

# Effect of doped Ni<sup>2+</sup> on the dielectric properties of NiO-BaTiO<sub>3</sub> composites

J. Q. Huang · P. Y. Du · W. J. Weng · G. R. Han

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**Abstract** NiO-BaTiO<sub>3</sub> composites were prepared by sintering BaTiO<sub>3</sub> together with NiO in air at 1300°C. Microstructure and morphology of the composites were detected by XRD and SEM, and the dielectric properties were measured by LCZ meter. The results indicate that the perovskite phase is formed in fact in status of solid solution doped with Ni<sup>2+</sup>, although only a small amount of Ni ions can dissolve into the perovskite phase. Ni doping decreases the formation temperature of the composite without inhibiting the grain growth of the crystalline phase. The dielectric constant decreases sharply and the dielectric loss decreases smoothly with increasing Ni<sup>2+</sup> below NiO addition of 0.5 wt.%. When NiO addition increases above 0.5 wt.%, the dielectric constant and loss correlate with mixing rule of the two phases. Meanwhile, the replacement of Ni<sup>2+</sup> for Ti<sup>4+</sup> decreases the Curie temperature of perovskite phase by 30°C.

**Keywords** NiO-BaTiO<sub>3</sub> · Composites · Dielectric property · Microstructure

## 1 Introduction

BaTiO<sub>3</sub> is conventionally an important ferroelectric material for its high permittivity, thus BaTiO<sub>3</sub> and its related compounds are used as high permittivity capacitor materials widely. In view of multilayer ceramic capacitors, the internal electrodes are usually sintered with the ceramic matrix at a high temperature. It demands usually high

melting point and well oxidation resistance. Some noble metals such as Pt, Ag, Pd and their alloys were normally used. In recent years, Ni is considered to replace these noble metals [1]. However, Ni is easily oxidized in the air during the high sintering temperature and even may be oxidized to form NiO during the powder processing [2]. A small amount of NiO can then dissolve into BaTiO<sub>3</sub> during sintering [2–4]. It is thus important to investigate the effect of NiO on BaTiO<sub>3</sub> matrix and even on forming NiO-BaTiO<sub>3</sub> composite.

The NiO-BaTiO<sub>3</sub> composites had been reported by some researchers [2–9]. It is indicated that Ni<sup>2+</sup> reduces the dielectric loss and leakage-current particularly [5–7]. And the NiO inclusion inhibits the grain growth of BaTiO<sub>3</sub> observably [8, 9], although only a small amount of Ni<sup>2+</sup> can dissolve into the perovskite phase of BaTiO<sub>3</sub>. The dielectric properties of the composites are mainly attributed to the grain size of BaTiO<sub>3</sub> phase by the previous researchers [2, 9].

In this paper, the effect of Ni on the dielectric properties of NiO-BaTiO<sub>3</sub> composites is investigated in detail.

## 2 Experimental

A conventional ceramic method was used for synthesizing the NiO-BaTiO<sub>3</sub> composites. BaTiO<sub>3</sub> powder was initially mixed with NiO powder and milled for 3 h to obtain the ceramic precursor powder. The precursor powder was then pressed into discs. The green discs were finally sintered at 1300°C for 10 h in air for obtaining the NiO-BaTiO<sub>3</sub> composites. After sintering, the ceramic samples were abraded and polished down to the thickness of about 1 mm. Silver electrode was then coated on the ceramic discs for measuring the dielectric properties.

The phase structure of NiO-BaTiO<sub>3</sub> composites were analyzed via X-ray diffractometry (XRD). The morphology

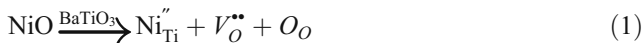
J. Q. Huang · P. Y. Du (✉) · W. J. Weng · G. R. Han  
State Key Lab of Silicon Materials, Zhejiang University,  
Hangzhou 310027, People's Republic of China  
e-mail: dupy@zju.edu.cn

of the composite ceramics were observed by scanning electron microscopy (SEM). The electrical properties of NiO-BaTiO<sub>3</sub> composites were measured using a Keithley 3330 LCZ meter.

### 3 Results and discussion

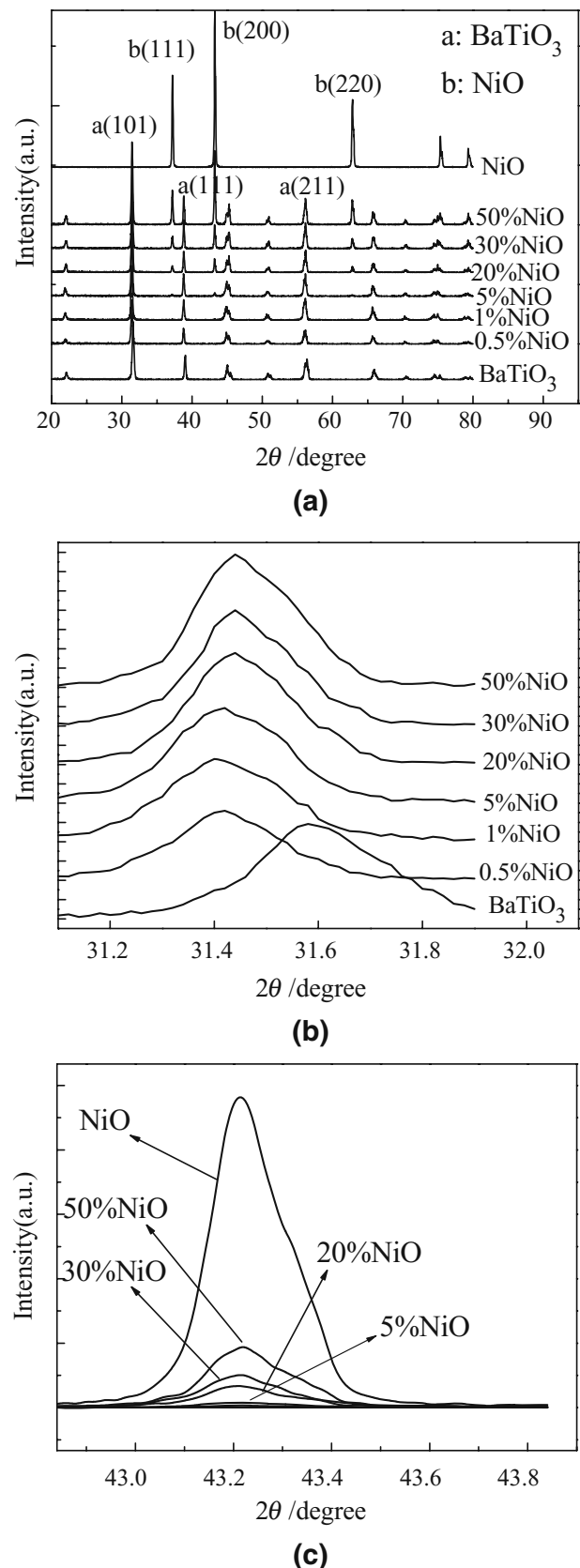
Figure 1(a) shows the XRD pattern of the composites with different mass fractions of NiO. When the NiO content is below 0.5 wt.%, there is only the perovskite phase of BaTiO<sub>3</sub> formed in the composite system. The NiO peaks then appear as NiO is above 0.5 wt.% and increase gradually with increasing NiO. Figure 1(b) shows the enlarged (110) peaks of the perovskite phase exhibited at about 31.6° in 2θ in Fig. 1(a). It is obviously that the peak position of (110) shifts toward low angle once NiO appears in the system and keeps unchangeable with increasing NiO concentration. Figure 1(c) shows the enlarged (200) peaks of the cubic NiO phase exhibited at about 43.2° in 2θ in Fig. 1(a). It indicates that the peak position of (200) is unchangeable with increasing NiO concentration.

It is well known that when a cation is added to the ABO<sub>3</sub> perovskite phase structure, there may be a substitution in A site or B site. Ni<sup>2+</sup> is apt to replace Ti<sup>4+</sup> due to their similar ionic radius of 0.072 and 0.068 nm when the NiO is compounded into the ceramic system. The defect reaction is therefore shown as follows:

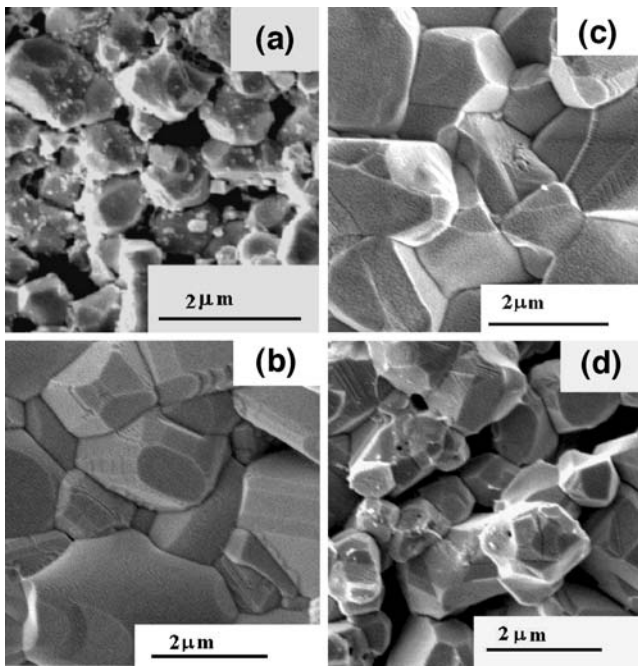


The crystal lattice of the perovskite phase will increase when a small Ti<sup>4+</sup> is substituted by a large Ni<sup>2+</sup>. It is very similar with that shown in another system [10, 11]. The peak position of the perovskite phase is hence low angle shifted as doping NiO. However, the solubility limit of Ni<sup>2+</sup> solved in the perovskite phase of BaTiO<sub>3</sub> occurs when NiO is above 0.5 wt.%. The peak of the perovskite phase is therefore unchangeable as NiO is above 0.5 wt.%, as shown in Fig. 1(b). It implies that the biphasic composite BaTiO<sub>3</sub>-NiO is formed exactly with two phases in which the perovskite phase is in fact the solid solution of Ni doped BaTiO<sub>3</sub>. However, NiO seems the phase with minor Ni ions inside in the phase structure due to almost no peak shifts exhibited as shown in Fig. 1(c).

The microstructures of the specimens with different compositions are shown in Fig. 2. The grain size of BaTiO<sub>3</sub> phase isn't restrained to grow exactly with introducing NiO phase into the ceramic system. It is clearly that the grain size of the biphasic composite seems to be a little bit larger than that of both the single phase ceramics of BaTiO<sub>3</sub> and NiO. It is significantly different from that reported by Tzing et al. [2, 9], which indicated that the NiO inclusion inhibits the grain growth of BaTiO<sub>3</sub> observably.

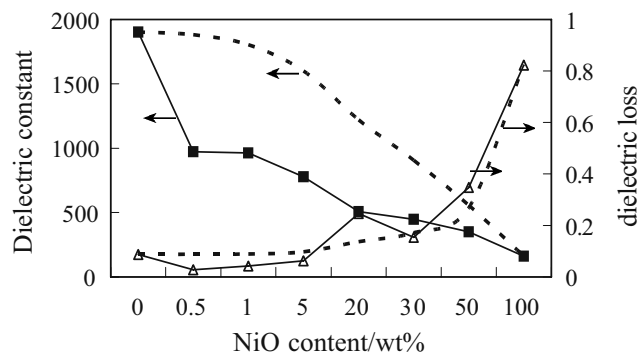


**Fig. 1** XRD patterns of (a) NiO-BaTiO<sub>3</sub> composite with different compositions, (b) that enlarged around 31.6°, and (c) enlarged around 43.2°

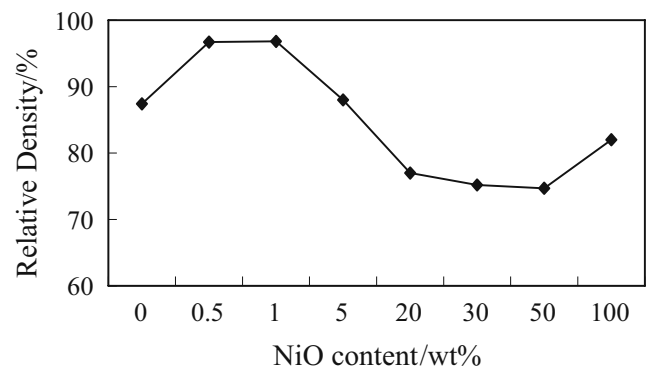


**Fig. 2** SEM graphs for specimens of (a) BaTiO<sub>3</sub> without NiO, (b) composites including 80% BaTiO<sub>3</sub> and 20% NiO, (c) composites including 50% BaTiO<sub>3</sub> and 50% NiO, and (d) NiO without BaTiO<sub>3</sub>

The dielectric properties of the BaTiO<sub>3</sub>-NiO biphas composite is in fact related to both the perovskite phase of BaTiO<sub>3</sub> having Ni addition and the cubic NiO phase. Fig. 3 shows the dielectric constant and dielectric loss of NiO-BaTiO<sub>3</sub>. The dielectric constant decreases sharply with increasing NiO until 0.5 wt.%. After NiO increases above 0.5 wt.%, the dielectric constant decreases smoothly with increasing NiO. Likewise, the dielectric loss decreases initially with increasing NiO to 0.5 wt.%. Afterward, as NiO is above 0.5 wt.%, it is turned to increase with increasing NiO through 100 wt.%. In fact, that the dielectric constant decreases sharply is due to the increase in Ni in the perovskite phase of BaTiO<sub>3</sub> initially below NiO of 0.5 wt.%. When a small amount of Ni is added to the perovskite

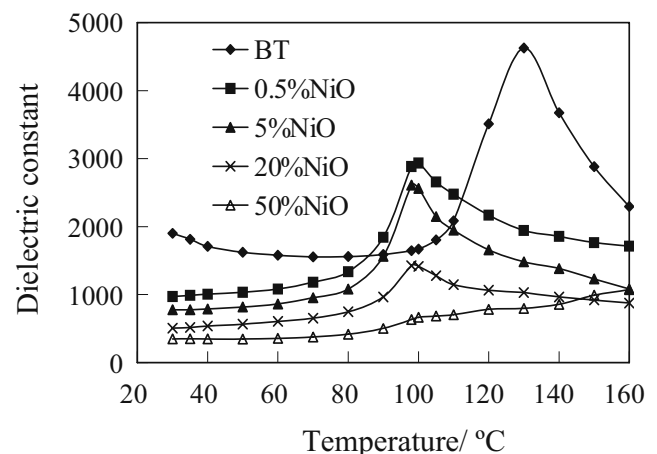


**Fig. 3** Plots of the dielectric constant and dielectric loss of NiO-BaTiO<sub>3</sub> as functions of NiO content at 10 kHz. Where the *solid lines* represent the experimental, and the *dotted lines* represent the theoretical from the mixing rule



**Fig. 4** A plot of the relative density of the composites as a function of NiO content

phase, the polarization actually decreases due to the substitution between Ti<sup>4+</sup> and Ni<sup>2+</sup>. As shown in Eq. 1, when the small Ti<sup>4+</sup> is replaced by the large Ni<sup>2+</sup>, the movement of Ti<sup>4+</sup> that nears to the Ni<sup>2+</sup> is limited and the ionic polarization is thus decreased [12]. The dielectric constant is therefore decreased with increasing Ni<sup>2+</sup> addition while the dielectric loss is decreasing due to small ionic polarization. Furthermore, it is also demonstrated by the sintering density of the ceramics, as shown in Fig. 4. Because a small amount of NiO addition can decrease the sintering temperature of BaTiO<sub>3</sub> ceramics due to the increase in concentration of oxygen vacancy as revealed in Eq. 1. The density of the composite therefore increases with increasing NiO content below 1 wt.%. It is well-known that high density generally correlates to high dielectric constant and lower dielectric loss. But it is obviously that the dielectric constant decreases sharply with adding a small amount of NiO to the BaTiO<sub>3</sub> matrix. This is practically due to the decrease of the polarization. It implies that the dielectric properties are actually dominated by BaTiO<sub>3</sub> doped with Ni ions in the perovskite phase below NiO addition of 0.5 wt.%. The dielectric constant decreases sharply and the loss decreases also with increasing Ni ions.



**Fig. 5** Variation of the dielectric constant as a function of temperature at 10 kHz

When the NiO addition increases above 0.5 wt.%, the second phase of NiO forms and the concentration of Ni ions dissolved in the perovskite phase is ended to increase. The dielectric constant decreases with increasing NiO smoothly due to the low permittivity of NiO phase. In this case, the apparent permittivity of the BaTiO<sub>3</sub>-NiO biphasic composite correlates with mixing rule of the two phases. The curve of the dielectric constant is therefore much more similar with that of the mixing rule theoretically calculated as shown in Fig. 3. And the similar relationship between the dielectric losses of these two cases is also shown in Fig. 3.

Meanwhile, the replacement between the two ions of Ni and Ti causes the distortion of the perovskite phase. It brings probably high inner stress in the phase structures and results in the decrease in stability of the perovskite phase. The Curie temperature ( $T_C$ ) of BaTiO<sub>3</sub> is thus shifted to low, as shown in Fig. 5. After the system reaches the solubility limit at NiO content of about 0.5 wt.%, the Curie temperature does not change again with increasing NiO. In consequence, the dielectric properties are actually related with the two phases of BaTiO<sub>3</sub> and NiO compounded together, in which the perovskite phase of BaTiO<sub>3</sub> is doped with the Ni ion. It seems that the dielectric properties not to be controlled by decreasing the grain size of the perovskite phase with increasing NiO reported by Tzing et al. [2, 9].

#### 4 Conclusions

NiO-BaTiO<sub>3</sub> ceramic composites were prepared successfully by sintering BaTiO<sub>3</sub> with NiO at 1300°C for 10 h in air. The perovskite phase in the biphasic composite is formed in

fact in status of solid solution doped with Ni<sup>2+</sup>, although only a small amount of Ni ions can dissolve in the perovskite phase. The grain size of the perovskite phase in the composite is larger than that of the BaTiO<sub>3</sub> without NiO, which is different from what was reported by Tzing et al. The dielectric constant of the composite decreases sharply and the dielectric loss decreases smoothly with increasing Ni<sup>2+</sup> below NiO addition of 0.5 wt.% due to substitution of Ni<sup>2+</sup> for Ti<sup>4+</sup>. Meanwhile, the replacement between Ni<sup>2+</sup> and Ti<sup>4+</sup> decreases the Curie temperature of the perovskite phase by about 30°C.

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