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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.

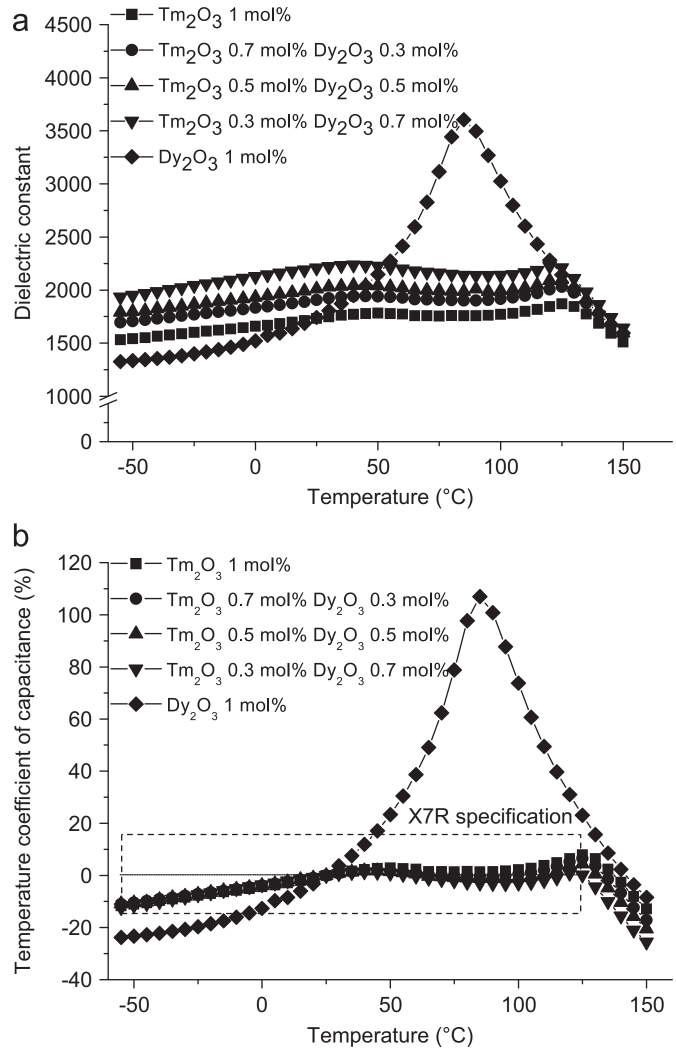

Fig. 1. (a) Temperature dependence of dielectric constant and (b) TCC of rare-earth doped $BaTiO_3$ ceramics as a function of Dy_2O_3 and Tm_2O_3 contents.

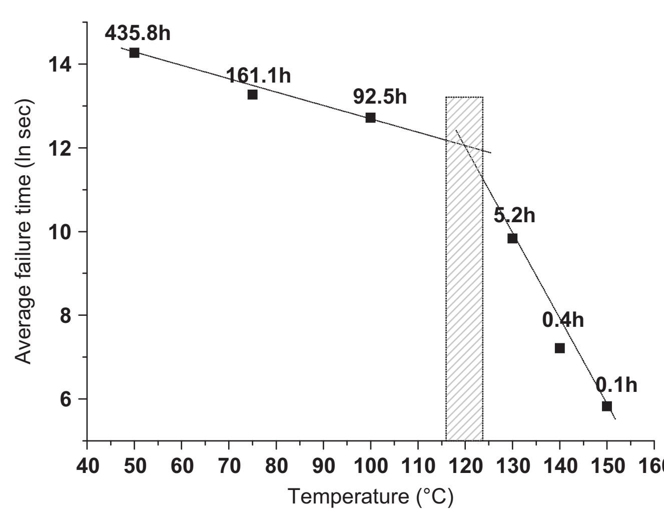

Fig. 2. Average failure time of the Dy_2O_3 and Tm_2O_3 co-doped $BaTiO_3$ specimens according to various temperatures.