The Research of Mixing Dielectric Capacitor Ceramic Materials *

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

Abstract: A new approach of improving the temperature coefficient of dielectric property was designed by using the principal of dielectric mixture, and this method was tested both theoretically and practically. In the end, a new version of the formula of dielectric mixture was proposed.

Key words: dielectrics; temperature coefficient; mixture
CLC number: TQ173　　**Document code:** A　　**Article ID:** 0529-6579(2003)S1-0081-03

1 Introduction

High temperature coefficient of dielectric constant is the most challenging problem in making high capacity ceramic capacitor. The common approach is modifying the composition by doping some additives to improve the temperature characteristic. Another approach is mixing two different dielectrics to achieve the goal of stable temperature properties. We found that the mixing of the dielectrics of SBT system does not conform to the law of mixture in dielectric property, and in some cases, the dielectric constant of the mixture is larger than that of any individual component.

2 Theoretical simulation

According to the law of mixing dielectrics, if the difference of dielectric constant is not large, and the two dielectrics are in homogeneous distribution, the following formula of ε and $T_{K\varepsilon}$ of the mixing dielectric constant should be satisfied.

$$\varepsilon = x_1 \ln \varepsilon_1 + x_2 \ln \varepsilon_2$$
$$T_{K\varepsilon} = x_1 T_{kK\varepsilon_1} + x_2 T_{K\varepsilon_2}$$

x_1, x_2 are the volume fractions of dielectric 1 and 2, $x_1 + x_2 = 1$. $\varepsilon_1, \varepsilon_2$ are the dielectric constants of dielectric 1 and 2; $T_{K\varepsilon_1}$, $T_{K\varepsilon_2}$ are the temperature coefficients of dielectric 1 and 2.

Two types of dielectric mixture are designed in our tests. The components of the mixture follow with the principle (1) that the temperature coefficients of these two dielectrics $T_{K\varepsilon_1}$ and $T_{K\varepsilon_2}$ keep reverse sign, or (2) that at least one of the dielectrics has very low $T_{K\varepsilon}$. Specifically the two types of mixture are (1) the Curie points of the two ceramic materials are different, while the temperature coefficients are just like the properties of SBTP system, as seen in the simulation figure, material a with Curie point of −5 ℃, and material b with 65 ℃, a + b is the mixed ceramic material. (2) One of the materials with lower Curie point has rather low dielectric constant and low temperature coefficient, such as the SBT system. Figure 1 and 2 are the simulation figures for these two types of mixture.

In Fig. 1, the dielectric constants of the two dielectrics are simulated according to the normal dielectric properties, and the dielectric constant of the mixed dielectric is calculated according to formula. In Fig. 2, a is the material with Curie temperature of −25 ℃, b is the material with curie temperature of 65 ℃, and a + b

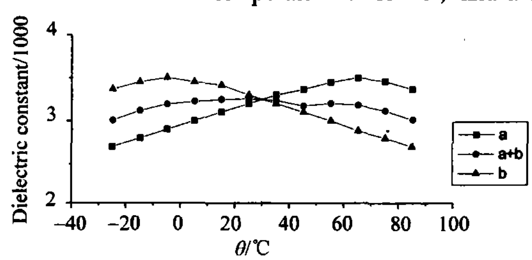

Fig. 1 Theoretical simulation 1

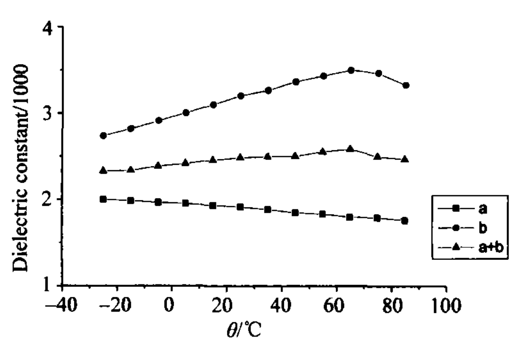

Fig. 2 Theoretical simulation 2

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

is the mixture. The simulation results of $TK\varepsilon_{-25℃}$ and $TK\varepsilon_{85℃}$ are shown in Tab.1.

Tab.1 The temperature coefficients of the mixing ceramic materials

item	a_1	b_1	a_1+b_1	a_2	b_2	a_2+b_2
$TK\varepsilon_{-25℃}/\%$	1.52	15.63	7.48	15.63	5.26	5.76
$TK\varepsilon_{85℃}/\%$	18.18	4.69	7.48	4.69	6.32	0.98

As seen from table 1, the simulation results indicate that mixing of the ceramic materials helps improve the temperature characteristics. In the above case, the temperature coefficients of a_1+b_1 and a_2+b_2 are below 10%. According to the principle and the simulation results, we have the following experiments with mixing ceramic materials.

2 Experiment simulation

2.1 Preparation of original materials

First, we prepare several ceramic materials. Material A is $0.90(Sr_{0.54}Pb_{0.26}Ca_{0.20})TiO_3-0.1Bi_2O_3\cdot3.5TiO_2$, without addition of $MnCO_3$, material B is $0.9(Sr_{0.6}Ca_{0.2}Pb_{0.2})TiO_3-0.08Bi_2O_3\cdot3.5TiO_2-0.02La_2O_3\cdot3.5TiO_2$, C is $0.90(Ba_{0.3}Sr_{0.3}Pb_{0.25}Ca_{0.15})TiO_3-0.1Bi_2O_3\cdot3.5TiO_2$, composition of D is $0.9(Sr_{0.55}Ca_{0.31}Pb_{0.31})TiO_3-0.10Bi_2O_3\cdot3.5TiO_2$, and composition E is $0.90(Sr_{0.51}Ca_{0.14}Pb_{0.35})TiO_3-0.10Bi_2O_3\cdot3.5TiO_2$. The composition B has much low dielectric constant and low temperature coefficient.

2.2 Mixing of A and B

From figure 3, the mixing experiments of A and B show that the mixing of two materials can improve the temperature characteristic. Through more accurate calculation, we can deduct the volume fraction of these two materials through the dielectric constant of the mixing material. The calculation indicates that the volume fraction calculated from the dielectric constant is different for different temperatures, as is apparently wrong in the case. Therefore, the mixture of A and B does not conform to the formula above.

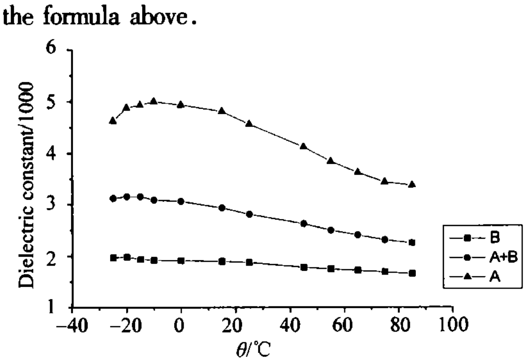

Fig.3 The acutal ε of the mixture A + B

2.3 Mixing of B and C

From Fig.4, C is the modified $BaTiO_3$ with high Curie temperature. In this experiment, we can see the aberration, especially under 0 ℃. It was unexpected that the dielectric constant of the mixed materials is larger than that of any individual material.

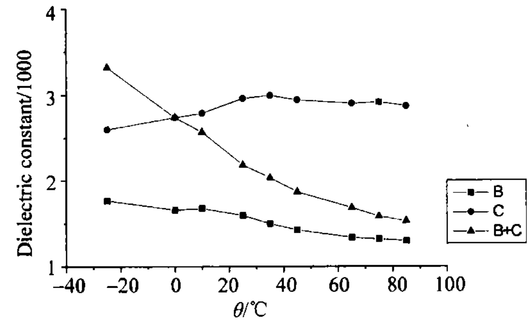

Fig.4 The acutal ε of the mixture B + C

2.4 Mixing of B and D

From Fig.5, as D has relatively high lead volume, composition D has a higher Curie temperature. The experiments indicate that the mixing will increase the dielectric constant without the expense of temperature coefficient, failing to satisfy the above formula. At about 10 ℃, the mixing dielectric has a higher dielectric constant than that of the individual material.

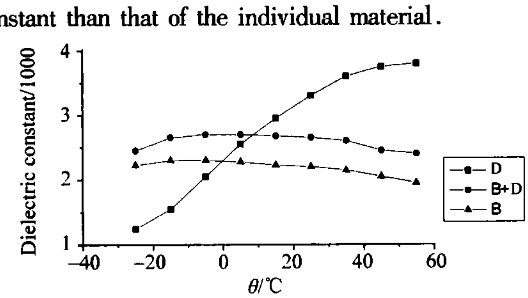

Fig.5 The acutal ε of the mixture B + D

2.5 Mixing of A_1, A_2 and E

From Fig.6, A_1 is composition A doped with $LiCO_3$ ($w=0.5\%$), E material is $0.90(Sr_{0.51}Ca_{0.14}Pb_{0.35})TiO_3-0.10Bi_2O_3\cdot3.5TiO_2$, A_2 is composition A doped with $MnCO_3$ ($w=0.4\%$) and LaO_3 ($w=0.5\%$). The experiment results indicate that this formula does not match this type of material. for the A_1+E, and A_2+E two mixing dielectric materials, when the temperature is below 5 ℃, there is also an abnormal dielectric constant: $\varepsilon_{A_1+E} > \max(\varepsilon_{A1}, \varepsilon_E)$, $\varepsilon_{A_2+E} > \max(\varepsilon_{A_2}, \varepsilon_E)$.

2.6 Mixing of A_3, B_1 and B

From Fig.7, B_1 is the material B doped with Li_2CO_3 ($w=2.0\%$), A_3 is the composition A doped with CuO ($w=2.0\%$). In this experiment, though there are not any results of the dielectric constants of the mixing dielectrics exceeding the larger of the individual component, there is still aberration from the formula, especially for the case of $A_3 + B$.

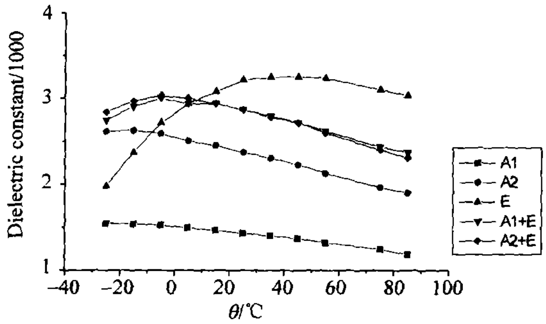

Fig.6 The acutal ε of the mixture $A_1 + E$ and $A_2 + E$

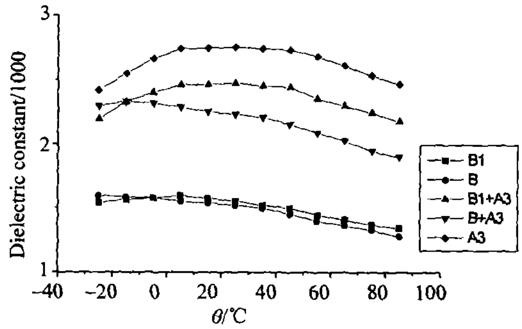

Fig.7 The acutal ε of mixture $B + A_3$ and $B_1 + A_3$

3 Conclusion

In conclusion, the mixture of this ceramic system does not conform to the above formula. The precondition is that the dielectric constant difference of these two phases is not too much, the mixture is homogenous, and there is no reaction in the boundary. The above experiments indicate that the mixture can not be homogenous, and there is some reaction in the boundary. In order to describe the mixing situation of the real ceramic materials, we try to make some modification for this formula and the new relationship is as follows:

$$\ln \varepsilon = x_1 \ln \varepsilon_1^* + x_2 \ln \varepsilon_2^* + x_3 \ln \varepsilon_3$$

$\varepsilon_1^* = f_1(T,x)\varepsilon_1$, $\varepsilon_2^* = f_2(T,x)\varepsilon_2$, $f_1(T,x)$, $f_2(T,x)$ are the factors that are related to temperature and others x_3, ε_3 are the volume fraction and dielectric constant of the new phase. The factors $f_1(T,x)$, $f_2(T,x)$ are related to the stress and the phase transformation. As for the stress factor, the grains are in a stress system in the ceramic polycrystalline. L.E. Cross had determined the dielectric constant of crystal $BaTiO_3$ at different axis. According to his experiment, the dielectric constant will increase with the increase of the stress, explaining the abnormal phenomena in the $BaTiO_3$ ceramic fine crystals ($< 1\ \mu m$), $\varepsilon > \max(\varepsilon_a, \varepsilon_c)$. In this ceramic system, the grains are very small ($< 1\ \mu m$), but the crystal of SBPT solid solution is very difficult to get, and no one has ever determined the dielectric constants of c axis and a axis, let alone the relationship between them and stress. Therefore, the dielectric constant of the dielectrics is not actually the arithmetic average of the dielectric constant of c and a axis, or the value calculated from the formula. We do not know the relationship of the dielectric constant of c and a axis with stress. As to the factor of phase transformation, when the two dielectrics of the different compositions (so different Curie temperature) mix, when the temperature declines to the higher Curie point, there is phase transformation in the ceramic body. In the phase transformation, the length of c axis will become longer, and that of a axis will be shorter, causing substantial stress in the system. Under the influence of this stress, the dielectric constant of the grain will increase, leading $\varepsilon > \max(\varepsilon_1, \varepsilon_2)$.

In the real process of mixing dielectrics, there is reaction at the boundary, especially when the difference is large in their properties. In fact, we can find there are small pores from the SEM cross section photo and there is a boundary reaction between two dielectrics. We can see the pore and new phase of the white rod like substances, different crystals intertwined together with different color in the photo.

In conclusion, for this system, the law of mixture is not suitable, actually $\varepsilon > \varepsilon_{\log}$ ($\varepsilon_{\log}$ is the logarithm average of the different dielectrics), even $\varepsilon > \max(\varepsilon_1, \varepsilon_2)$. We identify stress, phase transformation and boundary reaction as the key underlying factors in the process of mixing dielectrics. In the meantime, the experiments indicate that this mixing of the dielectrics can help improve the low temperature characteristics.

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

中高压介质电容瓷料迭加试验研究

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：利用混合物的介电性能的原理，设计了改善介电材料的温度系数的方法，进行了理论和实践的探讨，并对混合物的介电常数公式进行了修订。

关键词：介质材料；温度系数；混合物

中图分类号：TQ173 **文献标识码**：A