Influence of Cr_2O_3, La_2O_3, Li_2CO_3, and WO_3 on Dielectric Properties of Ceramic Capacitor Materials*

ZHANG Shao-hua, XIE Bing
(*Chemistry and Material School, Nanchang University, Nanchang* 330047, *China*)

Abstract: The influence of Cr_2O_3, Li_2CO_3, WO_3 on dielectric behaviors of the system $0.90(Sr_{0.54}Pb_{0.26}Ca_{0.20})TiO_{3-0.1}Bi_2O_3 \cdot 3.5TiO_2$ was investigated. The results showed that ① the incorporation of Cr_2O_3 makes the permittivity peak broader; ② the addition of Li_2CO_3 raises the permittivity peak and the dielectric loss below 45 ℃; ③ the doping of WO_3 makes the permittivity peak higher, in the meantime reduces the temperature coefficient of permittivity at higher temperature.

Key words: ceramic capacitor; doping; temperature coefficient
CLC number: TQ173 **Document code**: A **Article ID**: 0529-6579(2003)S1-0078-03

1 Introduction

High voltage ceramic capacitors are key components in many high-voltage electric circuits, and the performance of the capacitor depends primarily on the ceramic dielectrics. $BaTiO_3$-based and $SrTiO_3$-based ceramic dielectrics are two groups that have been mostly investigated. The latter exhibits a good temperature characteristic, low dielectric loss and high permittivity. We applied a general formula of $(1-z)(Sr_aPb_bCa_c)TiO_{3-z}Bi_2O_3 \cdot 3.5TiO_2$ to $SrTiO_3$-based dielectrics.

Generally, the following relations should be satisfied in order to obtain a good performance: $0.08 \leqslant z \leqslant 0.12$, $0.5 \leqslant a \leqslant 0.7$, $0.1 \leqslant b \leqslant 0.3$. Through a cross experimental design, a composition of good comprehensive performance was determined as $0.90(Sr_{0.54}Pb_{0.26}Ca_{0.20})TiO_{3-0.1}Bi_2O_3 \cdot 3.5TiO_2$, which was used as principal composition in our following experiments. In this paper, we studied the incorporation of Cr_2O_3, La_2O_3, Li_2CO_3 and WO_3 at different levels into the principal compositon for modification and obtained the optimum dielectric properties of the composition.

2 Experimental procedure

The principal dielectric ceramic materials were prepared according to the composition of $0.90(Sr_{0.54}Pb_{0.26}Ca_{0.20})TiO_{3-0.1}Bi_2O_3 \cdot 3.5TiO_2$, with addition of 0.2% CaF_2 and 0.2% ZrO_2, by wet-mixing the raw materials in the agate ball mill, drying, prefiring for 2 h at 950 ℃, grinding, sifting, incorporating of additives, again wet-mixing, drying, then palletizing, pressing at 100 MPa for $\phi 10 \times 1$ mm, sintering in the air at 1240 ℃, socking 2 h. Silver paste was coated on the surface of the samples and fired at 500 ℃. The capacitance and dissipation factors were measured using a CD-18 capacitance and loss-measuring device. The breakdown voltage was measured using a multifunctional breakdown device. Dmax/rb X-ray diffractometer was used for phase analyses, Ds-4 SEM for inspection of the microstructure of the material and CAMECA. BAX/MICRO EMPA for microanalyses.

3 Results and discussion

3.1 Incorporation of Cr_2O_3 at different levels

The former compositon was adopted for principal composition, incorporated with $w(Cr_2O_3) = 0.2\%$, 0.4%, 0.6%, 0.8%, respectively. Fig. 1 showed the temperature dependence curves of ε of these samples. From this figure, we know Cr_2O_3 has an effect of depressing the $\varepsilon - t$ peak. And other influences are not evident within the scope of observation. From the XRD figure of the sample doped with 0.8% Cr_2O_3, we can calculate the lattice parameters. And from the XRD figure, there is no any new phase existing. If Cr^{3+} enters into the lattice, it would be the position of Ti^{4+}. As we know $r(Cr^{3+}) = 0.064$ nm, $r(Ti^{4+}) = 0.064$ nm, the replacement between the ions with similar radius will not change the lattice structure. And we observe that the dielectric constant change following the change of dopants of Cr_2O_3 (see Fig. 1). We can see that dielectric constant will decrease as the dopants increase. That is because

* Received 10 December 2002; Accepted 18 April 2003
Corresponding author: zshaohua@vip.sina.com(ZHANG S H)

that the replacement of Ti^{4+} with Cr^{3+} can neutralize some of free (or qusi-free) electrons, leading to the decline of conductivity. The regional inbalance of electric charge causes the distortion of the lattice and the decline of the dielectric constant.

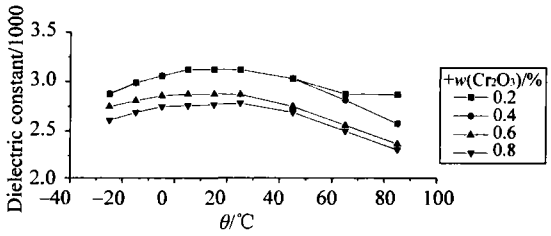

Fig.1 The temperature dependence of ε in Cr_2O_3

3.2 The incorporation of La_2O_3 at different levels

Also in the same principal composition as above, with the doping of 0.4% $MnCO_3$, before the second wet-mixing, La_2O_3 was incorporated at the levels of 0.5%, 1.0%, 1.5%, 2.0%. Fig. 2 is the temperature dependence curve of ε. We know from the figure that with the incorporation of La_2O_3, $\varepsilon - t$ peaks shift to lower temperature and are depressed. In the meantime, La_2O_3 also reduces the dielectric loss. From the XRD figure, we can calculate the lattice parameters.

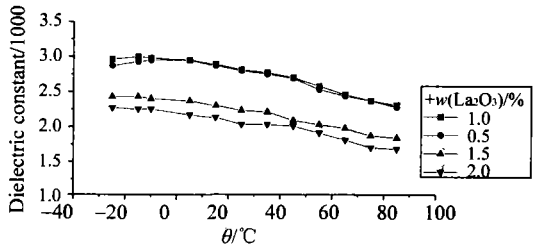

Fig.2 The temperature dependence of ε in La_2O_3

It was reported that the Curie temperture of (SrBi)TiO_3 is about 4 K, and for (SrLa)TiO_3, no ferroelectric phenomenon can be observed. We guess that the Curie temperature of $La_{2/3}TiO_3$ is lower than that of $Bi_{2/3}TiO_3$, and the addition of La_2O_3 will cause the decline of Curie temperature of the material, and the movement toward lower temperature. This result was also reported in other publishing. It was supposed that the replacement of La^{3+} with A site will lead to the widening of the peak. According to the articles, La^{3+} play the same role with Bi^{3+} in the system, and has the similar solubility(72.7% and 70% respectively). It is not ideal to broaden the peak through replacement of A site as Bi_2O_3 has made the vacancy of A site relatively saturated.

La_2O_3 has peak-depressing effect, and in the system there is limited soluability of Bi_2O_3, La_2O_3. The additional Bi_2O_3, La_2O_3 will precipitate as the second phase. On one hand, the second phase has low dielectric constant, minimize the grain size and increase the amount of the amorphous phase of low dielectric constant. On the other hand, as the amount of La_2O_3 increases, concentration of La^{3+} and V_{sr}'' are large enough to lower the concentration of free electron, causing the decline of dielectric constant and dielectric loss. At the moment, $La_{Sr}^{\cdot}$ and V_{sr}'' have been bound together. Although the combined structure of $La_{Sr}^{\cdot}$ and V_{sr}'' is very similar to dipole, but the distance between them is by far lower than that of non dipole. The decrease of dipole moment will diminish the contribution of dipole to dielectric constant, and the contribution of dipole relaxing effect, and the dielectric loss.

3.3 The incorporation of Li_2CO_3 at different levels

As the Li^+ can change the internal field of the system and increase the dielectric constant. Using the other principal composition with lower dielectric constant and low temperature coefficient, doped with 0.5% ZO_2 and 0.5% CaF_2 as flux. Fig. 3 is the relationship between ε and temperature. We know from this figure, with the addition of Li_2CO_3, and the dielectric constant also will increase, but no effect on temperature coefficient. And we have the figure of XRD of the sample doped and undoped with 2% Li_2CO_3, and we can calculate the lattice parameters.

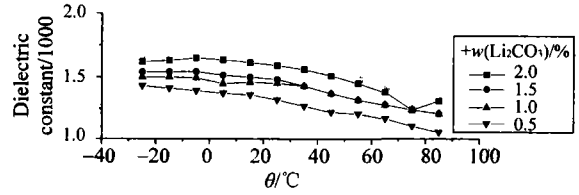

Fig.3 The temperature dependence of ε in Li_2CO_3

The incorporation of Li increases the dielectric loss. As $r(Li^+)$ is quite small, and with low quantity, very easy to mobilize in the electrical field, and result in the hike of dielectric loss. In other words, the incorporation of Li salt will increase the dielectric constant due to the change of internal electrical field in the system.

3.4 Incorporation of WO_3 at different levels

As we know from experience that ion of high valence and small ion radius oxides have evident peak raising and peak broadening effect. WO_3 was chosen as additive for experiment with B principal composition, and the temperature dependence of ε was shown in Fig. 4 with different addition of WO_3. We know from the figure that WO_3 have the effect of peak raising, and decrease the invincible high $T_{k\varepsilon}$ 85 ℃, bringing it below 10%. However, more WO_3 cannot increase further ε and decrease $T_{k\varepsilon}$. And there is no evident rule for dielectric constant. From the figure, we know when dopant is

0.3%, the loss is minimum, and dielectric constant is much small. From the XRD figure, we can calculate the lattice parameters. The incorporation of WO_3 reaction follows. The incorporation of WO_3 can hike the dielectric constant due to strengthening internal field in lattice of W^{6+}.

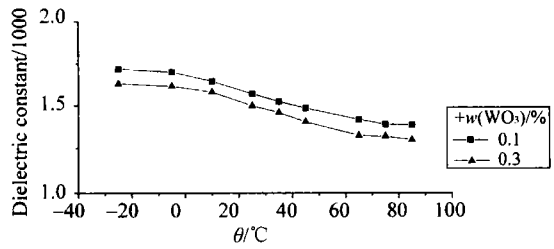

Fig.4 The temperature dependence of ε in WO_3

4 Conclusion

(1) The incorporation of Cr_2O_3 has peak depressing effect to A principal composition.

(2) The incorporation of La_2O_3 can move the $\varepsilon - t$ peak to lower temperature, and have peak depressing effect.

(3) The incorporation have the effect of peak-raising, the dielectric constant will increase with the addition of Li_2CO_3, and loss below 45 ℃ will increase with the addition.

(4) WO_3 have peak-raising effect, in the meantime can reducing $T_{k\varepsilon}$ 85 ℃.

Acknowledgment: This research was sponsored by the Science Funds of Jiangxi Province and Funds of Nanchang University.

Cr, Li, W 等添加物对瓷介电容瓷料性能的影响

章少华, 谢 冰

(南昌大学化学与材料科学学院,江西 南昌 330047)

摘 要: 研究了 Cr_2O_3, Li_2CO_3, WO_3 对于 $0.90(Sr_{0.54}Pb_{0.26}Ca_{0.20})TiO_3-0.1Bi_2O_3\cdot 3.5TiO_2$ 为系统的中高压瓷介电容瓷料的介电性能的影响,实验发现掺加 Cr_2O_3 对于该瓷料的 $\varepsilon - t$ 曲线有压峰作用;而 Li_2CO_3 的掺加有提升 $\varepsilon - t$ 峰作用,介电常数随着掺加量的增加而提高,损耗在 45 ℃以下随掺加量的增加而提高;WO_3 的添加也具有提峰作用,并且同时可以降低高温段 ε 的温度系数。

关键词: 瓷介电容器; 掺杂; 温度系数

中图分类号: TQ173 **文献标识码:** A