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Deterioration behavior analysis of dysprosium and thulium co-doped barium titanate ceramics for multilayer ceramic capacitors

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Abstract

An accelerated testing method for barium titanate ($BaTiO_3$) dielectrics was proposed to elucidate deterioration behavior of dielectric constant based on the life-temperature relation. The accelerated degradation test (ADT) which was designed using various temperature ranges below and above Curie temperature (T_c) was focused on the optimized composition of dysprosium (Dy) and thulium (Tm) co-doped $BaTiO_3$. The statistical analysis of the failure time data was performed to determine the optimum distribution as a goodness-of-fitness test. A scale parameter (η) and activation energy (E_α) were calculated in order to predict the life time of the co-doped $BaTiO_3$, and there was difference between the expected life times according to the acceleration temperature rating of the ADT. The difference of deterioration mechanism around T_c could be deduced from the change of lattice parameter and polarization behavior. The drastic decrease of tetragonality and ferroelectric property caused by the phase transition of the co-doped $BaTiO_3$ was verified in the temperature above T_c. Accordingly, the acceleration factor over T_c should be considered as reliability study of the $BaTiO_3$ dielectrics for multilayer ceramic capacitors (MLCCs).

Keywords: C. Dielectric properties; C. Lifetime; D. $BaTiO_3$ and titanates; D. Perovskite

1. Introduction

MLCCs having characteristics of miniaturization and high capacitance are required as an essential component with ongoing trend and development of portable electronic devices [1–4]. The researches about the development of additives composition for dielectrics and the reliability improvement of MLCCs have been progressed to meet these demands in electrical industry. Especially, rare-earth additives are generally applied to improve dielectric constant as well as to enhance life time and temperature stability due to the formation of core–shell structure [5–9]. And in reliability aspect, the electronic equipments should be guaranteed to satisfy its reliability, and the high durability of the individual components is needed because the negative effects by the failure of each part on the system are greatly influenced. The accelerated test which can cause failure and deterioration is used as a method for the reliability assessment considering time restriction and cost aspect. It is well known that the purpose of accelerated test is life time prediction through an adequate statistical method during short test time [10].

The $BaTiO_3$ ceramics which were used as the dielectrics for MLCC are a representative material having a phase transition property between cubic and tetragonal structure around T_c. Therefore, it is important to consider the verification of acceleration model assumption and the deterioration behavior according to the accelerated temperature conditions below and above T_c since the deterioration behavior of dielectric constant can be changed around T_c.

The content condition of Dy_2O_3 and Tm_2O_3 in the $BaTiO_3$ was confirmed through the research for the simultaneous improvement of dielectric constant and temperature stability previously [4]. In this paper, the

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reliability study on the Dy_2O_3 and Tm_2O_3 co-doped $BaTiO_3$ with the optimized content was carried out to elucidate the deterioration behavior of the dielectrics via the ADT. The life time prediction was conducted in the temperature ranges around T_c and the difference of deterioration mechanism was analyzed by the change of lattice parameter and polarization behavior.

2. Experimental

The researches about the optimum composition and the reliability assessment of Dy_2O_3 and Tm_2O_3 co-doped $BaTiO_3$ dielectrics were conducted with nominal compositions $BaTiO_3+xDy_2O_3+(1\%-x)\ Tm_2O_3$ where $x=0.0$, 0.3, 0.5, 0.7, and 1.0%. The $BaTiO_3$ specimens were prepared by using $BaTiO_3$ (Samsung Fine Chemicals, NBT-03), Dy_2O_3 (Aldrich, 99/9%), Tm_2O_3 (Aldrich, 99.9%), MgO (Aldrich, 98%), V_2O_5 (Junsei chemical Co. Ltd., 99.0%), SiO_2 (Aldrich, 99.9%), and MnO_2 (Aldrich, 99%). The dielectric constant and the temperature stability were measured by using an LCR meter (Agilent, E4980A), where the capacitance was measured at 1 kHz and 1 V from −55 to 150 °C.

The ADT was based on the dielectrics with optimum dielectric properties to confirm the difference of deterioration mechanism among the dielectric specimens tested in the temperature ranges below and above T_c which was determined as the inflection point of dielectric constant values. The constant accelerated temperature was applied to each specimen in a constant temperature and humidity chamber (AERO TECH) at 50, 75, and 100 °C as the temperature below T_c and at 130, 140, and 150 °C as the temperature above T_c.

The accelerated test for obtaining the failure time data continued until the point of time where the deterioration of dielectric constant was 10% of the initial value. Each $BaTiO_3$ specimen was tested 3 times repeatedly. In order to confirm the statistical analysis of the reliability data, we performed good-of-fitness verification about four typical life distributions to judge the optimum distribution's suitability of the achieving failure time data using MINITAB® statistical software. The acceleration model was based on Arrhenius's law about a chemical reaction rate and the life time prediction of the co-doped $BaTiO_3$ dielectrics was carried out after calculating η and E_α values in the temperature ranges below and above T_c. The lattice parameter was measured by a Rietveld refinement method (X'pert high score, Panalytical) through X-ray diffraction patterns using an X-ray diffractometer (MAC Science, M18XHF) for the failed specimens in order to verify the deterioration mechanism. The polarization behaviors were analyzed by a precision RC (Radiant Tech., USA) around T_c and finally, these results were compared with before and after the deterioration test.

3. Results and discussion

Fig. 1 shows the dielectric constant and the temperature stability of $BaTiO_3$ ceramics as a function of Dy_2O_3 and Tm_2O_3 contents over the temperature range of −55–150 °C.

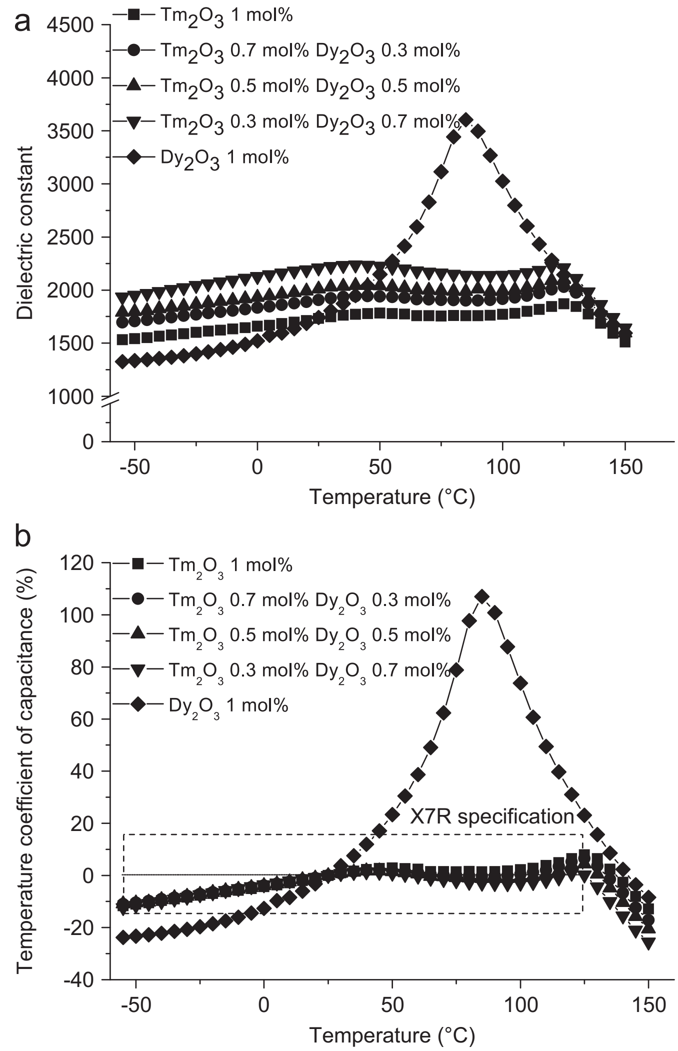

Fig. 1. (a) Temperature dependence of dielectric constant and (b) TCC of rare-earth doped $BaTiO_3$ ceramics as a function of Dy_2O_3 and Tm_2O_3 contents.

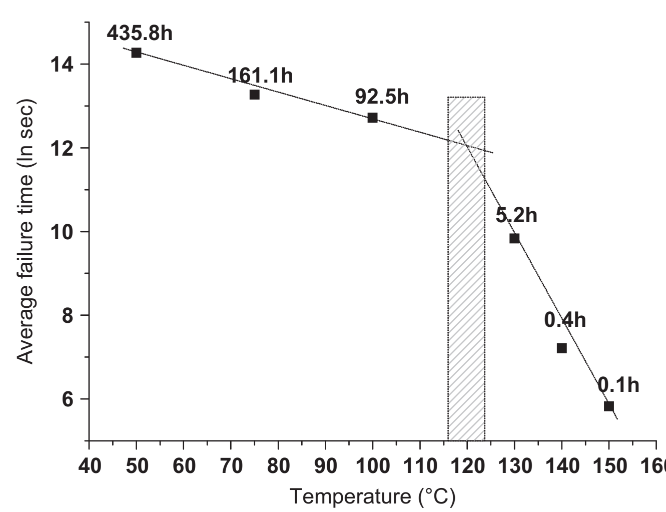

Fig. 2. Average failure time of the Dy_2O_3 and Tm_2O_3 co-doped $BaTiO_3$ specimens according to various temperatures.

The dielectric constant was enhanced with increasing Dy_2O_3 content but in case of the sample doped 1 mol% Dy_2O_3, the temperature stability drastically decreased. On the other hand, the addition of Tm_2O_3 can contribute to temperature coefficient of capacitance and all the Tm_2O_3 doped $BaTiO_3$ samples met the X7R specification (Fig. 1(b)). The specimen

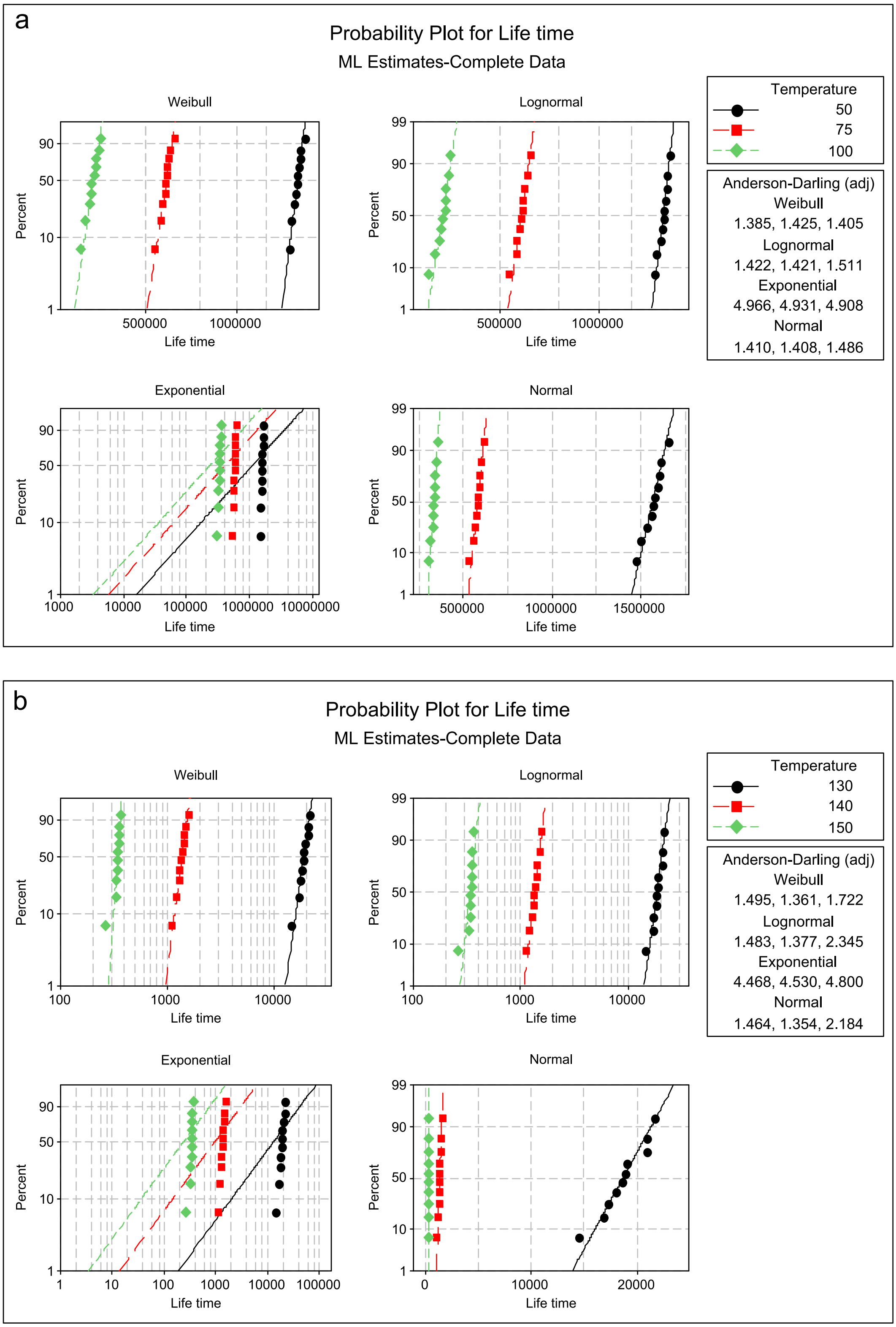

Fig. 3. Analysis of distribution suitability for failure time of Dy_2O_3 and Tm_2O_3 co-doped dielectric specimens in the temperature ranges (a) below and (b) above T_c.

co-doped with 0.7 mol% Dy_2O_3 and 0.3 mol% Tm_2O_3 exhibited the highest dielectric constant (≒2250) as shown in Fig. 1(a) at the room temperature having temperature stability (Fig. 1(b)). The dielectric property had a similar value with the previous researches which show the typical dielectric constant of 1500–4000 for the X7R material [9,11]. The dielectric constant of the dielectrics was improved with increasing the Dy_2O_3 content and the Tm_2O_3 addition contributed to the temperature stability. Therefore, the optimized condition of the co-doped $BaTiO_3$ could be obtained, which was satisfied with the improved dielectric constant and temperature stability simultaneously. The subject of the reliability assessment was 0.7 mol% Dy_2O_3 and 0.3 mol% Tm_2O_3 co-doped $BaTiO_3$ dielectrics whose composition was optimized by the analyses of microstructure and thermal properties [5].

Fig. 2 shows the average failure time of the Dy_2O_3 and Tm_2O_3 co-doped $BaTiO_3$ specimens according to various temperatures (50, 75, 100, 130, 140, and 150 °C). The failure time of the co-doped $BaTO_3$ was reduced with the increasing acceleration temperature, especially; the average failure time at the test condition above T_c was decreased rapidly shown in Fig. 2. It was expected by the fact that the deterioration behavior was changed around T_c where the slope of the average failure time suddenly increases.

From these results, we considered four kinds of life distribution: Weibull distribution, exponential distribution, normal distribution, and logistic distribution divided into two temperature ranges above and below T_c as shown in Fig. 3. Using the Anderson–Darling adjustments, the results indicated that the Dy_2O_3 and Tm_2O_3 co-doped dielectrics were adequately represented by a Weibull distribution. The Anderson–Darling adjustment values provide information about the goodness-of-fitness, such that the lower values indicated better correspondence with the distribution mode [12].

In order to predict the life time of the co-doped $BaTiO_3$ tested in the temperature ranges below and above T_c respectively, η and E_α values were calculated by follow equations applying the Arrhenius law,

$$\ln \eta = \ln \alpha + E_\alpha/k \cdot 1/T \quad (a)$$

$$v = \alpha_0 \exp(-E_\alpha/kt) \quad (b)$$

where η is the scale parameter, E_α is the activation energy, k is the Bolzman constant, v is the reaction rate, and α_0 is the constant. We achieved the scale parameter of $\eta = 4.0719 \times 10^6/1.8564 \times 10^{17}$ and the activation energy of $E_\alpha = 0.3195/2.9578$ applied the Arrhenius model in the temperature ranges below and above T_c, respectively, and confirmed the difference of each value. Also, as the results of life time prediction at 100 °C and 150 °C using these values, the life times of dielectrics had a considerable gap, which values are 1131 h and 5.156×10^{13} h (Table 1).

Table 1
Scale parameter (η), activation energy (E_α), and life time prediction at 25 °C values of dielectrics in the temperature ranges below and above T_c.

	Temp. below T_c	Temp. above T_c
Scale parameter (η)	4.0719 × 106	1.8564×10^{17}
Activation energy (E_α)	0.3195	2.9578
Life time prediction (25 °C)	1131 h	5.156×10^{13} h

The lattice parameter change of the $BaTiO_3$ tested at 100 °C and 150 °C was analyzed to define the difference of the predicted life time caused by the accelerated test in the temperature ranges below and above T_c. The tetragonality of the co-doped $BaTiO_3$ powders was calculated from the X-ray diffraction data [13] corresponding to (002) and (200) plans by using the Rietveld refinement method for comparison of c/a. Table 2 shows the variation of lattice parameters a and c of $BaTiO_3$ dielectrics before and after degradation at 100 °C and 150 °C. The lattice parameters of $BaTiO_3$ declined with deterioration and the decreasing rate of the tetragonality for $BaTiO_3$ degraded above T_c was lower than that of the dielectrics degraded below T_c. It could be identified that the co-doped $BaTiO_3$ degraded at 150 °C had the higher change rate of dielectric constant than that at 100 °C. Thus, the deterioration mechanism of the dielectrics was expected to vary around T_c, and this suggestion was experimentally verified with the failure time data shown in Fig. 2.

Fig. 4 shows the change of P–E hysteresis loops of the Dy_2O_3 and Tm_2O_3 co-doped dielectric specimens before (25 °C) and after (100 and 150 °C) deterioration. The co-doped $BaTiO_3$ degraded at 100 °C exhibited lower maximum polarization (P_{max}) up to 0.196 μC/cm^2 which was 10% lower than that of dielectrics in the room temperature (0.220 μC/cm^2) as shown in Fig. 4(a) and (b). On the other hand, the dielectrics degraded at 150 °C exhibited the abrupt reduction of the polarization behavior as well as the lowest P_{max} value (0.170 μC/cm^2) with the decline of 25% compared with the dielectrics in the room temperature (Fig. 4(c)). It can be explained in the phase transition

Table 2
Variation in lattice parameters and tetragonality of $BaTiO_3$ ceramics according to the testing temperature around T_c before and after deterioration.

Testing temperature	100 °C			150 °C		
	a	*c*	*c/a*	*a*	*c*	*c/a*
Before deterioration	4.00081	4.02643	1.00640	4.00074	4.02694	1.00655
After deterioration	4.00278	4.01963	1.00421	4.00487	4.00968	1.00120

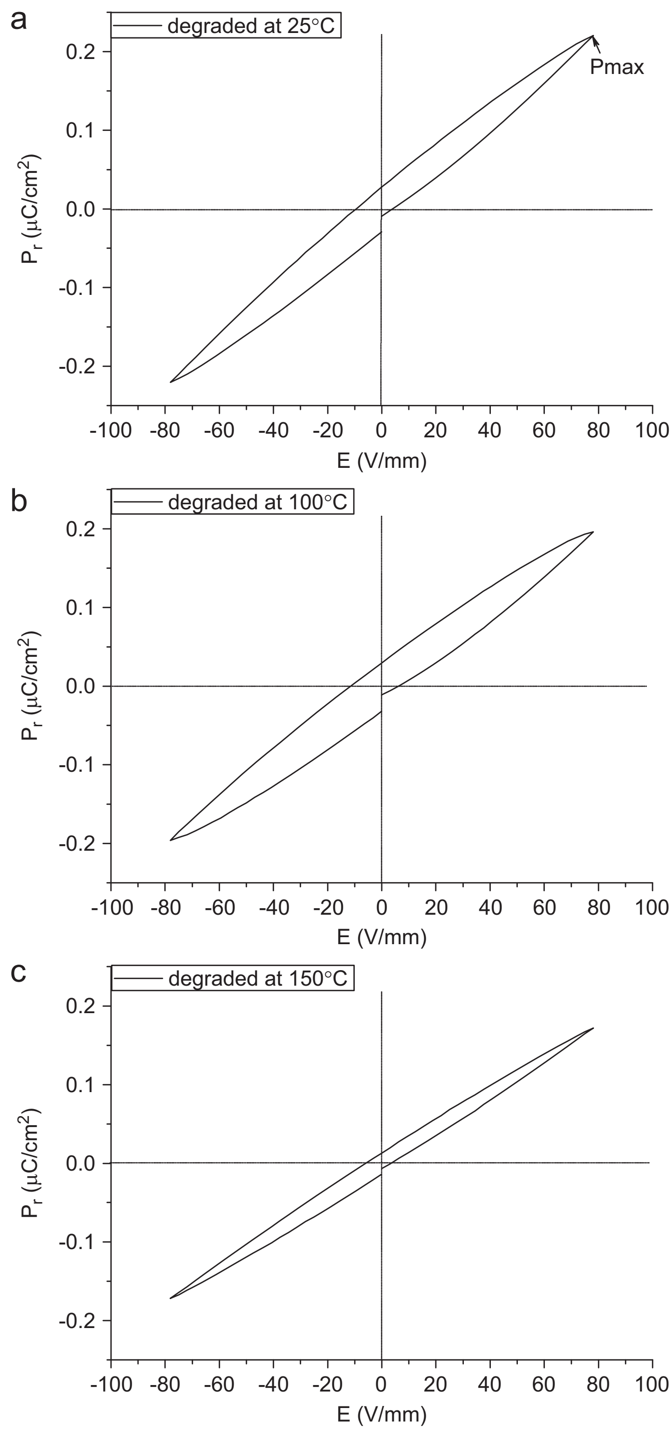

Fig. 4. Change of *P–E* hysteresis loops according to the temperature ((a) 25, (b) 100, and (c) 150 °C) of the Dy_2O_3 and Tm_2O_3 co-doped dielectric specimens.

of the co-doped $BaTiO_3$ since the dielectric property is changed from ferroelectric to paraelectric around T_c.

The difference of the predicted life time of the co-doped $BaTiO_3$ shown in Table 1 could be demonstrated in terms of the decrease of tetragonality and polarization behavior above T_c, and the deterioration mechanism of the co-doped $BaTiO_3$ around T_c could be changed according to the acceleration temperature. For such reasons, it is difficult to conduct the life time prediction due to the difference in η and E_α and finally the change of deterioration mechanism could be considered certainly during the accelerated test of $BaTiO_3$ ceramics having the phase transition temperature.

4. Conclusions

The reliability assessment on the 0.7 Dy_2O_3 and 0.3 Tm_2O_3 co-doped $BaTiO_3$ with the optimized content was carried out to elucidate the deterioration behavior by the ADT according to various temperature ranges. The average failure times at the test conditions above T_c were decreased rapidly, and it was expected by the fact that the deterioration mechanism was changed around T_c where the slope of average failure time suddenly increases. The Weibull distribution was selected as the goodness-of-fit test, and η and E_α values were calculated for the life time prediction respectively. As the results of the prediction at 100 °C and 150 °C using these values, the considerable gap of the expected life times of the co-doped $BaTiO_3$ was identified. In order to analyze the reason for the difference of predicted life time, the change of tetragonality and polarization curves was measured around T_c before and after the deterioration. The deterioration rate of tetragonality and P_{max} value was rapidly increased in the temperature above T_c, and the difference of deterioration mechanism in the temperature ranges below and above T_c could be verified by the change of lattice parameter and polarization behavior due to the phase transition of $BaTiO_3$ ceramics. Thus, the acceleration factor over T_c should be considered as the reliability assessment of $BaTiO_3$ for MLCCs.

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