

Mechanism of capacitance aging under DC-bias field in X7R-MLCCs

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Abstract Capacitance aging under DC electric fields has been studied on multilayer ceramic capacitors (MLCCs) with the X7R characteristics. The capacitance change with time was divided into two stages, the first- and the second-stage. The first-stage was due to the nonlinear permittivity of dielectrics and it should not be involved in the aging phenomenon. The second-stage depended on the MnO content, grain size and firing condition of dielectrics. From the behavior of the second-stage, it was concluded that the capacitance aging was caused by the 90-degree domain switching in BaTiO₃ in the core. The first-stage was due to the nonlinear permittivity but the domain switching was also included in the first-stage if the domain walls moved by the first application of DC field. The change in the aging behavior with the intensity of DC field could be explained by separating capacitance change into the nonlinear permittivity and the domain switching according to the mechanism proposed in this study.

Keywords Multilayer ceramic capacitor · Ferroelectric domain · Barium titanate · Nonlinear dielectricity · X7R

1 Introduction

Multilayer ceramic capacitors (MLCCs) have been used for surface-mounted chip capacitors in various electric circuits. In order to increase the capacitance density of MLCCs, the dielectric layer thickness has been reducing every year and it has reached under 1 μm [1, 2]. The reduction of the dielectric layer thickness directly implies the increase in the electric field applied to the dielectric layers [3, 4]. The dielectrics in MLCCs with the EIA X7R specification have the “core-shell” structure in one grain, where the core in a grain consists of almost pure BaTiO₃ while the shell around the core consists of BaTiO₃-based relaxor-like dielectrics [5, 6].

Recently, a serious problem has been coming out in the dielectric properties of X7R-MLCCs with ultra thin dielectric layers, which is the capacitance aging under DC electric fields. The capacitance of MLCCs somehow decreases with time under the continuous application of DC fields. Although this problem is extremely important for the usage of MLCCs in electric circuits, studies on the capacitance aging under DC fields have been extremely limited so far except the report of Nomura et al. [7] They indicated that the capacitance aging without DC fields could well be explained by a Richter-type relaxation curve, while the aging behavior under DC fields was explained by two-step relaxations, short-term relaxation and long-term relaxation. However, the mechanism of the capacitance aging under DC fields was not understood yet.

In this study, we have measured the capacitance aging for X7R-MLCCs with different grain sizes, firing conditions and MnO content under various experimental conditions in order to understand the mechanism of the capacitance aging under DC fields.

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2 Experimental procedure

The dielectric compositions employed here were $100\text{BaTiO}_3-0.5\text{Ho}_2\text{O}_3-0.5\text{MgO}-x\text{MnO}-1.5\text{BaSiO}_3$, where the amount of MnO (x) was changed from 0.0 to 0.8 mol%. The addition of Ho_2O_3 was considerably effective in prolonging the lifetime of capacitors [1, 8]. These dielectrics show a temperature-stable dielectric permittivity and satisfy the X7R characteristics. The MLCCs were formed by a sheet method using paste of the dielectric materials and nickel for internal electrodes. After printing nickel electrodes, green sheets were laminated and pressed to form 10 or 20 dielectric layers. The thickness of dielectric layers after sintering was 2–4 μm . The core-shell structure was observed in dielectric layers in all MLCCs. The domain structures observed in the core were almost the same in size for all specimens.

The capacitance aging of the MLCCs was measured as a function of temperature and DC field at 1 kHz and 5–10 mV(rms) in AC voltage using an impedance analyzer (Agilent Tech., hp4294A). The measurement of capacitance aging in this study is that the capacitance of MLCC was measured as a function of time under continuous application of a certain DC field at fixed temperature.

3 Results and discussion

Figure 1 shows a typical capacitance aging behavior of X7R-MLCCs under a DC electric field. The δC (%) means $\delta C = (C - C_0)/C_0 \times 100$, where C_0 is the capacitance measured without DC field at the temperature shown in the figure. It is possible to see that the reduction of the capacitance proceeds with two stages as Nomura et al. [7] pointed out. The first-stage ends before 10 s in this figure. We have measured the δC at very early time less than 1 s

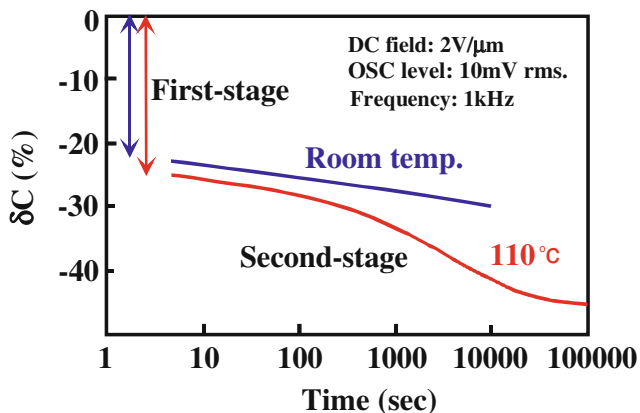


Fig. 1 Typical examples of the capacitance aging in X7R-MLCCs measured at room temperature and 110 °C

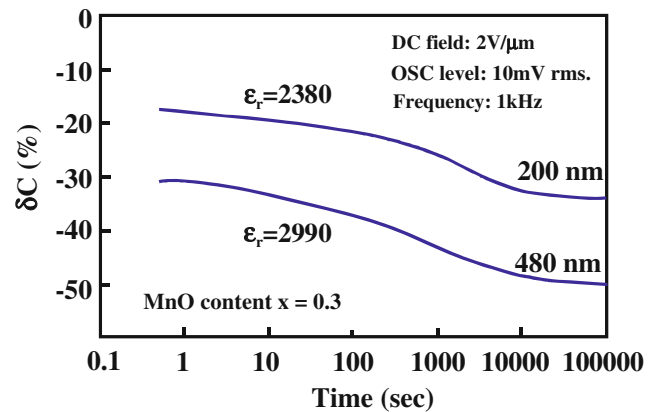


Fig. 2 Capacitance aging at 110 °C of dielectrics with the grain size of 200 and 480 nm. Relative permittivity shown in the figure was measured without DC field

but the δC in the first-stage was consistent. This indicates that the reduction of the capacitance in the first-stage takes place at the application of DC field without a time delay. The first stage is therefore attributable to the nonlinear dielectric permittivity of dielectric materials and it should not be included in the capacitance-aging phenomenon. The second-stage starts after the first-stage and continues up to 10^5 s and more. The δC in the second-stage depends on temperature, indicating that a thermal activation process concerns with the aging phenomenon.

We can consider two possible mechanisms for the capacitance aging in the second stage. The one is the effect of internal fields or space charges caused by trapped charge carriers at the grain boundaries. As the dielectrics are fired in a reducing atmosphere to prevent the oxidation of nickel electrodes, a lot of defects and charge carriers are produced in the dielectrics. These carriers are moved by the external DC fields and trapped at the grain boundaries to form internal fields or space charges that may change the dielectric permittivity. The other mechanism is the switching of 90-degree domains in tetragonal BaTiO_3 in the core because no domains are observed in the shell. It is known that the dielectric permittivity of tetragonal BaTiO_3 along c-axis (ϵ_{33}) is much smaller than that along a-axis (ϵ_{11}). The external DC field switches the 90-degree domains to align the c-axis to the field, which gives rise to the reduction of dielectric permittivity.

The grain size dependence of the aging behavior is shown in Fig. 2. The first-stage was enhanced in the specimen with a large grain size but the second-stage was independent of the grain size. The enhancement in the first-stage can be understood by the difference in the dielectric permittivity. The dielectric layer with the large grain size has a high permittivity as shown in Fig. 2. The high permittivity usually results in the high nonlinear permittivity of dielectric ceramics: consequently the first-stage in the

specimen with a large grain size was enhanced. It is important that the second-stage was less dependent on the grain size. If the trapping of charge carriers at grain boundaries plays an important role in the aging phenomenon, the second-stage should be changed with the grain size. Therefore, the result in Fig. 2 indicated that the internal field or space charges caused by trapped charge carriers less related with the aging phenomenon.

The aging behavior measured at different temperatures is shown in Fig. 3. It should be noted that the capacitance aging was markedly depressed at 150 °C which is above the Curie temperature of BaTiO₃. In the report of McQuarrie and Buessem [9], it was shown that the aging behavior was peculiar to the ferroelectric states. If the migration and trapping of charge carriers were the origin of the aging, the aging behavior would change monotonously with temperature. It is obvious that the dielectrics do not have ferroelectric domains above the Curie temperature. Consequently, the suppression of the aging in the specimen without domains strongly supports the mechanism of the 90-degree domain switching as the origin of the aging phenomenon.

Figure 4 shows the change in the aging behavior with MnO content (x). The relaxation time of the aging obviously decreased with increasing MnO content. It was reported that the capacitance change by the aging increased with increasing Mn content [7]. However, it was found in this study that the δC of MLCCs with different Mn contents tended to saturate to a certain value after a long time aging. Most of Mn ions are incorporated into the shell but a slight amount of Mn ions are located in the core in MLCCs. The Mn ions with a multi valence state substitute the Ti ions at the B site of Perovskite lattice as acceptors. The addition of a large amount of Mn produces a large amount of defects in the dielectrics. This should enhance the capacitance change if the trapped charge carriers concerns with the aging phenomenon. The result in Fig. 4 shows that the δC after a long time aging is independent of the Mn content, which

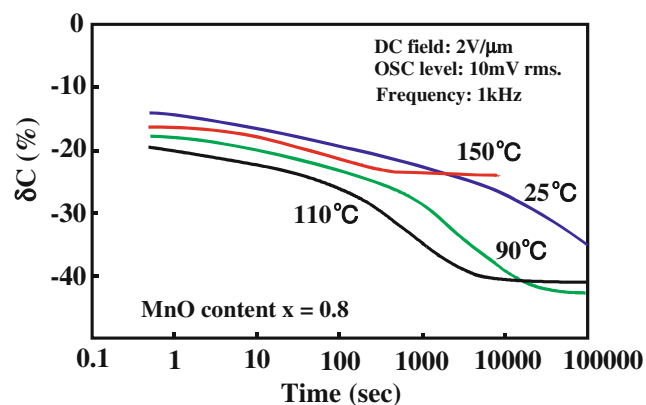


Fig. 3 Capacitance aging measured at different temperatures

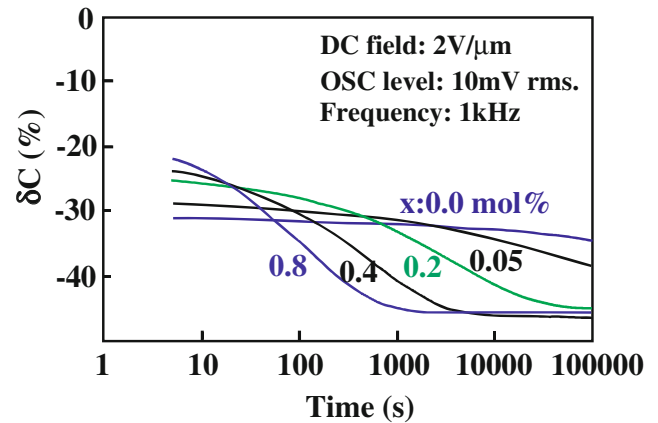


Fig. 4 Effect of MnO addition on the capacitance aging at 110 °C. The chemical composition of dielectrics is given by 100 BaTiO₃–0.5 Ho₂O₃–0.5 MgO–xMnO–1.5 BaSiO₃

indicates that the internal field or space charges less related with the aging phenomenon.

In Fig. 5, the aging behavior was compared for MLCCs fired in reducing or air atmosphere. In the latter, Ag–Pd internal electrodes were used to prevent the oxidation of the electrodes. The aging in the second-stage is markedly depressed in the air-fired specimen. It is also notable that the δC after the aging is almost consistent for the two specimens. In other words, the aging in the second-stage could be moved to the first-stage by firing in air atmosphere. The Mn ions in the core of the reduced specimen have trivalent (Mn³⁺) or divalent (Mn²⁺) state, which clamp the domain-wall motion. It is well known that Mn is an effective additive to makes the ‘hard’ PZT ceramics, in which the domain-wall motion is clamped by the defect dipoles associated with Mn³⁺ and/or Mn²⁺ substituted with B site ions in Perovskite structure [10, 11]. In the MLCCs fired in air atmosphere, Mn³⁺ and/or Mn²⁺ are possibly changed to Mn⁴⁺ that is not effective to clamp the domain-wall motion. This change results in a relatively free

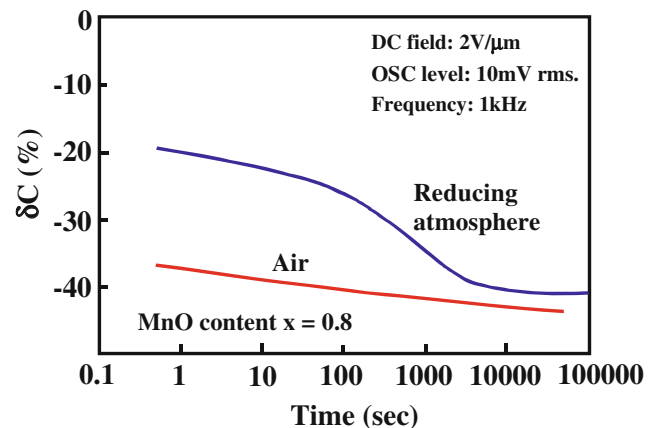


Fig. 5 Effect of firing condition on the capacitance aging at 110 °C

movement of domain walls by the first application of DC field, therefore, the δC in the second-stage moved to the first-stage in the air-fired specimen. The δC after the aging was consistent for two specimens because the firing condition did not much affect the nonlinear permittivity and the domain switching of MLCCs.

From the results obtained above, we have concluded that the capacitance aging in the second-stage is caused by the 90-degree domain switching in BaTiO₃ in the core. The mechanism of the capacitance aging in X7R-MLCCs is shown in Fig. 6. Most of domains walls in the core are clamped by the defect dipoles formed by negatively charged Mn sites and positively charged oxygen vacancies. The movement of unclamped domain walls may be involved in the δC in the first-stage, although the δC in the first-stage mainly is due to the nonlinear dielectric permittivity of the relaxor-like shell. In the second-stage, the continuous application of DC fields moves the electrons on Mn sites to eliminate the defect dipoles with time. This enhances the domain-wall motion to align the c-axis of BaTiO₃ to the electric field direction, resulting in the reduction of dielectric permittivity due to the permittivity difference between the ϵ_{33} and ϵ_{11} . The movement of electrons is thermally activated hopping process. And, the increase in Mn sites in the core enhances the hopping of electrons, therefore, the relaxation time reduced with increasing MnO content (x). The difference between the ϵ_{33} and ϵ_{11} is almost independent of the Mn content, so the

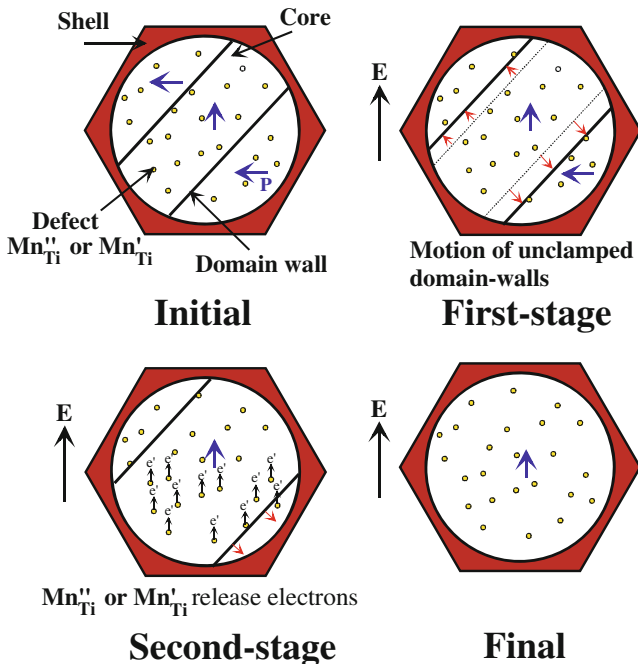


Fig. 6 A proposed mechanism for the capacitance aging. Each hexagon shows one grain in the dielectric layer

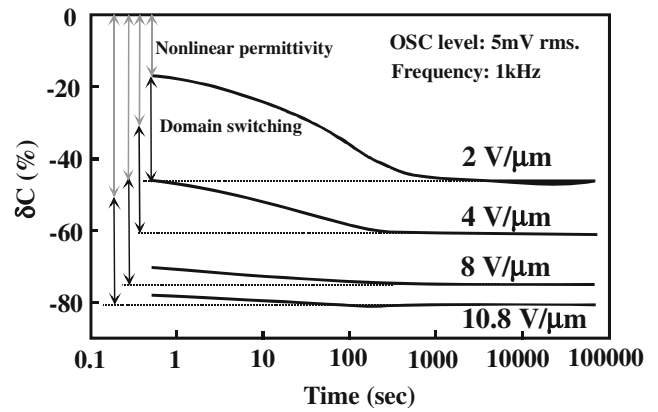


Fig. 7 Capacitance aging curves of the specimen with $x=0.8$ at 110 °C measured under different DC fields. The effects of the nonlinear permittivity and the domain switching on the δC was shown as arrows

δC after the aging tends to saturate to a certain value as shown in Fig. 4.

Figure 7 shows the change in the aging behavior with the DC field. It should be noted that the first-stage enhanced but the second-stage depressed to disappear when a high DC field was applied. This is because the high DC field moves the domain walls quickly in the first-stage in spite of the clamping of domain walls by defect dipoles. The same phenomenon is normally observed in ferroelectrics when an applied DC field exceeds the coercive field. The difference in the δC after the aging is purely due to the effect of nonlinear permittivity because the domain switching is completed after the second-stage. Figure 8 shows an electric displacement (D) vs. electric field (E) curve measured for the specimen in Fig. 7. A clear hysteresis observed in the D – E curve indicates that the domain switching definitely takes place in the dielectrics. By assuming that the difference in δC after the aging in Fig. 7 was caused only by the nonlinear permittivity, it was possible to

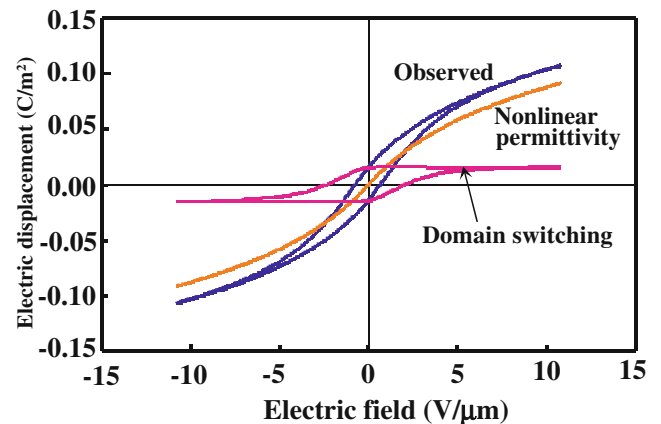


Fig. 8 Electric displacement (D) vs. electric field (E) curve of the specimen in Fig. 7

separate the effect of the nonlinear permittivity and that of the domain switching from the experimental results. The two additional curves in Fig. 8 show the both effects. The D – E curve observed could be explained by the sum of the nonlinear permittivity and the domain switching. The effects of the nonlinear permittivity and the domain switching were also separated and shown in Fig. 7. It is important that the domain switching effect on the δC is consistent for all curves in the figure and the δC due to the nonlinear permittivity increases with increasing DC field.

4 Conclusion

The mechanism of the capacitance aging in X7R-MLCCs was clarified in this study. The first-stage is due to the nonlinear permittivity and the second-stage is due to the domain switching, but the domain switching is also included in the first-stage if the domain walls move by the first application of DC field.

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