Defence Science Journal, Vol. 60, No. 6, November 2010, pp. 683-686

SHORT COMMUNICATION

Effect of Temperature on Aging of Ferroelectric Lead-Strontium-Zirconate-Titanate Ceramics

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ABSTRACT

The effect of aging on Sr^{2+} modified lead-zirconate-titanate (PSZT) ceramics has been studied. Aging was assessed by the measurement of dielectric constant and dielectric loss tangent as a function of time and temperature. Dielectric constant and dielectric loss tangent were measured at different temperature ranges. Absolute rate of aging and relative rate of aging were determined. The PSZT ceramic showed sharp dielectric peak at 300 °C. The results shows that with increase temperature, both the dielectric constant and rate of aging increase.

Keywords: Aging, dielectric constant, dielectric loss tangent, temperature, ferroelectric ceramics, PSZT ceramics

1. INTRODUCTION

Aging is a time-dependent phenomenon leading to changes in piezoelectric properties of ferroelectric materials[1-2]. The changes tend to be logarithmic with time after poling[3]. Some external stimulation can also affect the aging rate of the ferroelectric ceramics[4]. It was observed that with increase in temperature electromechanical coupling coefficient (k_p) and piezoelectric charge coefficient (d_{33}) of poled piezoceramics decreases considerably[5-7]. This is due to the structural changes in ferroelectric ceramics as function of temperature as approaching the Curie temperature[8]. For understanding of the aging mechanism and development of ferroelectric devices, the study and knowledge of aging is considered to be an important aspect of research[9].

Over the period of past forty years, different aging models have been proposed by different authors to describe the time-dependent changes. However no uniform model exists which can necessarily explain the possible contributions of the dielectric constant. Earlier investigations on dielectric aging in $BaTiO_3$ ceramic indicate that there may exist more than one aging mechanism[10].

The following aging models have been proposed by different authors to describe the time dependent changes.

1. Aging may involve stabilisation of domain pattern by the segregation of impurities and vacancies on domain walls[11,12].
2. Space charge field in poled ceramics increases gradually with aging because of the effect of the depolarising field[13].
3. Poled ceramics are stabilised by space charge polarisation at the grain boundaries that arises from the interaction between the polarity of the domain and the polarity of space charge[14].

Although much work has been done on $BaTiO_3$, PLZT and PMN-PT, no dielectric aging has been reported on Sr^{2+} modified PZT, a hard category of piezoelectric ceramic. In the present work, the authors have studied the aging of dielectric constant (K^T_3) and dielectric loss tangent (tanδ) as a function of both time and temperature.

2. EXPERIMENTAL

The composition selected for the study of was $Pb_{0.94}Sr_{0.06}(Zr_{0.53}, Ti_{0.47})$. The ferroelectric ceramics were prepared from powders of $SrCO_3$, PbO, ZrO_2, and TiO_2 by mixed oxide route. The powders were weighed and mixed with zirconia grinding media and distilled water for 24 h in roller mill. Calcination was carried out at 1000 °C for 4 h. The powder was pressed into the discs 10 mm in diameter and 1 mm in thickness by applying a pressure of 121 MPa. The discs were sintered between 1260 °C – 1300 °C for 1h in a closed alumina crucible. Sintered discs were lapped for smooth surface and subsequently silver electroded. The sample were poled by applying dc electrical field 3 kV /mm in silicon oil bath at 80 °C for 30 min. Direct Current (dc) electrical field was applied by high voltage power supply (Brandenburg make, USA).

Particle size of calcined powder was measured using Particle Size Analyser (Master Sizer model 2000 MU (A)). K^T_3 and tanδ were measured at different time interval. Temperature dependence of K^T_3 and tanδ was measured at temperature range from 100 °C to 400 °C. Aging of K^T_3 and tan δ was also studied at 150°C and 200°C at regular time intervals which lied between the poling temperature

Received 11 August 2009, Revised 9 September 2010

and Curie point. K^T_3 and tan δ were measured using HIOKI 3532 – 50 LCR HITESTER (Japan).

3. RESULT AND DISCUSSION

Some properties of PSZT evaluated before and after the sintering are listed in Table 1.

Table 1. Properties of the PSZT

Property	Value
Particle size (μm)	1.179
Green's density (gm/cc)	4.95
Sintered density (gm/cc)	7.58
Curie temperature (°C)	320

XRD pattern of calcined powder is shown in Fig. 1. Figure 2 represents XRD pattern of: (a) Sintered sample, (b) poled sample, and (c) poled sample heated above T_c. Poled sample (b) shows the intense peak by (110) plane indicating the formation of perovskite phase. Splitting of (h00), (h01) and (h11) types peak, i.e., (002) and (200); (102) and (201); and (112) and (211), respectively indicates the co-existence of ferroelectric rhombohedral (F_R) and ferroelectric tetragonal (F_T) crystal structure. More splitting of these peaks were seen in sintered samples than in calcined powder. In case of poled sample, (200) peak intensity increased, at the same time that of (002) peak decreased indicates the tetragonality increases. The XRD pattern of

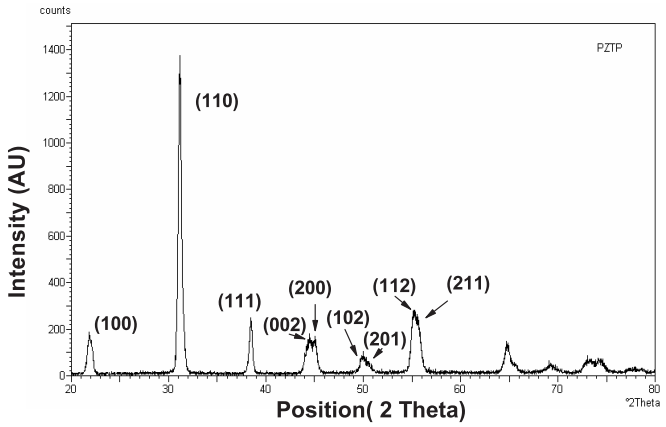

Figure 1. XRD of PSZT calcined powder.

the sample heated above the T_c (i.e., 400 °C) was taken at room temperature and it was observed that the peak intensity of $(200)_T$ has reduced to the large scale. Additional $(200)_R$ peak also appeared.

Figure 3 shows the SEM of the fractured surface of the unpoled sample in which a dense microstructure can be seen. After analysis it is seen that the grains are polygonal in shape having average grain size 2.1 m.

Figure 4 shows the aging of K^T_3 and tan δ. Both of them decreased with respect to logarithmic time. This decrease was because of domain moving to lower energy state leads to aging. The driving force is the mechanical and electrical stresses, which arises during poling. The aging behavior for K^T_3 and tan δ follows the logarithmic law. The

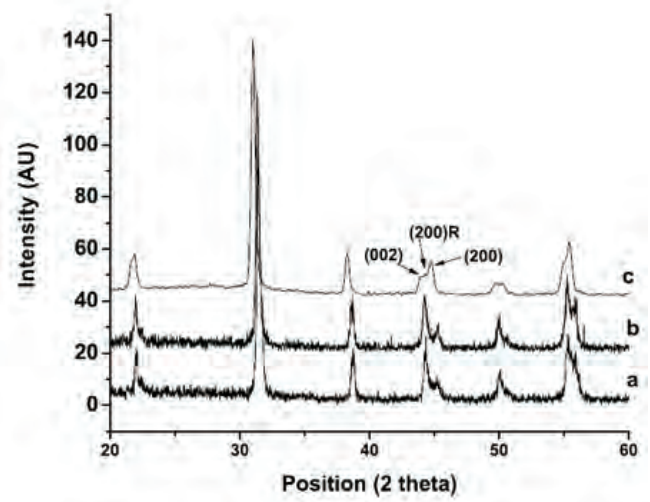

Figure 2. XRD of samples: (a) unpoled, (b) poled and (c) heated above T_C.

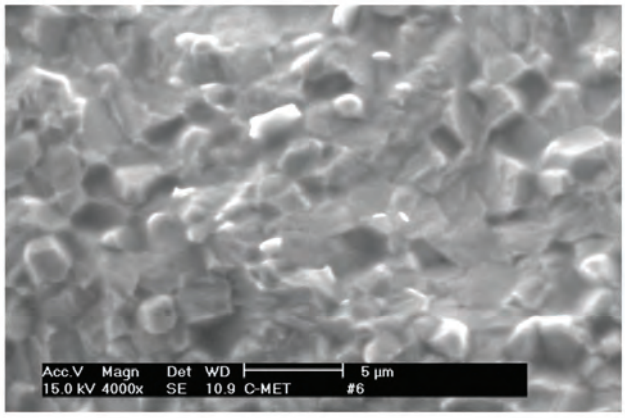

Figure 3. SEM of fractured sample.

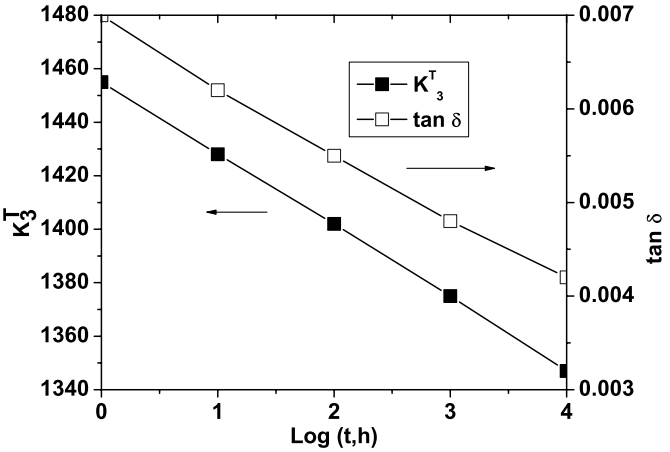

Figure 4. Aging of K^T_3 and tan δ at 25 °C.

Absolute aging rate (A) and Relative aging rate (R) for ferroelectric PSZT ceramics were calculated according[15] to Eqns (1) and (2).

$$K_t = K_0 - A \log (t) \quad (1)$$

$$R = A \times 100 / K_0 \quad (\% \text{ decade}) \quad (2)$$

where K_t is dielectric constant after time t, K_0 is dielectric constant measured at t = 1 min.

A is the absolute aging rate relating to the absolute decrease in property in one decade. The values of A and R for K^T_3 were determined using Eqns (1) and (2) and plotted against Log(t). Both the absolute aging rate and relative aging rate are used to characterise the aging behaviour.

Figure 5 represent A and R as a function of log(t) for K^T_3. It is seen that as the log (t) increases, the difference in (K_0 -K_t) also increases, indicating the domain has moved to lower energy state. Initially, the decrease in A was rapid, this is because after poling, the rate of domain movement to lower energy state was higher and log(t) was minimum. However as the time elapsed, the domain stabilised, the difference in (K_0 -K_t) was increased but log(t) was also increased. That increase in log(t) was responsible for slowdown of the rate of decrease in A. R thus also shows the same behaviour as A, since R is completely dependent on A.

Figure 6 shows temperature dependence of K^T_3 and tan δ. The figure shows that as the temperature increases, K^T_3 also increases. Because, with increasing temperature the ferroelectric ceramics undergo structural changes. Sharp peak of the dielectric constant was observed at 300 °C. This indicates that at this temperature, phase transition from ferroelectric tetragonal to paraelectric cubic occurs.

The tan δ increase slowly with increasing temperature up to phase transition temperature. After this temperature the tan δ suddenly increases. This has been attributed to the disappearance of the domain structure at this temperature.

Figure 7 shows the aging of K^T_3 and tan δ as a function of temperature for longer time. A considerable decrease in the K^T_3 is observed when the ferroelectric ceramics are aged for longer times at temperature 150 °C and 200 °C. It was clear that aging was accelerated by exposing the ceramics to the temperature that approaches the Curie point. This is due to the fact that aging process is thermally activated and aging occurs more rapidly at higher temperatures. Increasing the temperature from 150 °C to 200 °C activates the K^T_3 from domain wall motion and aging from defect dipole reorientation leads to increasing both K^T_3 and rate of aging. For both the temperatures aging clearly begins to slow down after 6 h. This may be due to another mechanism of aging that may start from this time.

The behaviour of the tan δ as a function of temperature showed the same trend as that of K^T_3. At higher temperatures, the properties tend to deteriorate rather rapidly as the temperature is raised. This is true in PSZT, which has Curie temperature of 320 °C. The considerable decrease in tan δ was observed when PSZT wasaged for long time at temperatures 150 °C and 200 °C. Here also for both the temperatures, aging starts to slow down after 6 h. This may be due to another mechanism of aging that may start from this time.

4. CONCLUSION

Aging follows the logarithmic law for both dielectric constant and dielectric loss tangent (tan δ). The absolute aging rate and relative aging rate for K^T_3 was decreased with Log(t). The rate of aging accelerated by exposing ceramics to high temperature. Peaks of the dielectric constant K^T_3 and dielectric loss tangent (tan δ) were observed at the same temperature.

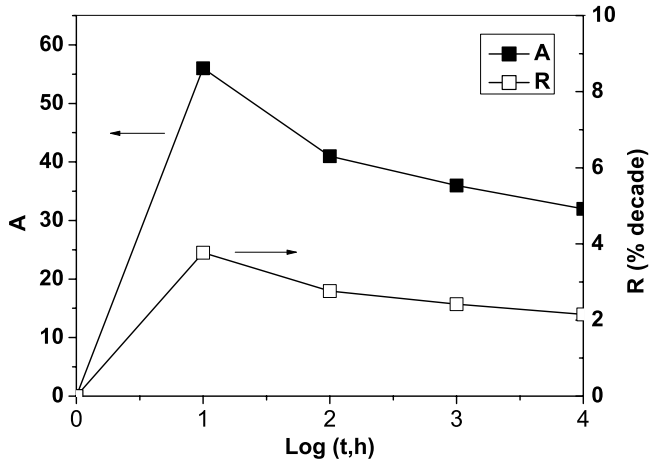

Figure 5. Absolute aging rate (A) and relative aging rate (R) as a function of log(t) for K^T_3.

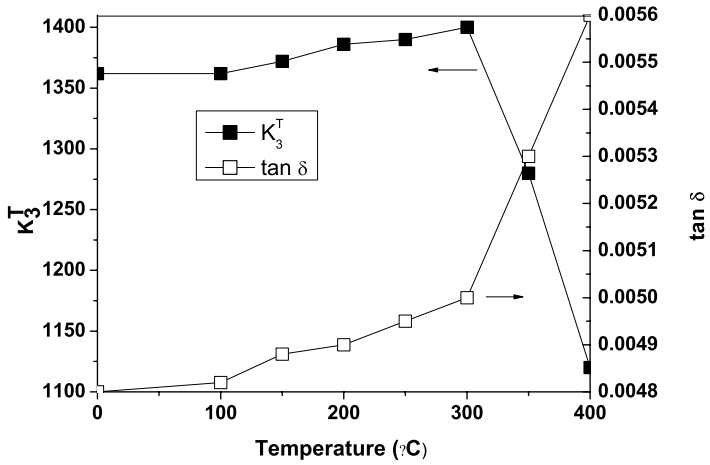

Figure 6. Effect of temperature on K^T_3 and tan δ.

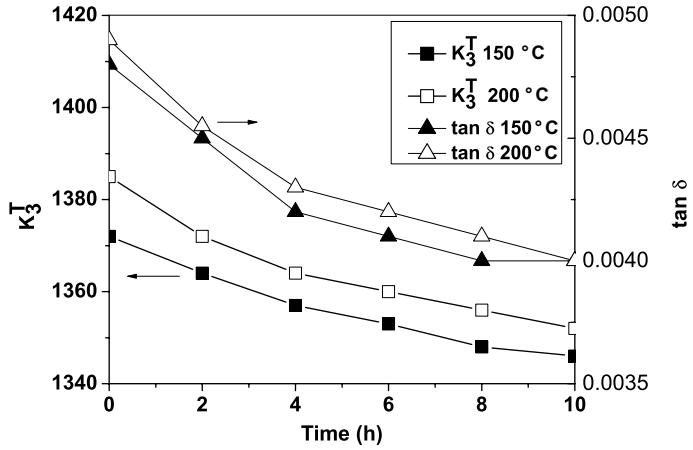

Figure 7. Aging of K^T_3 and tan δ at 150 °C and 200 °C.

ACKNOWLEDGMENTS

The authors express their sincere gratitude to Director, ARDE for providing necessary support to carry out the research work and for the permission to publish the work. Thanks are also due to the members of PZT Centre of ARDE for their technical help for characterisation of the material.

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