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Study on dielectric ageing behaviour of antiferroelectric $(Pb_{1-x}Ba_x)ZrO_3$ $(0 \leq x \leq 0.10)$ ceramics

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Abstract Ageing phenomena on dielectric constant and dielectric losses of pure and compositionally modified $PbZrO_3$ by Ba^{2+} ions are presented both in antiferrolelectric and ferroelectric phases. It is shown that the room temperature stable antiferroelectric phase of the samples gets inhibited on cooling after a heating cycle. The phase recovers from metastable ferroelectric phase on long-term ageing at room temperature. The antiferroelectric $(Pb_{1-x}Ba_x)ZrO_3$ system having higher internal stress has a great driving force for higher ageing rate. It is also shown that the ageing process is more pronounced if the sample is thermally activated and the room temperature ageing leads to linear dependence of dielectric constant and dielectric losses upon logarithmic of time. It is proposed that the decrease in dielectric constant with time is due to the motion of domain walls coming from the domain nucleation as well as the stress relaxation.

Introduction

Recently there has been considerable interest in the research and study of ageing of ceramic samples. Ageing is the spontaneous change of physical and chemical properties with time under zero external field and isothermal conditions. Ageing indicates normally the changes that may be troublesome in maintenance of device tolerance. In ferroelectrics, it is observed that ageing can be reversed or setback to 'time equals zero' by thermal cycles of reasonable duration above Curie temperature [1]. The time dependent change of dielectric constant of $BaTiO_3$ ceramics was the evidence of ageing in the early capacitor applications.

Mark [2] established that the ageing of capacitance or dielectric constant was a linear function of logarithm time. It is also shown that the capacitance would drop by 5% per decade in time. Roup [3] recognized dielectric ageing as a problem in the stability of $BaTiO_3$ based capacitors. It is also speculated that the dielectric ageing is caused by delayed inversion of the various domains that make up the structure of the ceramics. With the study of ceramic and flux-grown single crystal of $BaTiO_3$, Misarova [4] concluded that the rate of ageing depends on processing conditions and level of types of impurities in the host $BaTiO_3$ structure. Cooke et al. [5] have studied the effect of precipitation of a dispersed $CaTiO_3$ rich phase on the shape organization and thickness of ferroelectric (FE) domains in $BaTiO_3$ and concluded that it is not a simple thermally activated process. Sawaguchi and Charters [6] reported that asymmetric P-E hysteresis loop observed in $(Pb–Ca)TiO_3$ ageing at room temperature several hours after cooling from 200 °C is due to interaction between the two phases which are formed as the ageing proceeds. Bradt and Ansell [7] studied the ageing phenomenon of tetragonal $BaTiO_3$ using optical microscopy and dielectric data which concluded that ageing is the relief of the residual stress of FE transition by the thermally activated nucleation of 90° domains.

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Vincent et al. [8] have revealed the ageing effect in spin glasses and frustrated ferromagnetic sample and have suggested that the spin-glass dynamics is dominated by mechanism of the type wall reconstructions but not by domain growth [9]. Recently, Mitoseria [10] has studied dielectric ageing of pure and (Hf, Zr) doped $BaTiO_3$ ceramics and concluded that the ageing of the samples imposes the twinning rate and rearrangement of FE domains minimizing the elastic energy of the lattice. More recently, Miga et al. [11] found inherent large ageing effects in the uniaxial ferroelectric relaxor strontium-barium niobate (SBN) system. It is also noticed that the ageing effects are much larger in this system than that reported on systems like lead magnesium niobate-lead titanate (PMN–PT) [12], potassium-lithium tantalate (KLT) [13], etc.

The ceramics based on antiferroelectric (AFE) $PbZrO_3$ are found to be important materials for various electronic devices due to their high dielectric constant, large volumetric expansion [14] and having not only AFE to FE but also FE to paraelectric (PE) phase transitions. Such materials have been investigated for high displacement electromechanical actuators applications, energy conversion as well as high and low field switching devices. It is possible to reduce AFE to FE phase transition temperature and enhance the relative stability of the FE phase by chemical substitutions of Ba^{2+} at Pb^{2+} site [15]. It is also reported that in compositionally modified $PbZrO_3$ ceramics i.e. $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ), the AFE to FE phase switching field can considerably be reduced [16]. In lead zirconate titanate stanate (PZTS) ceramics, Pan et al. [17], have studied such effect by doping La^{3+} and found that the switching times are less than 1 μs and nearly 2 μs for AFE to FE and FE to AFE transitions respectively for 30 kV/cm. It is also noted that upon removal of electric field , field induced AFE to FE phase transition in PZTS ceramics, samples do not return as to its virgin AFE state [18] confirming the irreversibility. Pokharel and Pandey [14] have also shown such irreversibility in the temperature induced AFE to FE transition in PBZ10 ($x = 0.10$) ceramic. In the present work, we have shown that Ba^{2+} doped $PbZrO_3$ for $x = 0$, 0.05 and 0.10 which shows not only irreversibility in AFE to FE phase transition on cooling but also ageing phenomena of the samples.

Experimental procedure

The samples used in this work are prepared by semi-wet route, the details of which are reported elsewhere [19]. In this method, first $(Pb_{1-x}Ba_x)CO_3$ solid solution precursors were prepared by chemical co-precipitation technique to ensure uniform distribution of Ba^{2+} and Pb^{2+} ions. These precursors were mixed with extra pure ZrO_2 powders and ball milled using acetone as mixing media. The powder is first calcined at 750 °C in air atmosphere for 6 h which is then compacted in the form of pellets in a steel die of 13 mm diameter using hydraulic press at an optimized load of 80 kN. Polyvinyl alcohol (PVA) was used as binding agent which was burnt at 500 °C for 12 h. The pellets so obtained were sintered at optimized temperature 1,050 °C for 3 h in a covered crucible with PbO atmosphere to prevent the PbO loss at such high firing temperature. The PbO atmosphere was maintained using optimized amount [20] of $PbZrO_3$ as a spacer powder and MgO as a sealing agent to avoid the PbO evaporation from the sample. The typical weight loss due to possible PbO escape was less than 2%. The density of sintered pellets measured using liquid displacement method were close to or in excess of 99% of the theoretical density.

The solid solution of carbonate precursors and structure of PBZ compound were checked using CuK_α radiation on a 12 kW rotating anode based Rigaku powder diffractometer fitted with a curved crystal graphite monochromator. The dielectric data were obtained measuring capacitance and loss tangent of fired silver pasted pellets using Solartron 1260 Impedance Gain/Phase analyzer and Hioki 3532-50 LCR HiTester at 10 kHz. The temperature of the measurement was controlled within ±1 °C using temperature controller. The heating and cooling rates of the experiments were kept at 1 °C/min.

Results and discussion

Quenching of AFE phase in FE matrix

Figure 1a–c depict the variation of real and imaginary parts of dielectric constant with temperature during heating and cooling of virgin $(Pb_{1-x}Ba_x)ZrO_3$ samples for $x = 0$, 0.05, and 0.10 respectively. In Fig. 1a, there are two dielectric anomalies at 226 °C and 231 °C in heating and 215 °C and 222 °C for cooling corresponding to the AFE to FE and FE to PE transitions respectively of pure $PbZrO_3$ ceramic which is similar as observed by Goulpeau [21] and Handerek et al. [22] in single crystal. The anomaly corresponding to the AFE to FE transition during heating at 226 °C is very weak which can be clearly seen from the inset to this figure. The hysteresis of about 11 °C and 9 °C in the AFE to FE and FE to PE phase transitions respectively obtained during heating and cooling cycles confirm both the anomalies as the first order nature of phase transition of the sample. These dielectric anomalies are known to be due to phase transitions sequence from orthorhombic(AFE) to rhombohedral (FE) to cubic (PE) phases [23]. Both anomalies are seen at the same temperature in both real and imaginary parts of the dielectric constant as

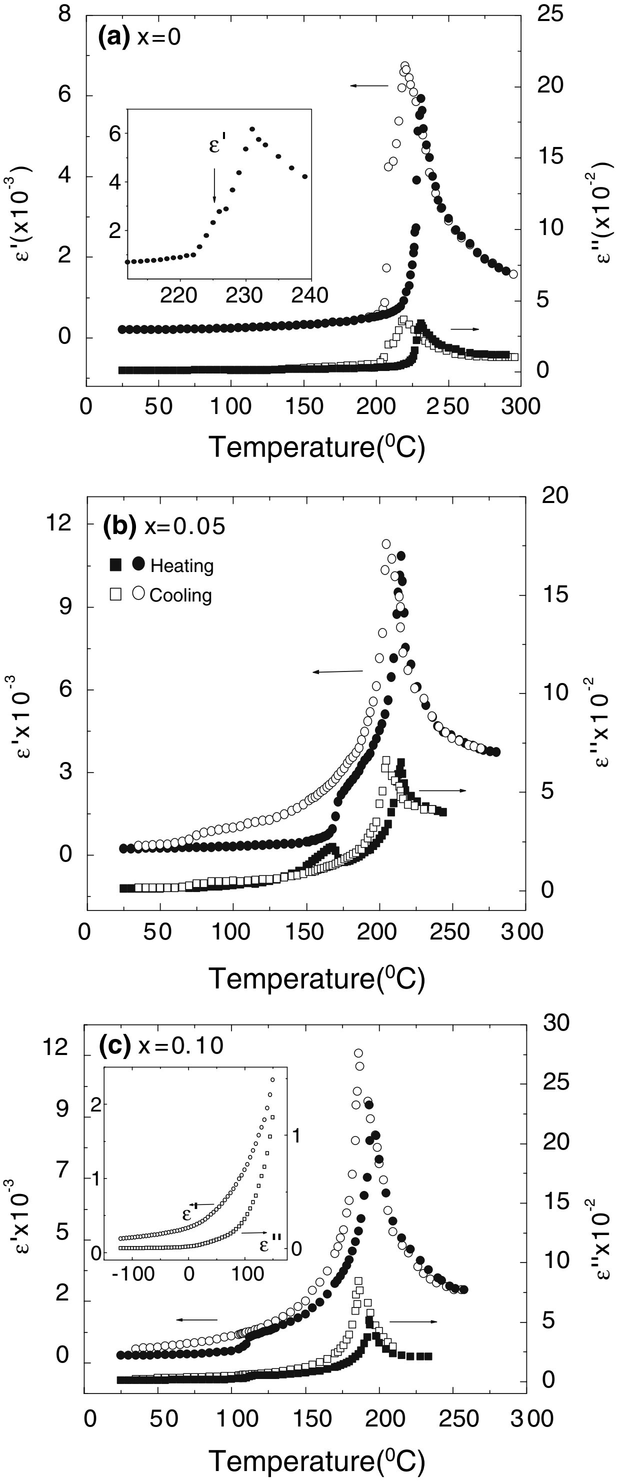

Fig. 1 Variation of real and imaginary parts of dielectric constant of virgin ($Pb_{1-x}Ba_x$) ZrO_3 ceramics (**a**) $x = 0$, (**b**) $x = 0.05$ and (**c**) $x = 0.10$ as a function of temperature during heating and cooling cycles at 10 kHz for various compositions. The insets (**a**) shows the zoom portion of the ε′ dielectric data in heating cycle and (**c**) that of ε′ and ε″ data in cooling cycle

expected on the basis of Kramers–Kronig relationship [24]. The jump in the real part of dielectric constant at the transition temperature is found to be 2,170 for AFE to FE phase and about 6,000 for FE to PE phase transitions in pure $PbZrO_3$ during heating cycle.

The substitution of Ba^{2+} ion, lowers the AFE to FE as well as the FE to PE phase transition temperatures. The AFE to FE and FE to PE phase transition temperatures of PBZ for $x = 0.05$ and 0.10 are 176 °C and 114 °C as well as 215 °C and 196 °C respectively on heating which can be seen in Fig. 1b and c. The jumps in the real part of dielectric constant at transition temperatures during heating cycle are found to be 1,430 and 720 in AFE to FE transition and about 9,000 and 10,000 in FE to PE phase transitions for $x = 0.05$ and 0.10 respectively. This confirms that due to substitution of barium ions AFE phase destabilizes and FE phase gets stabilized. In general, during phase transition, the jump in dielectric constant for cooling cycle is more pronounced than for heating cycle as per simple Landau theory arguments. For $PbZrO_3$, this is indeed the case as can be seen in Fig. 1a for both AFE to FE and FE to PE transitions, but for PBZ05 the jump of the dielectric constant for cooling cycle is 488 which is considerably lower than the value 1,430 for heating cycle. The thermal hysteresis of PBZ05 sample in this transition for heating and cooling cycles is observed about 100 °C whereas for $PbZrO_3$ it was only 11°C. In case of FE to PE transition the thermal hysteresis remains nearly same for all these three compositions.

However, for AFE to FE transition, it is more anomalous in PBZ10. No dielectric anomaly in FE to AFE transition is observed in cooling cycle. On the basis of thermal hysteresis of about 11 °C in $PbZrO_3$ and 100 °C in PBZ05, we expect the FE to AFE transition during cooling cycle to occur around –86 °C for PBZ10. But up to –120 °C, no anomaly either in ε′ and ε″ versus temperature plots is observed which can be seen from the inset in Fig. 1c. The dielectric result shown in the inset of Fig. 1c down to –120 °C has confirmed that none of the observation of the AFE phase up to room temperature is not due to very wide thermal hysteresis pushing the FE to AFE phase transition temperature below room temperature which is described in detailed elsewhere [14]. It clearly indicates the quenching of FE phase to room temperature.

We repeated the second dielectric measurements of the same samples ($Pb_{1-x}Ba_x$)ZrO_3 for $x = 0$, 0.05 and 0.10 just after the first heating cum cooling cycles to verify the quenching. The results are shown in Fig. 2a–c. The weak dielectric anomaly observed during first heating cycle at 226 °C for $PbZrO_3$ is totally missing, however, in the

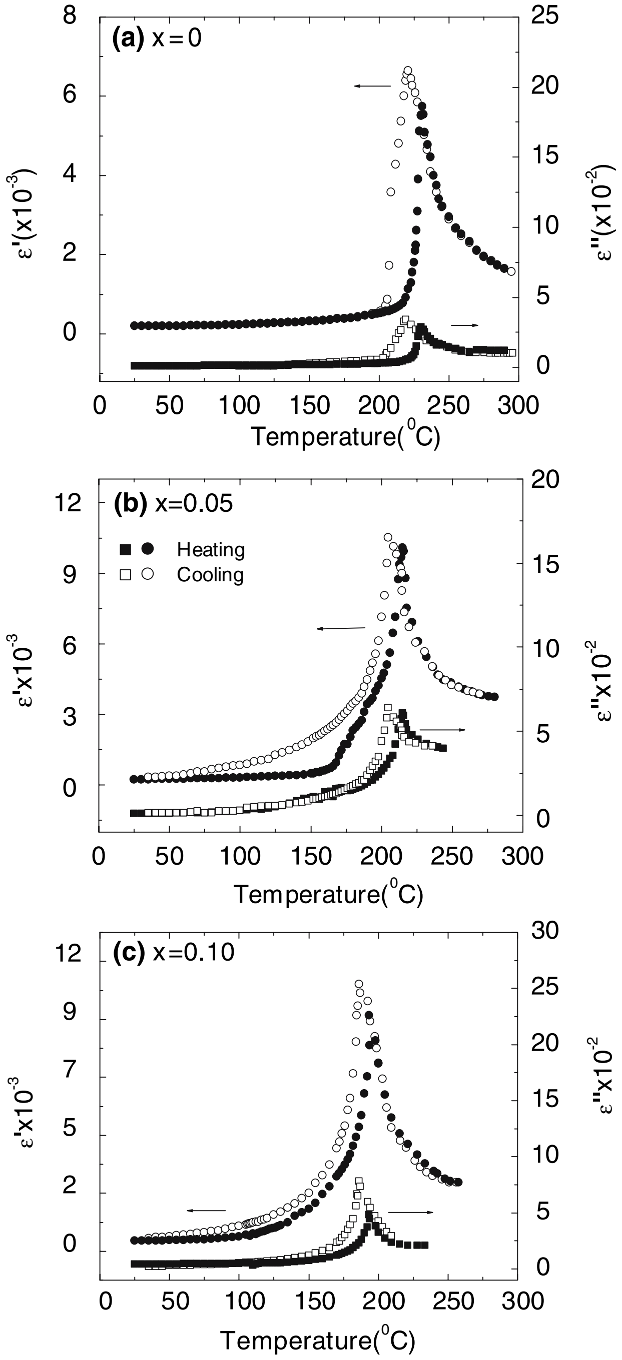

Fig. 2 Variation of real and imaginary parts of dielectric constant of $(Pb_{1-x}Ba_x)ZrO_3$ ceramics as a function of temperature for second heating cum cooling cycles just after first cycle at 10 kHz for various compositions

cooling cycle, the weak anomaly is still observed as can be seen in Fig. 2a. Even the values of dielectric constant in FE to PE and PE to FE phase transitions have been decreased. In contrast to the result of $PbZrO_3$ in AFE to FE phase transition, we observed a weak anomaly in heating cycle for PBZ05 ($x = 0.05$) at around 176 °C and the anomaly observed at around 76 °C in first cooling cycle (see Fig. 1b) is totally missing which can be seen in Fig. 2b. It also indicates that the AFE phase is getting destabilized on increasing the substituted Ba^{2+} content in Pb^{2+} site in PBZ system. In PBZ10 ($x = 0.10$), dielectric anomaly observed during the first heating cycle in AFE to FE phase transition at 114 °C is totally missing in second heating cycle which is shown in Fig. 2c, which confirms that the FE to AFE phase transition is suppressed during the cooling cycle with the increase of Ba^{2+} contents in the $PbZrO_3$ matrix.

The PBZ10 sample is then allowed to age at room temperature and dielectric data were again taken after one year. The result of the dielectric measurement of this aged sample is shown in Fig. 3. It is evident from this figure that the dielectric anomaly reappears exactly at 114 °C corresponding to AFE to FE phase transition during heating cycle but it is still absent in cooling cycle data. However, the jump of the dielectric constant near the AFE to FE phase transition in heating cycle is slightly reduced indicating the effect of ageing and partial recovery of the AFE phase ageing at room temperature for 12 months. The FE to PE transition temperatures at 196 °C and 186 °C during heating and cooling cycles are also reproduced in the aged sample but the jump of dielectric constant is slightly reduced by partially recovered AFE phase at 114 °C. Figure 4 represents the variation of real and imaginary parts of dielectric constant with temperature of the PBZ10 pellets aged for 5 days at room temperature after heating cum cooling cycle. In this case a weak dielectric anomaly has reappeared at 114 °C only in ε'' versus T plot but not in ε' versus T plot. This gives better idea about the kinetics of

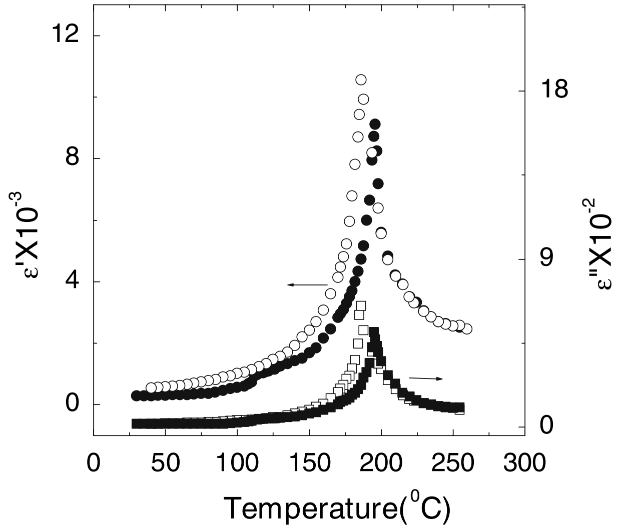

Fig. 3 Variation of real and imaginary parts of dielectric constant during heating and cooling cycles at 10 kHz of PBZ10 ceramic as a function of temperature aged for 12 months at room temperature after cooling cycles

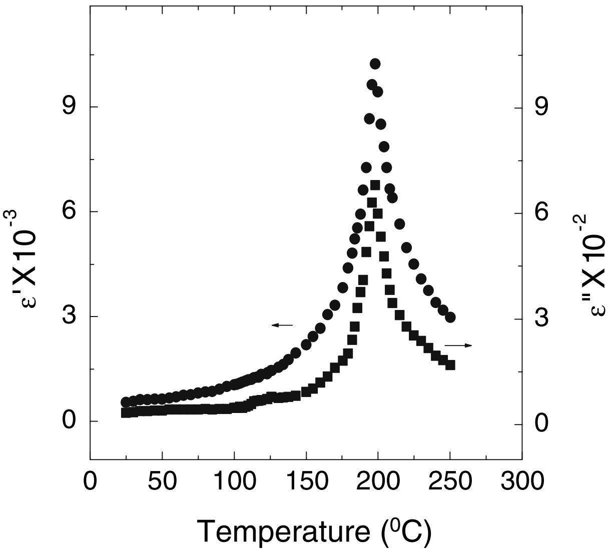

Fig. 4 Variation of real and imaginary parts of dielectric constant during heating cycle of PBZ10 ceramic pellet as a function of temperature aged for 5 days at room temperature after cooling cycles. (●) and (■) represent the real and imaginary parts of dielectric data respectively

recovery of the AFE phase from the metastable FE matrix and demonstrates that the rate of recovery is extremely slow on ageing at room temperature.

We feel that the phenomenon of FE phase quenching is intimately linked with the problem of nucleation of the AFE phase in the FE matrix. It is well known that the AFE to FE phase switching is accompanied by a large volume change [23]. High temperature XRD studies on PBZ10 samples have shown that the volume expansion at the AFE to FE phase transition temperature (114 °C) is about 0.8%. It has also been shown that this volume change is mainly due to the discontinuous expansion of the pseudocubic c-parameter of the orthorhombic AFE phase since the pseudocubic a-parameter remains nearly temperature independent. Such a large and highly anisotropic expansion at the AFE to FE transition in sintered polycrystalline samples can be accommodated in grains near the surface but not in the grains located in the interior of the specimen. The large transformation strains may, in fact, lead to a very fine scale fragmentation of all the grains (except those near the surface) similar to well known at the cubic to tetragonal transition in $PbTiO_3$ ceramics [25]. Such a fragmentation will reduce the size of the FE domain with a concomitant increase in the surface area which contains broken and dangling bonds. These broken and dangling bonds effectively behave like Pb^{2+} and O^{2-} vacancies [26], which are known to stabilize the FE phase in pure $PbZrO_3$. As a result, the FE phase does not transform to the AFE phase during cooling. On ageing at room temperature, there appears to be a healing process which not only restores the contact between the FE phase domains but also eradicates the broken and dangling bonds thereby tilting the subtle energy difference between the FE and AFE phases in favour of the AFE phase. As a result of this the AFE phase slowly recovers from the metastable FE matrix.

Decrease in dielectric constant and loss factor

In order to get the better idea on ageing mechanism of these samples, we chose only PBZ10 sample and carried out dielectric measurement as a function of time at room temperature and FE to PE phase transition temperature. No special ageing treatment was made before the measurement. Figure 5a and b show the variation of real part of dielectric constant and tanδ of PBZ10 ceramics with logarithm of time. The data is linearly fitted. It is evident from these figures that the dielectric constant and tanδ in both temperatures decrease linearly with the increase of logarithm of time which is similar to that reported by Mitoseriu [10] for ferroelectric $BaTiO_3$ ceramics. It is evident from the figures that the rates of decrement dielectric data during ageing are about 2.0 and 2.5% per decade and about 3.9 and 4.7% per decade in tanδ at room temperature and transition temperature respectively. These ageing rates are very high as compared to the reported data [27] for PMN–$BaTiO_3$–$PbTiO_3$ ferroelectric ceramics. The changing rate of tanδ is greater than the dielectric changing rate in which complex mechanisms of ageing are involved. It is also noted that there is a little more rate of change of dielectric constant and tanδ at transition temperature than at room temperature similar to that reported by Zhang et al. [28]. It concludes that in thermally activated process, ageing rate is more pronounced.

Most proposed ageing mechanisms relate ageing process with a slow gradual change of domain wall configuration with time towards more energetically stable equilibrium states. This process is affected by mechanical and electrical stresses as well as electric and anisotropic elastic defects. It is known that ageing cannot be attributed to 180° domain boundaries because the time constant of phenomenon is much too long. By microscopy study of $BaTio_3$, Bradt and Ansell [7] reported that the dislocation effect to the ageing process can be regarded as negligible. They also remarked that the 90° domain splitting is a form that the nucleation of 90° domains can assume when moving 90° domains encounter another domain boundaries at a right angle to their direction of motion. If the two directions of polarization are opposing splitting occurs to reduce the confrontation. Thus, polarization decreases resulting the decrease in dielectric constant. The dominate contribution to dielectric constant is the intrinsic ionic motion which affects the domain wall motion. However, the contribution from the stress relaxation of the dipoles probably

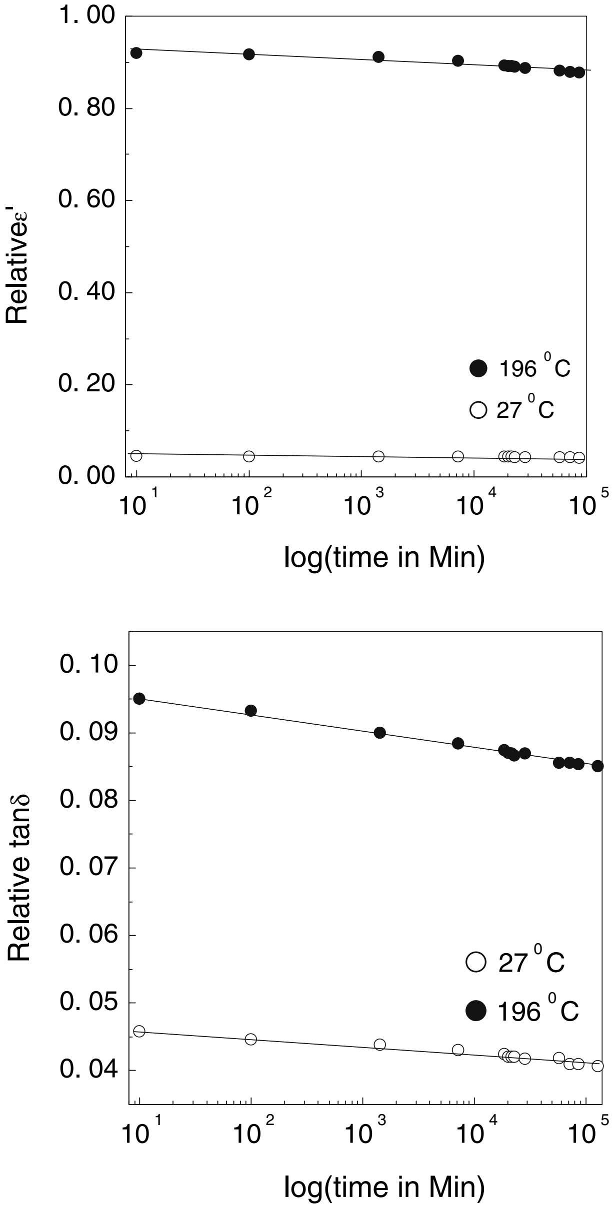

Fig. 5 Relative variation of (**a**) dielectric constant and (**b**) dielectric losses upon logarithm of time for PBZ10 ceramics

responsible for the drop in dielectric constant. Stresses both external and internal are very important to the dielectric properties of antiferroelectric materials. High temperature XRD study of PBZ (x = 0.05 and 0.10) [23] shows that the transformation strains associated with AFE to FE transition increases with Ba^{2+} content from a value of 0.6% for x = 0.05–0.9% for 0.10, which also confirms the idea of stress relaxation effect in the ageing of our sample. It is interesting to note that polycrystalline material apparently has a higher internal stress, as well as a greater driving force for higher ageing rate. In polycrystalline anisotropic material having different crystallographic directions, logarithmic scale is applicable in averaging the directions.

Conclusions

Highly dense lead–barium zirconate ceramic samples were prepared using semi-wet route and carried out their dielectric measurements as a function of temperature and time. Temperature dependant dielectric data shows that the stable AFE phase of $PbZrO_3$ gets inhabited on cooling after heating cycle and FE phase gets stabilized with the increase of Ba^{2+} contents. The time dependant dielectric data confirms the dielectric ageing behaviour of the samples. The average ageing rate observed for dielectric constant and loss factor are 2.2 and 4.3, respectively. It also reveals that the quenched AFE phase recovers from FE phase on long-term ageing.

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