Improvement of temperature-stable $BaTiO_3$-based dielectrics by addition of Li_2CO_3 and Co_2O_3

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Abstract

The influence of Co_2O_3 and Li_2CO_3 on the dielectric constant-temperature characteristic of the $BaTiO_3$–Nb_2O_5–La_2O_3–Sm_2O_3 system (BNLS) was studied. The Co element is useful to flatten the dielectric constant-temperature curve at low temperature. Compared with the influence of Co_2O_3, Li_2CO_3 is an effective additive that can improve the dielectric constant of this system at high temperature near the Curie temperature. This is very helpful for this ceramic system to satisfy the requirement of EIA X7R specification on TCC and still keep a relatively high dielectric constant at room temperature. The possible mechanism of the phenomenon was also discussed. © 2001 Published by Elsevier Science Ltd.

Keywords: $BaTiO_3$; Co_2O_3; X7R; Dielectric constant; Dielectric properties; Li_2CO_3

1. Introduction

It is well known that the research on temperature-stable $BaTiO_3$-based dielectrics is now under fast development because it is harmless to the environment both in production and in application. This kind of material is commonly used as multilayer ceramic capacitors (MLCC) of EIA X7R specification.[1]

Some systems based on $BaTiO_3$ have been developed successfully. They can satisfy the requirement of X7R on TCC ($\leqslant \pm 15\%$ from -55 to $125°C$).[2] But usually their dielectric constants at room temperature are not very high because depressors are used to depress the dielectric constant peaks to make them satisfy the requirement of X7R on TCC. In recent years, the material developed for MLCCs is required to have large dielectric constant and small dispersion factor. So depressors are not agreeable to X7R capacitors with high dielectric constant now.

Much work has been done on the development of the $BaTiO_3$–Nb_2O_5–La_2O_3–Sm_2O_3 system (BNLS) as a novel material for X7R specification. This system has a relatively high dielectric constant and its dielectric constant-temperature curve is relatively flat. However, its dielectric constant will be much lower both at low temperature and at high temperature near the Curie temperature than that at room temperature, which can not satisfy the requirement of X7R specification. The Co element is very effective to flatten the dielectric constant-temperature curve at low temperature, which will make the system satisfy the requirement at low temperature. So, to improve the dielectric constant of the system at high temperature near the Curie temperature will be the key of getting novel dielectrics with higher dielectric constant at room temperature for X7R. So, the influence of Li_2CO_3 on the dielectric constant-temperature characteristic of the $BaTiO_3$–Nb_2O_5–La_2O_3–Sm_2O_3–Co_2O_3 (BNLSC) system was studied and the possible mechanism of the phenomenon was discussed.

2. Experimental

2.1. Preparation of samples

Reagent-grade $BaTiO_3$, Nb_2O_5, La_2O_3, Sm_2O_3, Co_2O_3 and Li_2CO_3 were used as raw materials. To examine the effects of Co_2O_3 and Li_2CO_3 as dopants with the BNLS system and to compare their different effects, a series of Co-doped BNLS and Li-doped BNLSC samples were prepared.

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The samples were prepared by the conventional method as follows. $BaTiO_3$ was pre-calcinated at 1150°C for 2 h. According to the chemical formula of $BaTiO_3 + 0.005$ $Nb_2O_5 + 0.003La_2O_3 + 0.0015Sm_2O_3 + xCo_2O_3 + yLi_2CO_3$, the raw materials were weighted, mixed by ball milling and dried. Then the dried powder was pressed into disks and the disks were fired at 1250°C for 2 h in air.

2.2. Measurements

An X-ray diffraction experiment was conducted to check the phase structure of the ceramics. The microstructures of the samples were observed by scanning electron microscope (SEM). Both surfaces of the disks were coated with silver paste, and then sintered at 800°C for 30 min. Their dielectric properties were measured by HP-41 92A. The dielectric constant-temperature characteristics of the samples were measured by a measuring system, also using HP-4192A, developed by our laboratory, in which the temperature range is from −60 to 135°C.

3. Results and discussion

3.1. The comparison of the effects of Co_2O_3 and Li_2CO_3 on the $BaTiO_3$-based system

Through XRD, the phase of all the sintered ceramics were perovskite. The grain size of the samples is as fine as 5 μm by the observation of SEM. Fig. 1 shows the dielectric constant-temperature characteristics of the samples doped with different contents of the Co element.

It is obvious that the overall dielectric constant of BNLS will become lower with increasing Co element contents. So, cobalt oxide is a very good depressor for this system. It could be concluded from this figure that with more Co element content, the system's overall dielectric constant could be depressed low enough so cobalt oxide is helpful to make the system satisfy the requirement of EIA X7R specification on TCC.
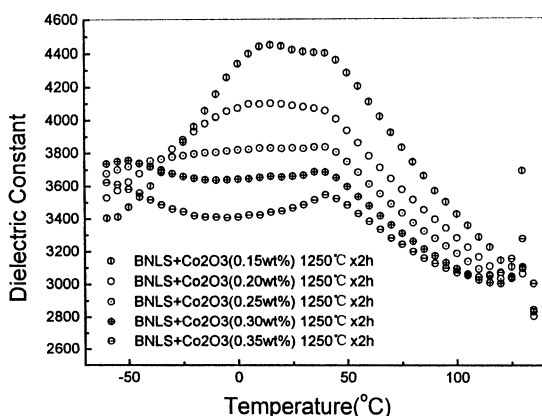
But this method will result in a lower dielectric constant of this system at room temperature. It is useless for the improvement of this system's whole dielectric properties. More detailed information can be got from Fig. 1. At low temperature, the dielectric constant-temperature curve is comparatively flat. This is due to the effect of the Co element's depressing effect. But, in the high temperature near the Curie temperature, there is a huge trough on the dielectric constant-temperature curve. It seems that the Co element is not very effective to flatten the curve at this range of temperature.

Fig. 2 shows the effect of doping Li_2CO_3 into the BNLSC system. From Fig. 2, the dielectric constant of this system at high temperature near the Curie temperature is enhanced highly by doping 0.5 wt.% Li_2CO_3 into the BNLSC system. So, it is obvious that it is helpful to improve the dielectric constant of this system at this range of temperature by doping proper content of Li_2CO_3 into the BNLSC system.

The contents of Co_2O_3 and Li_2CO_3 were adjusted to get a detailed graph of the effect of Li_2CO_3 on the dielectric constant-temperature characteristic of the BNLSC system. The contents of Li_2CO_3 are 0.10, 0.15 and 0.20 wt.%. The dielectric constant-temperature characteristic is shown in Fig. 3.

So, the rule of the effect of doping Li_2CO_3 on the dielectric constant-temperature characteristic of the BNLSC system is as follows. With more Li_2CO_3 added into the BNLSC system, the dielectric constant of this system at high temperature near the Curie temperature was improved. Also, the dielectric constant of this system at low temperature will be depressed at the same time. However, with proper content of Li_2CO_3 the dielectric constant at room temperature will not be influenced very much. So this is very helpful for this ceramic system to satisfy the requirement of EIA X7R specification on TCC and still hold a relatively high dielectric constant at room temperature.
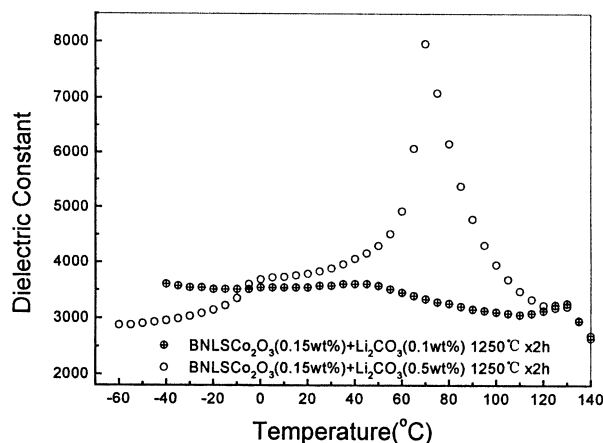

Fig. 1. The effects of CO_2O_3 on the BT-based system.

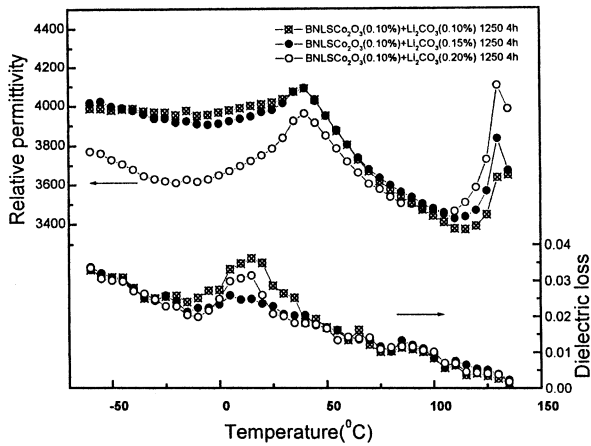Fig. 2. The effects of Li_2CO_3 on the BNLSC system.

Fig. 3. The dielectric constant-temperature characteristic after doping Li_2CO_3.

The dielectric loss of Li_2CO_3-doped BNLSC ceramics alters with temperature, as is shown in Fig. 3. With the increase of Li_2CO_3 dopant, the dielectric loss shows undetectable change at higher temperature. On the contrary, the dielectric loss varies remarkably with the dopant content. The dielectric loss decreases to less than 0.0250 at room temperature with the Li_2CO_3 content of 0.15%, which can satisfy X7R specification.

Then it could be concluded that Li_2CO_3 is an effective additive that can improve the dielectric constant of this system at high temperature near the Curie temperature and does not affect the dielectric constant of this system at low temperature very much.

3.2. The mechanism of the effect of Li_2CO_3 on the $BaTiO_3$-based system

Li_2CO_3 has been used as a sintering agent in the $BaTiO_3$-based system for some time. It can introduce the presence of a liquid phase. So it is helpful to the sintering process. As the volume of this liquid phase is not large enough for a uniform distribution on the surface of all the grains, a segregation can then result and the concentration gradient of this liquid phase may lead to an abnormal grain growth.[3]

As discussed before, the Li^+ cations will tend to occupy the octahedral sites of the perovskite lattice, forming additional anionic vacancies, according to the equation

$$Li_2CO_3 \rightarrow 2Li_{Ti}^{'''} + V_o^{\bullet\bullet} + CO_2(g) \uparrow \qquad (1)$$

The anionic vacancies coming from Li_2CO_3 will then be partially occupied by oxygen. This is helpful to the grain growth.

It has been apparent that the flattening ability of additives in X7R materials is associated with the inhomogeneous chemical distribution in the matrix grains.[4] It is well known that matrix grains consist of a ferroelectric phase
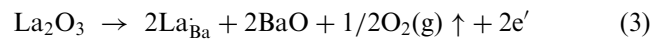
as the "core" and a nonferroelectric phase as the "shell". This microstructure is formed during the sintering process and is due to an inhibitive reaction between $BaTiO_3$ grains and the liquid phase materials. Unreacted grain core is pure $BaTiO_3$ and the grain shell consists of reacted $BaTiO_3$ severely doped with additives.[5]

In the BNLSC system, the Nb^{5+} cation is bigger than the Ti^{4+} cation and when it replaces the Ti site, the crystal lattice will expand. This will bring high inner-stress in the crystal lattice. Nb and La elements are donor additives. When their concentrations are low, free electrons will be produced in the matrix.
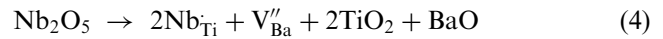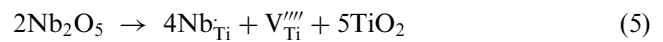
For Nb_2O_5,

$$Nb_2O_5 \rightarrow 2Nb_{Ti}^{\cdot} + 2TiO_2 + 1/2O_2(g) \uparrow + 2e' \qquad (2)$$

For La_2O_3,
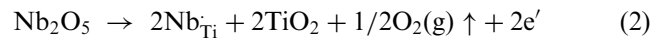
$$La_2O_3 \rightarrow 2La_{Ba}^{\cdot} + 2BaO + 1/2O_2(g) \uparrow + 2e' \qquad (3)$$

When their concentrations are higher, V_{Ba}'' or V_{Ti}'''' will be produced, which will make the crystal lattice distorted and produce inner-stress.

For Nb_2O_5,

$$Nb_2O_5 \rightarrow 2Nb_{Ti}^{\cdot} + V_{Ba}'' + 2TiO_2 + BaO \qquad (4)$$

or

$$2Nb_2O_5 \rightarrow 4Nb_{Ti}^{\cdot} + V_{Ti}'''' + 5TiO_2 \qquad (5)$$

For La_2O_3,

$$La_2O_3 \rightarrow 2La_{Ba}^{\cdot} + 3BaO + V_{Ba}'' \qquad (6)$$

or

$$2La_2O_3 \rightarrow 4La_{Ba}^{\cdot} + 4BaO + TiO_2 + V_{Ti}'''' \qquad (7)$$
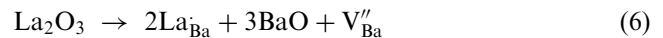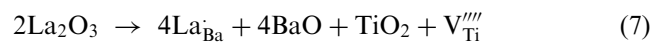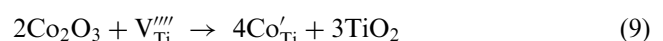
This will have an effect on the dielectric constant-temperature curve of the system, result in the rise of dielectric constant at low temperature as detailed previously.

The effects of Co and Li elements are different from those above. Co^{3+} and Li^+ cations act as acceptor additives, with low valance and small radius. They can compensate for the V_{Ba}'' or V_{Ti}'''' as Eqs. (8)–(11) show.

For Co_2O_3,

$$1/2O_2 + Co_2O_3 + V_{Ba}'' \rightarrow 2Co_{Ti}' + 2TiO_2 \qquad (8)$$

or

$$2Co_2O_3 + V_{Ti}'''' \rightarrow 4Co_{Ti}' + 3TiO_2 \qquad (9)$$

For Li_2CO_3, when Li^+ occupies Ba-sites:

$$Li_2CO_3 + V''_{Ba} \rightarrow 2Li'_{Ba} + BaO + CO_2(g) \uparrow \qquad (10)$$

or

$$2Li_2CO_3 + V''''_{Ti} + O_2 \rightarrow 4Li'_{Ba} + 4BaO + 2CO_2(g) \uparrow$$

$$\qquad (11)$$
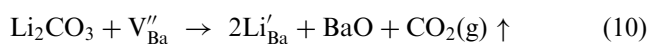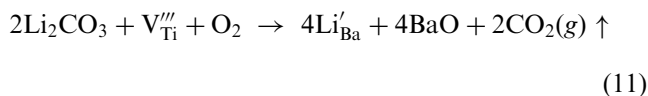
When Li^+ occupies Ti-sites:

$$3/2O_2 + Li_2CO_3 + 3V''_{Ba}$$

$$\rightarrow 2Li'''_{Ti} + 2TiO_2 + CO_2(g) \uparrow \qquad (12)$$

or

$$2Li_2CO_3 + 3V''''_{Ti} \rightarrow 4Li'''_{Ti} + TiO_2 + 2CO_2(g) \uparrow \qquad (13)$$
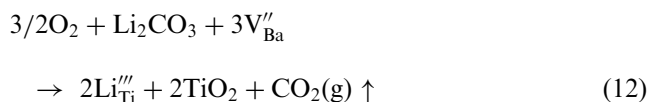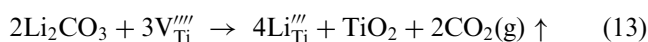
So they will be helpful to release the inner-stress.

As the "core–shell" structure discussed before, the grain shell consists of reacted $BaTiO_3$ severely doped with additives. So the distortion mainly occurs at the "shell" region in the BNLS system.

Because the Li^+ and Co^{3+} act as acceptors and eliminate the cation vacancies, it is helpful to reduce the high inner-stress caused by doping Nb^{5+} and La^{3+} cations into the crystal lattice.

The Li^+ cation is smaller and has a lower valance than the Co^{3+} cation. More cation vacancies were compensated as discussed in Eqs. (8)–(13). The effect of the Li^+ cation on releasing inner-stress of the system is more distinct than the Co^{3+} cation. So the dielectric constant-temperature curve will turn towards the original one of pure $BaTiO_3$, which will bring the improvement of the dielectric constant of this system at high temperature near the Curie temperature.

Another reason for Li_2CO_3 being a useful additive is that the Li^+ cation can shift the dielectric constant peak at high temperature towards the low temperature end as shown in Fig. 2. This is also very helpful to the temperature stabilization of the dielectric constant of this system.

4. Conclusions

The rule of the effect of doping Co_2O_3 and Li_2CO_3 on the dielectric constant-temperature characteristic of the BNLS system was found. The Co element is very effective to flatten the dielectric constant-temperature curve at low temperature. Also, the influence of Li_2CO_3 on the dielectric constant-temperature characteristic of the BNLSC system was compared with the influence of Co_2O_3. The function of Li_2CO_3 on improving the dielectric constant of the BNLSC system at high temperature near the Curie temperature is very helpful in developing novel temperature-stable dielectrics based on $BaTiO_3$ with relatively high dielectric constant at room temperature. This result has been used successfully to develop novel materials satisfying the EIA X7R specification.

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