sintering temperature increases, the powders activity decreases, then the grains grow slowly, and the grain size is small, which is consistent with the BEI results. In addition, the reduced activity will

also hinder the ion diffusion between the particles, which is detrimental to the grains growth and the final sintering density.

Figure 5 is the dielectric temperature spectrum at 10kHz, showing the function relationship between dielectric permittivity( $\epsilon$ ) and loss tangent( $\tan\delta$ ) with pre-sintering temperature. The relevant dielectric properties of composite ceramics were summarized in Table 1. The results show that the dielectric properties of the samples are greatly affected by the pre-sintering temperature of BST. Compared with the samples pre-sintered in 1100°C and 1150°C, the dielectric permittivity of that pre-sintered in 1200°C and 1250°C decreased significantly, and the dielectric peaks were strongly suppressed and broadened. This is because the grain size decreases and grain boundary composition increases when the pre-sintering temperature increase, resulting in the domain wall pinning effect that may reduce the dielectric permittivity[21]. The Curie temperature increases with the increase of pre-sintering temperature. On the one hand, it is the reason for the grain size; the phonon momentum distribution increases, and lattice vibration becomes more difficult with the grain size decreases, resulting in increased internal stress. To break this equilibrium state requires more heat energy, which needs to be obtained from the external environment, so that the Curie temperature moves to a higher temperature [22]. In addition, compared with pure BST, the ion diffusion phenomenon in ferroelectric-dielectric composite system makes  $T_c$  to move to a lower temperature[23]. As the pre-sintering temperature increases, the Curie temperature of the sample is closer to that of pure BST.  $T_c$  changes from 243.5K to 251.5K, as the pre-sintering temperature increased from 1200°C to 1250°C. This is because the excessively high pre-sintering temperature reduces the sintering activity of BST, and the ion diffusion is inhibited. Therefore, inhibiting the ion diffusion can make the system show more composite effects[4]. Besides it can be observed from Table 1 that the increase of BST pre-sintering temperature increases the dielectric permittivity at room temperature. Obviously, the dielectric permittivity at about 20°C changes sensitively with the Curie temperature. And the dielectric loss increases with the increase of the pre-sintering temperature. This is mainly because the extrinsic loss caused by the change of pre-sintering temperature, which is related to density and crystal order degree. In addition, we noticed that the loss tangents of all samples at room temperature were kept at a low level.

$$T = \frac{\epsilon(0) - \epsilon(E)}{\epsilon(0)} \times 100\%$$

Tunability is usually defined as: . Among them, when no electric field is applied, the dielectric permittivity is recorded as  $\epsilon(0)$ ; when an electric field is applied, the dielectric permittivity is recorded as  $\epsilon(E)$ . Fig. 6 shows the tunability of MgO-doped BST ceramic samples with different pre-sintering temperatures measured at room temperature and 10 kHz DC electric field. As the pre-sintering temperature increase, the material activity and the ion diffusion decrease, which leads to the  $T_c$  not moving to the low temperature, and the decrease of the crystal grain size makes the  $T_c$  move to the high temperature. As shown in Fig. 6, with the pre-sintering temperature increase, the tunability of the ceramic sample increase, which is attributed to the  $T_c$  shifted to the high temperature. It's documented that the tunability is considerable in the temperature range near  $T_c$  [24]. When  $T_c$  is close to the test

temperature, the more PNRs generated by the acceptor doping, the polarization domain as an external contribution increases the tunability [25]. In addition, the reduction in grain size increases the connectivity level of BST, while enhancing the interaction between  $Ti^{4+}$ . This is also a reason for the increase of the tunability. The tunability of the composite ceramic is up to 29% when the pre-sintering temperature is 1250°C.

The dielectric properties of BST-MgO ceramic sample at microwave and low frequencies were summarized in Table 1. Compared with the results at low frequencies (less than 1 MHz), the dielectric permittivity of ceramic sample decreased significantly at microwave frequency. With the increase of the pre-sintering temperature, the quality factor Q shows an upward trend. It can be concluded that when the BST pre-sintering temperature is too high, the sintering activity is reduced, resulting in a low ion diffusion. The low ion diffusion degree will not affect the long-range ordering of the B site in BST, which makes the Q value enhanced at the microwave frequency, and especially evident when the pre-sintering temperature reaches 1250°C. Proper pre-sintering temperature can improve the tunability of BST, reduce the dielectric permittivity, and obtain decent Q value.

The occurrence of irregular lattice, lattice defects, lattice strain, etc. affect the equilibrium state of chemical reaction[26]. Different degree of the ion diffusion affects the sintering activity of the pre-sintered powders. The crystal grains becomes finer and their shapes tend to be more irregular. Excessively high pre-sintering temperature will reduce the powder activity, weaken the sintering driving force, and affect the dielectric permittivity and tunability. Therefore, the pre-sintering process of the composite ceramic is very important to control the stability of the preparation, keep the sintering quality and guarantee the dielectric properties.

## 4. Conclusions

$Ba_{0.6}Sr_{0.4}TiO_3$ -MgO composite ceramic was synthesized by solid-state reaction method with different pre-sintering temperature. The microstructure and microwave dielectric properties of the composite ceramic is obviously affected by different pre-sintering temperatures. With the increase of the BST pre-sintering temperature, the activity of the sample decreases, which reduces the grain size and hinders the ion diffusion between the particles. The dielectric permittivity and loss tangent at room temperature are decreased with the increase of pre-sintering temperature. The tunability and Q value of the ceramic samples is significantly increased, manifesting that the microwave dielectric properties of the samples are improved. Comprehensive analysis shows that the higher the sintering temperature, the lower the ion diffusion, the more significant the composite effect between the ferroelectric-dielectric phase, which improves the tunability and Q value, but a higher pre-sintering temperature has a certain influence on the sintering activity and grain uniformity.

## Declarations

## Acknowledgments

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## **Conflicts of interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## **Availability of data and material**

All data generated or analysed during this study are included in this article

**Code availability:** Not applicable

## **Authors' contributions**

Mingwei Zhang, Jingjing Jin contributed to the conception of the study;

Jingjing Jin performed the experiment;

Mingwei Zhang, Jingjing Jin, Shiting Shen, Luchao Ren contributed significantly to analysis and manuscript preparation;

Jingjing Jin performed the data analyses and wrote the manuscript;

Le Xin, Zhengxin Li, Yuze Xue, Xue Guo, Long Chen, Jiwei Zhai helped perform the analysis with constructive discussions

All authors read and approved the final manuscript.

**Ethics approval:** Not applicable

**Consent to participate:** Written informed consent was obtained from individual participants..

**Consent for publication** Written informed consent for publication was obtained from all participants.

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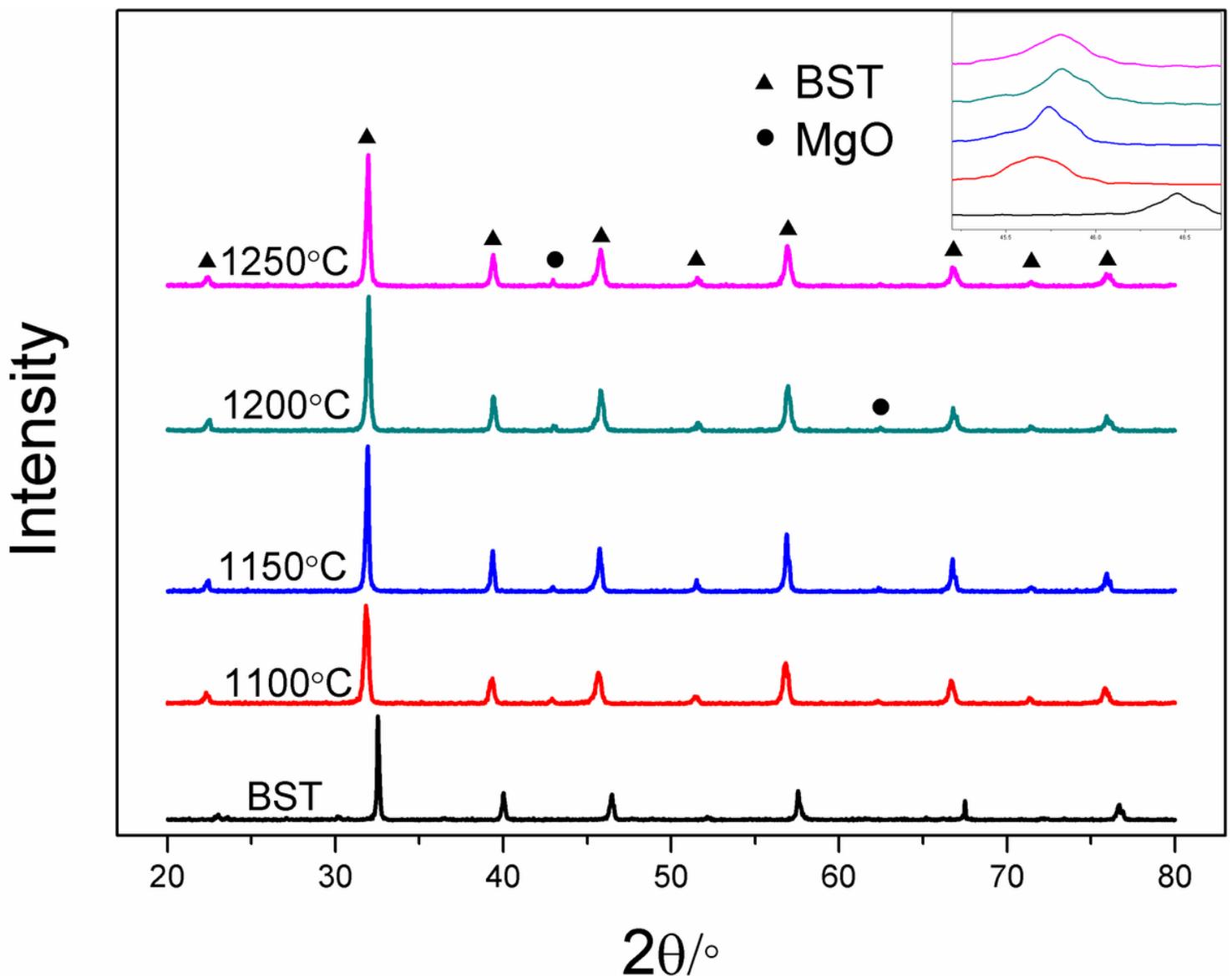
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## Tables

Table 1 Microwave and low frequency dielectric properties of the BST60-MgO composite ceramics.

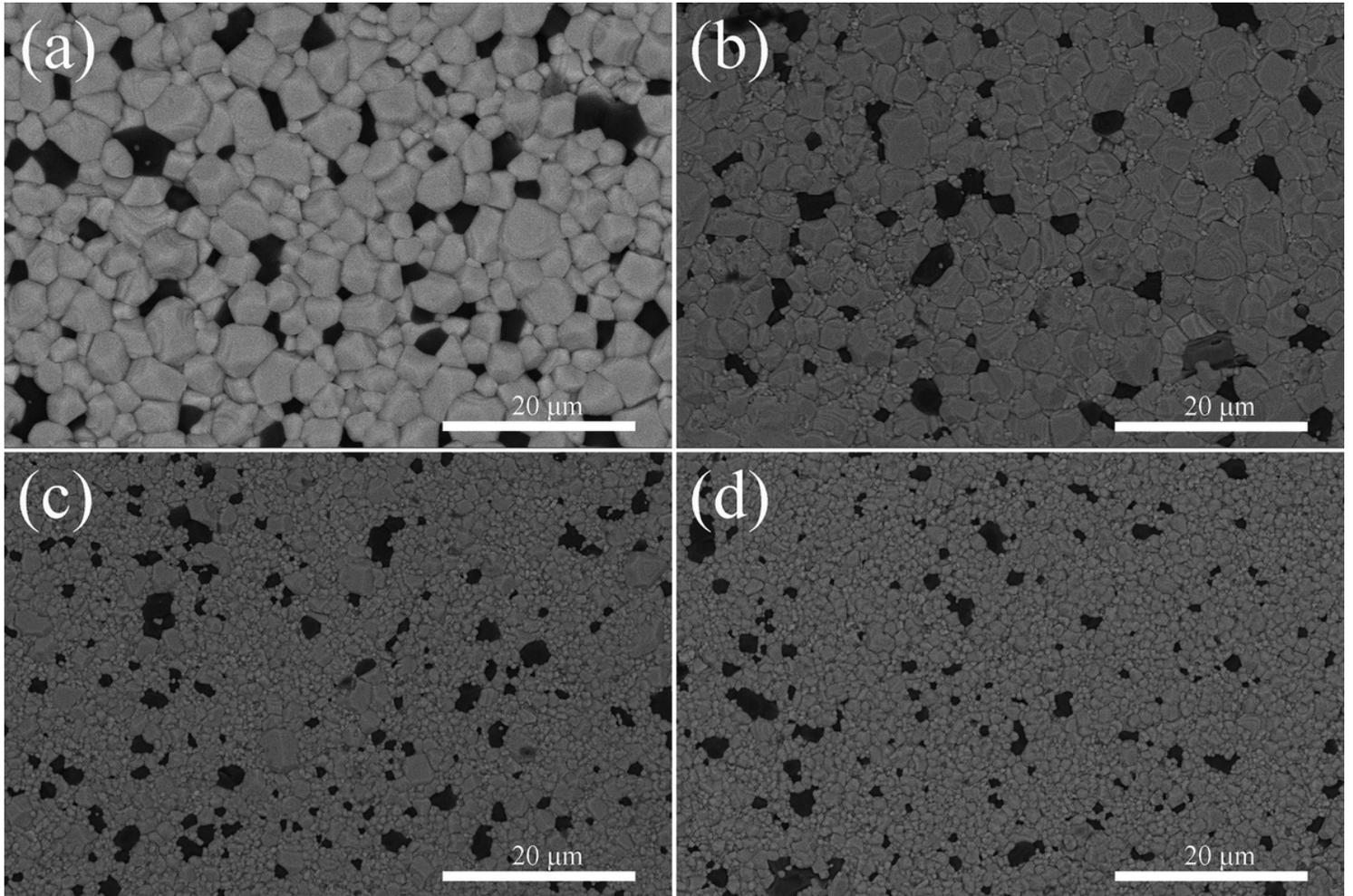
Temperature	Dielectric properties (at 10 kHz)				Microwave properties		
	T <sub>c</sub> (K)	At about 20 °C			Resonant frequency (GHz)	ε (at resonant frequency)	Q (1/ tanδ)
		ε'	tanδ	Tunability(%) at 30kV/cm bias			
1100	241.5	1633	0.00092	12.6	1.28	1324	108
1150	243.8	1678	0.00089	14.0	1.21	1399	114
1200	243.5	1872	0.00248	18.5	1.31	1546	110
1250	251.5	2224	0.00474	29.0	1.37	1721	132

## Figures



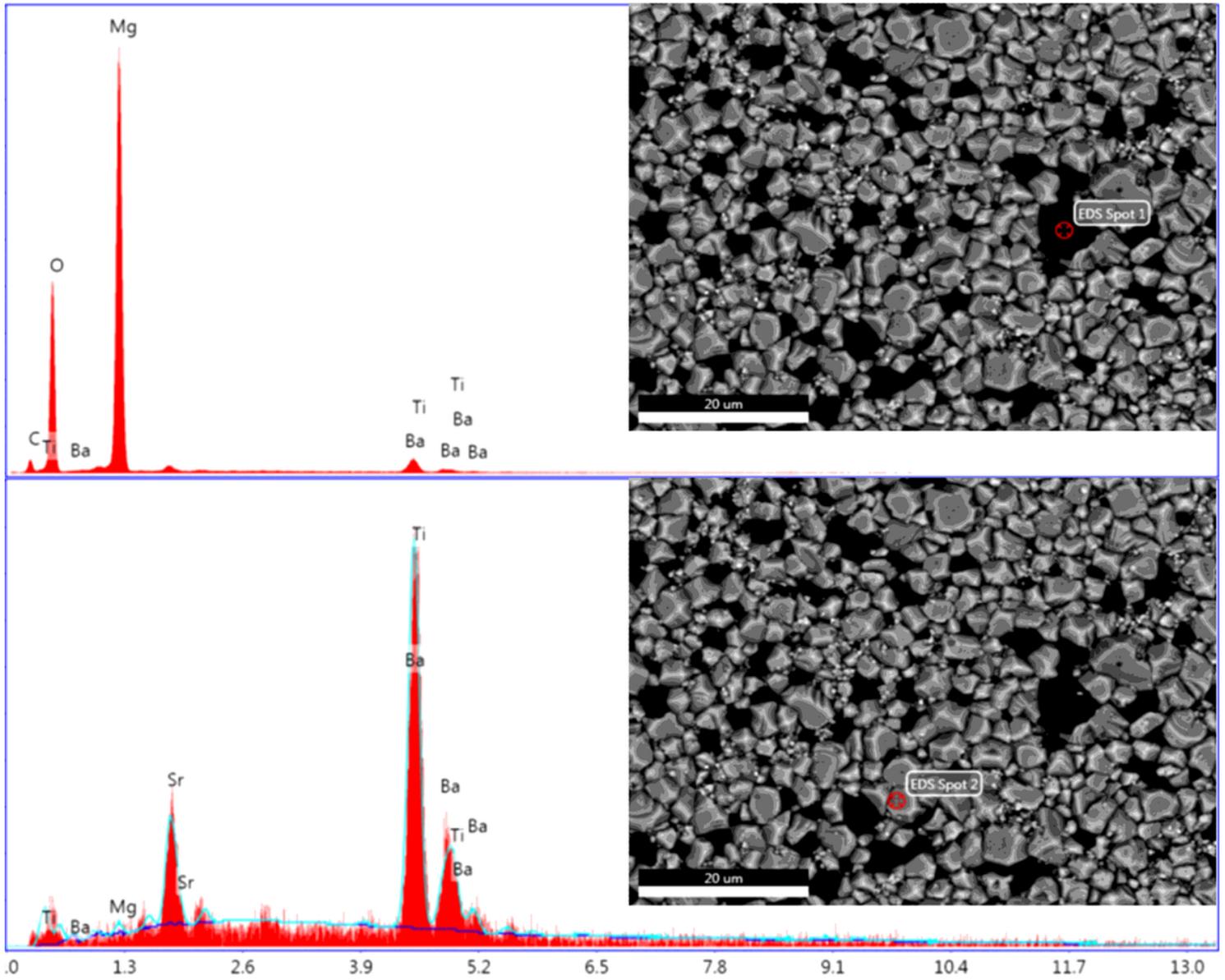
**Figure 1**

XRD patterns of the 92.5 wt %Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub>-7.5 wt %MgO ceramic sample



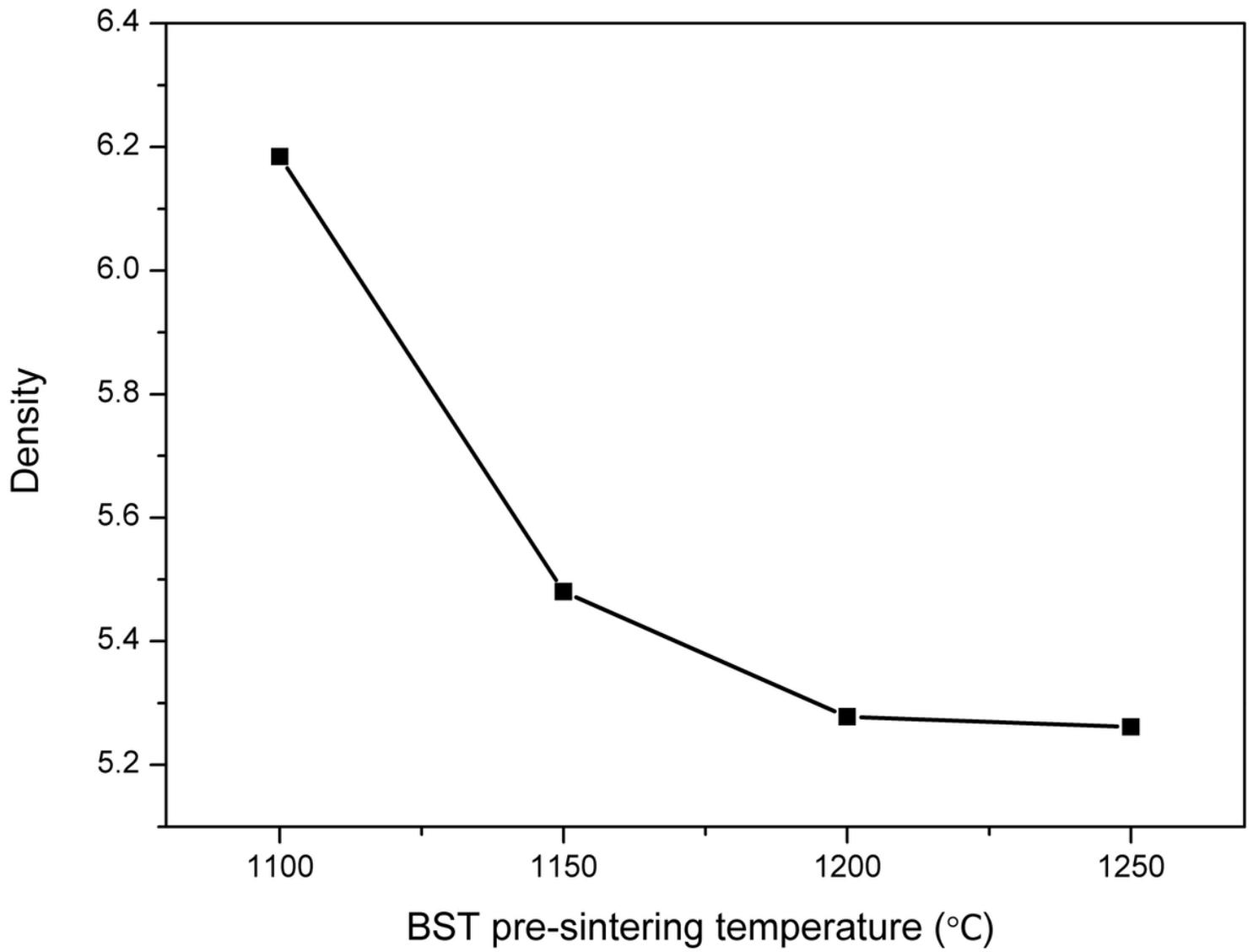
**Figure 2**

BEI micrographs of the 92.5 wt %Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub>-7.5 wt %MgO ceramics: (a)T=1100°C (b)T=1150°C (c)T=1200°C (d)T=1250°C.



**Figure 3**

EDS spectra of the BST60-MgO composite ceramics.



**Figure 4**

Density of BST60-MgO composite ceramics as a function of BST pre-sintering temperature.

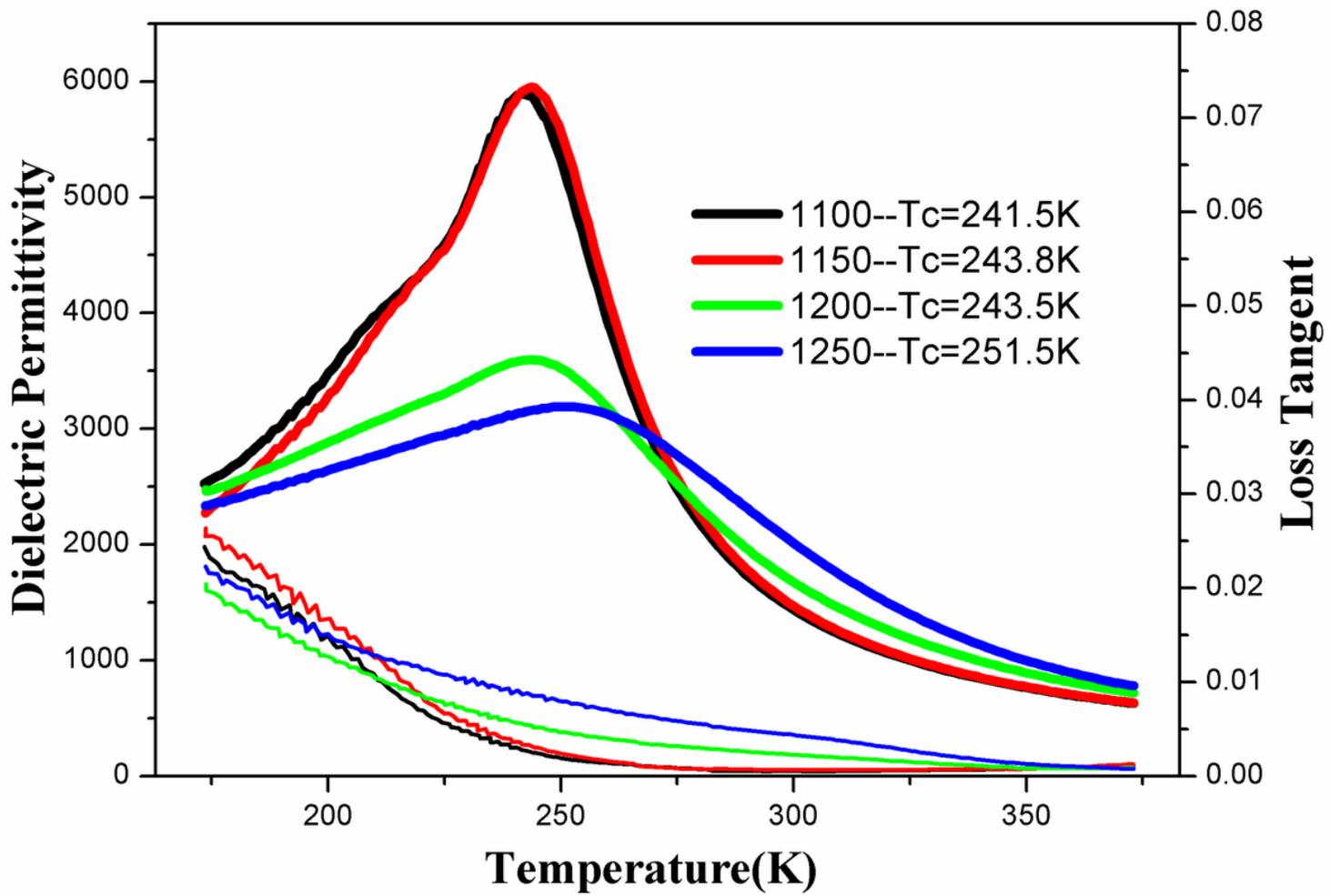


Figure 5

Temperature dependence of dielectric properties (dielectric permittivity and loss tangent) for the 92.5wt%Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub>-7.5wt%MgO composite ceramics at 10kHz.

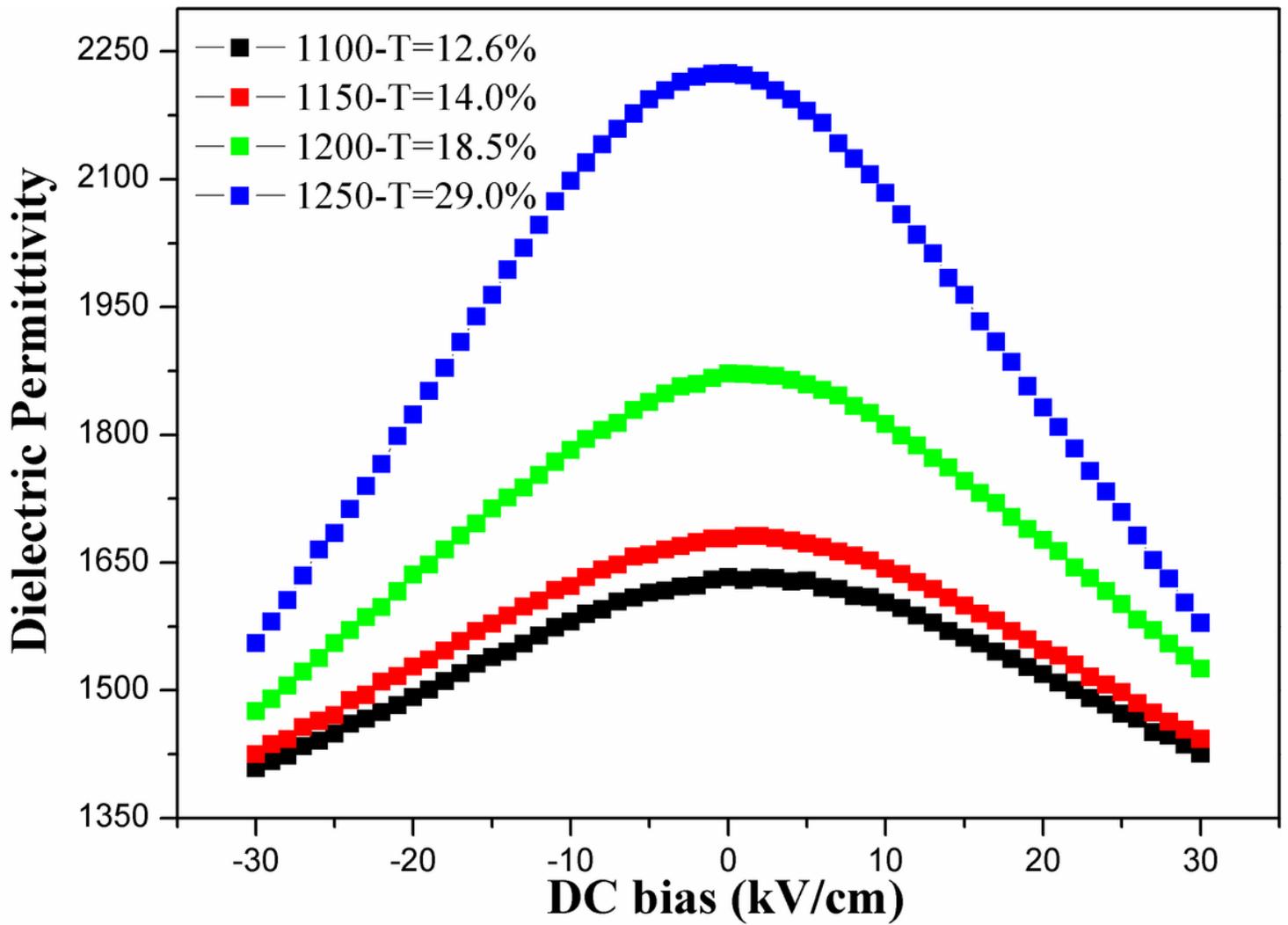


Figure 6

DC bias field dependence of the dielectric permittivity of samples at different pre-sintering temperatures measured at 10kHz and room temperature.