# Roles of Nano-Domains on Uniaxial Stress Dependence of Dielectric Properties of Ferroelectric Ceramics

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## ABSTRACT

*Roles of nano-domains on the uniaxial stress dependence of dielectric properties of ferroelectric ceramics in three different systems, i.e., BT-PZT, PMN-PT and PMN-PZT were studied. The dielectric properties were observed at room temperature under the compressive pre-stress levels up to 15, 22 and 5 MPa for BT-PZT, PMN-PT and PMN-PZT, respectively, using a homebuilt uniaxial compressometer. Dielectric constant of the BT-PZT ceramics increased significantly with increasing applied stress. Larger changes in the dielectric properties with the applied stress were observed in the PZT-rich compositions. However, for PMN-PT and PMN-PZT ceramic systems, changes in the dielectric properties with the stress were found to depend significantly on the ceramic compositions. The experimental results could be explained by both intrinsic and extrinsic mechanisms, involving domains, domain wall motions and de-aging phenomenon from the application of the compressive stress. Roles of different types of domains, i.e., micro-domains and nano-domains were also discussed.*

**Key words:** Dielectric Properties, Ferroelectrics, Nano-Domains, Uniaxial Stress

## INTRODUCTION

Among perovskite ferroelectric materials, barium titanate ($BaTiO_3$ or BT), lead titanate ($PbTiO_3$ or PT), lead zirconate titanate ($Pb(Zr_{1-x}Ti_x)O_3$ or PZT) and lead magnesium niobate ($Pb(Mg_{1/3}Nb_{2/3})O_3$ or PMN) ceramics have been investigated extensively and continuously since the late 1940s (Jaffe and Cook, 1971; Cross, 1996; Haertling, 1999; Moulson and Herbert, 2003). BT and PT, PMN, and PZT are representative perovskite normal ferroelectrics, relaxor ferroelectric, and piezoelectric prototypes, respectively, because of their excellent electrical properties. These ceramics possess distinct characteristics that make each of them suitable for different applications. Forming a composite of these ferroelectrics has been one of the techniques employed to improve the properties of ferroelectric ceramics for specific requirements for each application.

One of the most-studied piezoelectric compounds, $Pb(Zr_{0.52}Ti_{0.48})O_3$, a morphotropic phase boundary (MPB) compound of PZT, has great piezoelectric properties with a high Curie temperature ($T_C$) of ~390ºC. BT exhibits high dielectric constant and superior electrostrictive responses with a lower $T_C$ (~ 120ºC) (Jaffe and Cook, 1971; Cross, 1996; Haertling, 1999; Moulson and Herbert, 2003). In addition, BT is mechanically superior to PZT (Chaisan et

al., 2004), whereas PZT ceramics can be easily sintered at temperature much lower than BT ceramics which usually require as high sintering temperature as 1400ºC (Chaisan et al., 2004). With their complementary features, the composites between PZT and BT are expected to exhibit better properties than the single-phase PZT and BT (Jaffe and Cook, 1971; Cross, 1996; Haertling, 1999; Moulson and Herbert, 2003). Furthermore, the properties can also be tailored over a wider range by changing the compositions to meet the strict requirements for specific applications (Jaffe and Cook, 1971; Cross, 1987, 1996; Haertling, 1999; Moulson and Herbert, 2003).

PMN exhibits high dielectric constant and a broad range transition of dielectric constant, with temperature as a function of frequency (Haertling, 1999). In addition, PMN ceramics exhibit low loss and non-hysteretic characteristics. These make PMN a good candidate for a large number of applications, such as multilayer capacitors, sensors and actuators. However, it is difficult to form a single-phase PMN. It is widely accepted that forming a solid solution between PMN-PT results in ceramics with high dielectric constant and large electrostrictive coefficients (Lejuene and Boilot, 1985; Choi et al., 1989; Choi et al., 1996). In addition, PMN ceramics have relatively low electromechanical coupling coefficients, as compared to PZT which are found in several actuator and transducer applications due to the latter's high electromechanical coupling coefficients and higher temperature of operation (Jaffe and Cook, 1971; Moulson and Herbert, 2003). However, PZT ceramics also possess highly hysteretic behavior which makes them unsuited for applications that require high delicacy and reliability. Furthermore, PZT ceramics normally have very high Curie temperature ($T_C$) in the vicinity of 400°C. Usually many applications require that $T_C$ is close to ambient temperature. Therefore, there is a general interest to reduce the $T_C$ of PZT ceramics to optimize their uses. With the complementary features of PMN and PZT, the composites between PMN and PZT are expected to synergetically combine the properties of both ceramics, which could exhibit more desirable piezoelectric and dielectric properties for several technologically-demanding applications than single-phase PMN and PZT (Yoo et al., 1998; Shilnikov et al., 1999). With the reasons outlined above, it is therefore of interest to investigate the PMN-PT and PMN-PZT systems.

In many applications, these ferroelectric ceramics are often subjected to mechanical loading, either deliberately in the design of the device itself or because the device is used to change shapes as in many smart structure applications or the device is used under environmental stresses (Cross, 1987; Xu, 1991; Viehland and Powers, 2001). Despite the fact, material constants used in any design calculations are often obtained from a stress-free measuring condition, which in turn may lead to incorrect or inappropriate actuator and transducer designs. It is therefore important to determine the properties of these materials as a function of applied stress. Previous investigations on the stress-dependence dielectric and electrical properties of many ceramic systems have clearly emphasized the importance of the matter (Zhao et al., 1996; Zhao et al., 1999). More importantly, since these three ceramic systems possess very distinct dielectric characteristics, they display significantly different ranges of Curie temperature ($T_C$). BT-PZT has a range of $T_C$ between 120 and 400°C (Chaisan et al., 2005), while the range extends from -10 to 490°C for PMN-PT (Lejuene and Boilot, 1985; Choi et al., 1989; Choi et al., 1996) and from -10 to 400°C for PMN-PZT (Yimnirun et al., 2004, 2005). The experimental results of the uniaxial stress dependence of the room temperature dielectric properties of these ceramic systems will provide a tool in assessing the

roles of different domain mechanisms in these important ferroelectrics. Therefore, this study is undertaken to investigate the influences of the uniaxial stress on the dielectric properties of ceramics in BT-PZT, PMN-PT and PMN-PZT systems.

## MATERIALS AND METHODS

The ceramic composites with formula $BaTiO_3$–$Pb(Zr_{0.52}Ti_{0.48})O_3$ or BT-PZT, $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ or PMN-PT and $Pb(Mg_{1/3}Nb_{2/3})O\pm$–$Pb(Zr_{0.52}Ti_{0.48})O_3$ or PMN-PZT were prepared from the starting BT, PT, PZT and PMN powders by a mixed-oxide method. BT, PT and PZT powders were first prepared by a conventional mixed-oxide method. On the other hand, perovskite-phase PMN powders were obtained via a well-known columbite method (Swartz and Shrout, 1982). Subsequently, the $(x)BaTiO_3$–$(1-x)Pb(Zr_{0.52}Ti_{0.48})O_3$ (when x = 0.0, 0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95, and 1.0), the $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$ – $(x)Pb(Zr_{0.52}Ti_{0.48})O_3$ (when x = 0.1, 0.2, 0.3, 0.4, and 0.5) and the $(x)Pb(Mg_{1/3}Nb_{2/3})O_3$ – $(1-x)Pb(Zr_{0.52}Ti_{0.48})O_3$ (when x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0) ceramic composites were then prepared from the starting BT, PT, PZT and PMN powders by the similar mixed-oxide method described above at various processing conditions. The detailed descriptions of powders and ceramics processing and characterizations were presented thoroughly in the earlier publications (Yimnirun et al., 2004, 2005; Chaisan et al., 2005).

For dielectric property characterizations, the sintered samples were lapped to obtain parallel faces, and the faces were then coated with silver paint as electrodes. The samples were heat-treated at 750°C for 12 min to ensure the contact between the electrodes and the ceramic surfaces. The samples were subsequently poled in a silicone oil bath at a temperature of 120°C by applying a dc field of 20 kV/cm for 30 min for BT-PZT ceramics, while for PMN-PT and PMN-PZT ceramics, the poling condition was 25 kV/cm for 30 min and field-cooled to room temperature. To study the effects of the uniaxial stress on the dielectric properties, the uniaxial compressometer was constructed. The uniaxial compressive stress applied parallel to the electric field direction was supplied by the servohydraulic load frame and the applied stress level was monitored with the pressure gage of the load frame. The details of the system were described elsewhere (Yimnirun et al., 2003a; Yimnirun et al., 2003b). The dielectric properties were measured through spring-loaded pins connected to the LCZ-meter (Hewlett Packard, model 4276A). The capacitance was determined at frequency of 1 kHz and room temperature (25°C). The dielectric constant was then calculated from a parallel-plate capacitor equation, e.g., $\varepsilon_r = Cd / \varepsilon_0 A$, where C is the capacitance of the sample, d and A are the thickness and the area of the electrode, respectively, and $\varepsilon_0$ is the dielectric permittivity of vacuum ($8.854 \times 10^{-12}$ F/m).

## RESULTS AND DISCUSSION

The experimental results of the uniaxial compressive stress dependence of the dielectric constant of the ceramics in BT-PZT, PMN-PT and PMN-PZT systems are shown in Figures 1-3.
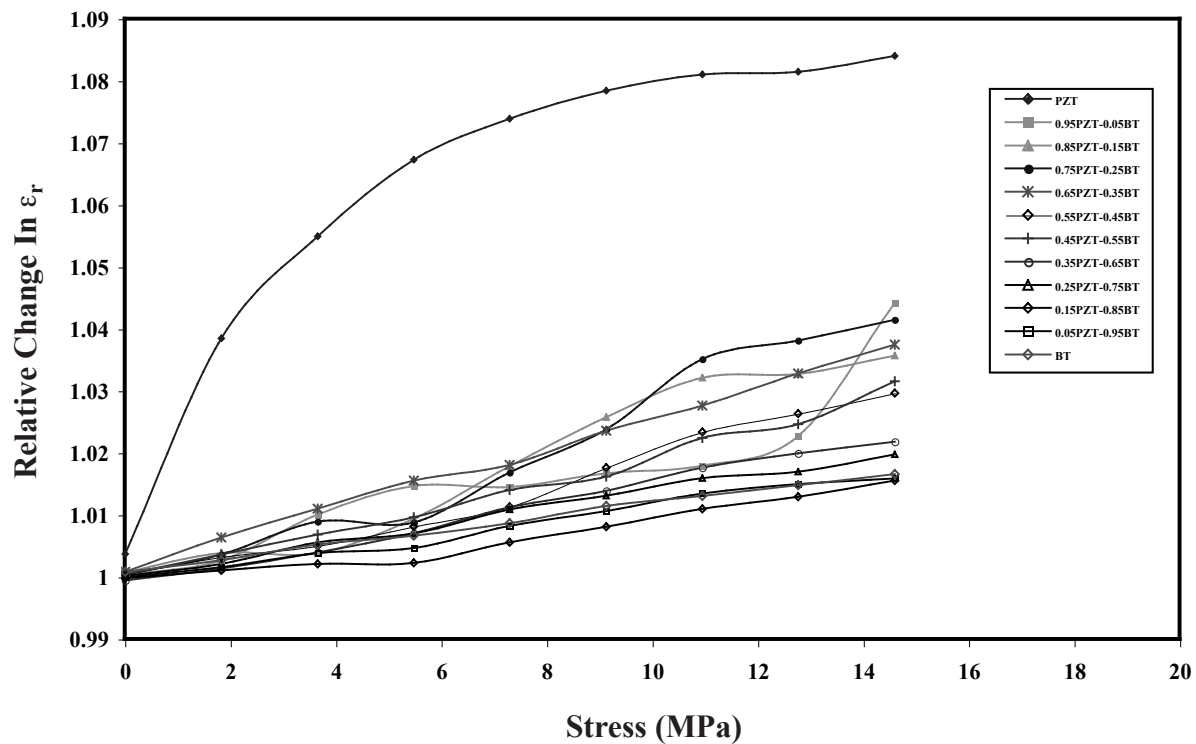
**Figure 1.** Relative changes of dielectric constant ($\varepsilon_r$) as a function of compressive pre-stress for ($x$)BT-($1$-$x$)PZT ceramics.

For BT-PZT system (Figure 1), there is a significant change of the dielectric constant of the ceramics when the applied stress increases from 0 to 15 MPa. The changes of the dielectric constant with the applied stress can be divided into three different groups. For PZT ceramic, the dielectric constant increases exponentially with applied stress. It can be seen that dielectric constant is enhanced by approximately 8% at 15 MPa applied stress. For PZT-rich compositions (0.05BT-0.95PZT, 0.15BT-0.85PZT, 0.25BT-0.75PZT, 0.35BT-0.65PZT and 0.45BT-0.55PZT), the dielectric constant increases rather linearly with increasing applied stress. The changes in the dielectric constant between 2 to 4% at 15 MPa applied stress are obviously smaller than that observed in PZT. For BT-rich compositions (BT, 0.95BT-0.05PZT, 0.85BT- 0.15PZT, 0.75BT-0.25PZTand 0.65BT-0.35PZT), the dielectric constant only rises slightly (< 2%) and in a linear manner when the applied stress increases to the maximum amplitude. Similar experimental results have been reported previously for soft PZT (Calderon-Moreno, 2004; Zhou et al., 2005) in which the dielectric properties are found to increase with increasing magnitude of the compressive stress.

The experimental result for the PMN-PT ceramics is shown in Figure 2. The changes of the dielectric constant with the applied stress can be divided into two groups. For 0.9PMN-0.1PT ceramic, the dielectric constant decreases drastically with applied stress. The change is more than 70% decrease when the applied stress increases to 22 MPa. On the other hand, for other PMN-PT ceramics, i.e., with x values of 0.2-0.5, the change is minimal. The dielectric constant is actually rather stable within this range of the applied stress
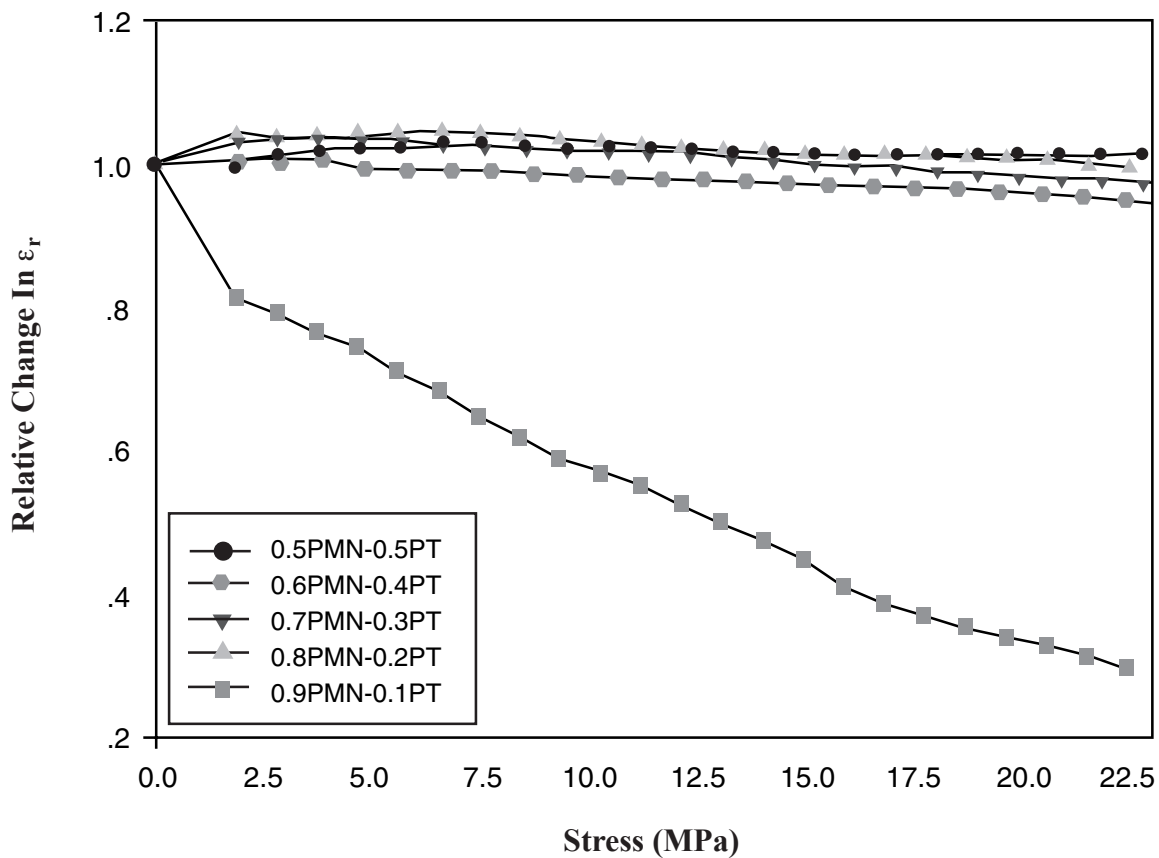
**Figure 2.** Relative changes of dielectric constant ($\varepsilon_r$) as a function of compressive pre-stress for ($x$)PT-($1$-$x$)PMN ceramics.

Figure 3 displays the experimental results for the PMN-PZT ceramics. To prevent mechanical failures usually occurring in PMN-PZT, the experiments are carried out at the compressive stress levels up to 5 MPa only. However, there is already a significant change of the dielectric constant of the ceramics even the maximum applied stress is only 5 MPa. The changes of the dielectric constant with the compressive pre-stress can be divided into two different groups. For PMN-rich compositions (PMN, 0.9PMN-0.1PZT, and 0.7PMN-0.3PZT), the dielectric constant generally decreases with increasing applied stress. However, it should be noticed that only PMN and 0.9PMN-0.1PZT compositions show definite decreases in the dielectric constant while the dielectric constant of the 0.7PMN-0.3PZT composition initially increases, then decreases with very little difference in the dielectric constant between the 0 and 5 MPa. On the other hand, for PZT-rich compositions (PZT, 0.1PMN-0.9PZT, 0.3PMN-0.7PZT, and 0.5PMN-0.5PZT), the dielectric constant rises slightly when the compressive pre-stress increases from 0 to 1 MPa, and becomes relatively constant when the pre-stress level increases further.
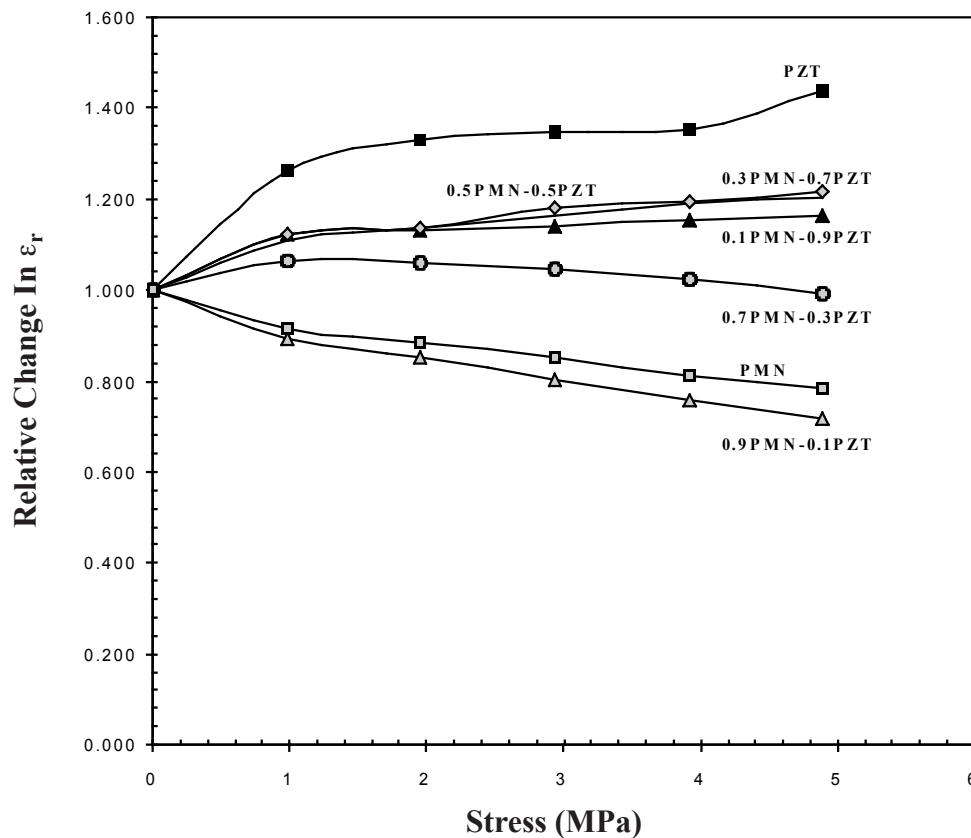
**Figure 3.** Relative changes of dielectric constant ($\varepsilon_r$) as a function of compressive pre-stress for ($x$)PMN-($1$-$x$)PZT ceramics.

To understand these experimental results, various effects have to be considered. Normally, the properties of ferroelectric materials are derived from both the intrinsic contribution, which is the response from a single domain, and extrinsic contributions, which are from domain wall motions (Zhao et al., 1999; Yang et al., 2000a; Yang et al., 2000b). Intrinsically, these ferroelectric materials consist of different types of domains, depending upon temperature. In normal ferroelectrics such as BT, PT and PZT, the domains called "micro-domain" are present when the temperature is below $T_C$, and the domains are non-existent above $T_C$. On the other hand, in relaxor ferroelectric like PMN, the domain size gradually changes from nano-domain to micro-domain when the temperature decreases from far above temperature with maximum dielectric constant ($T_{max}$) to below depolarization temperature (Td), as depicted in Figure 4. Normally, the responses of nano-domains to the external compressive stress result in the decrease in the dielectric constant with stress (Steiner et al., 1999). The extrinsic contribution is also very important. When a mechanical stress is applied to a ferroelectric material, the domain structure in the material will change to maintain the domain energy at a minimum; during this process some of the domains engulf other domains or change shape irreversibly. Under a uniaxial stress, the domain structure of ferroelectric ceramics may undergo domain switching, clamping of domain walls, de-aging and de-poling (Yang et al., 2000b).
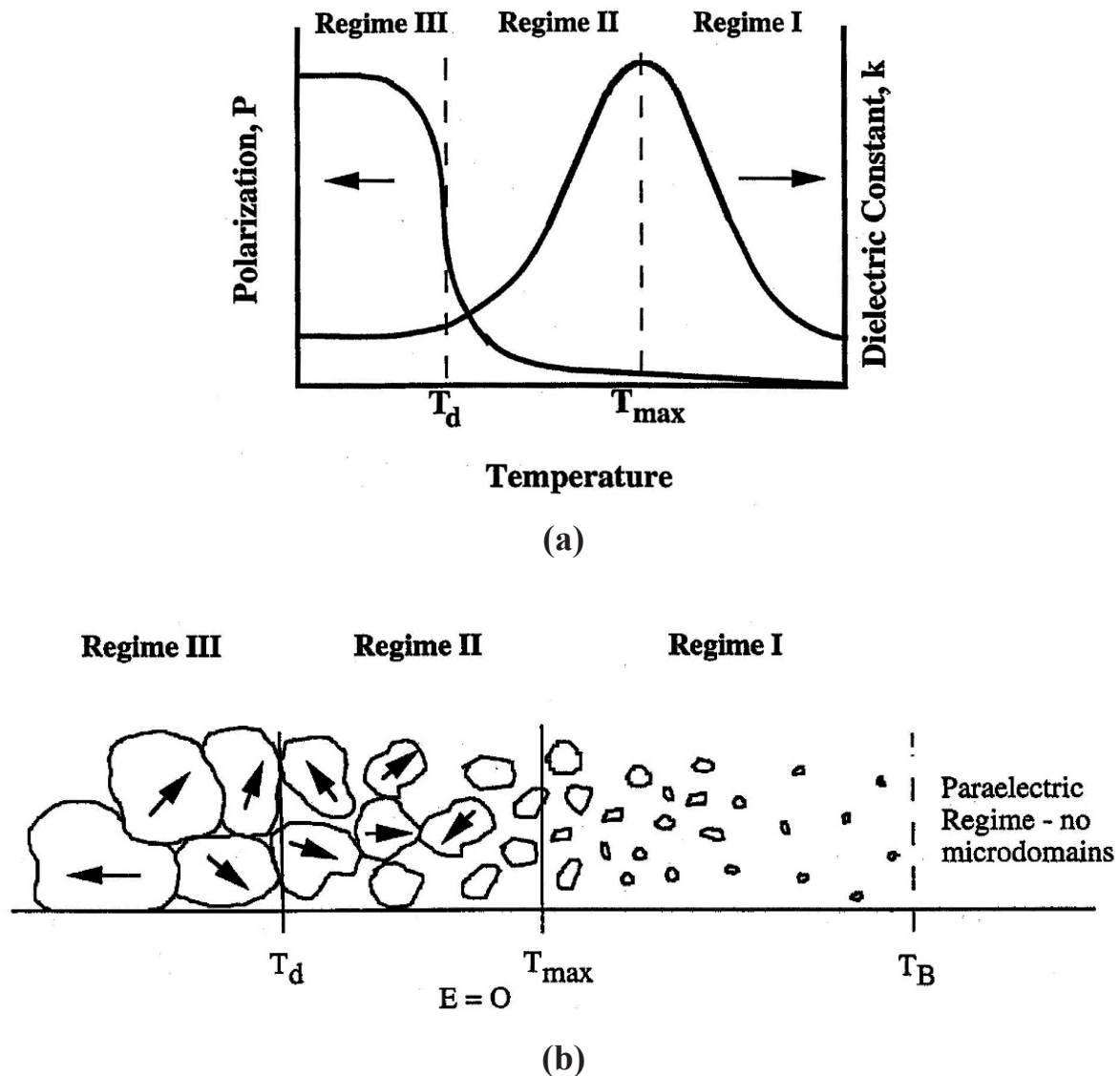
**(a)**



**(b)**

**Figure 4.** Changes of (a) polarization and dielectric constant (b) sizes of domains in different temperature regimes for realxor ferroelectric materials (Cross, 1987).

For the case of BT-PZT system which exhibits normal ferroelectric behavior, the results on the uniaxial compressive stress dependence of the dielectric constant can easily be explained with the contribution from the extrinsic contribution because the range of $T_C$ for these ceramics is far above the room temperature, at which the experiment was carried out. Therefore, the main contribution is from micro-domains and the domain walls. When the uniaxial compressive stress is applied in the direction parallel to the polar axis (poling) direction, the stress will move some of the polarization away from the poling direction, resulting in a change in domain structures (Zhao and Zhang, 1996; Yang et al., 2000a; Yang et al., 2000b). This change increases the non-180º domain wall density. Hence, the increase of the dielectric constant with the applied stress can be observed. The de-aging mechanism is also expected to play a role here. However, the stress clamping of domain walls and the de-poling mechanisms are not expected at this relatively-low stress level used in this study (Zhang et al., 1997). Therefore, a combination of the domain switching and the de-aging mechanism

is believed to be a reason for the increase of the dielectric constant with increasing applied stress in the BT-PZT system, as shown in Figure 1.

The situation for the PMN-PT system is a little more complex because this system is a mixing between the normal ferroelectric PT and the relaxor ferroelectric PMN. Therefore, there is a competing mechanism between the two types of materials, depending upon the temperature and the composition. Since the $T_{max}$ for 0.9PMN-0.1PT is ~ 30°C and the experiment was performed at ~ 25°C, the nano-domains contribute greatly to the dielectric response, hence a significant decrease in dielectric constant with increasing stress is observed. For other compositions with higher $T_{max}$ (110°C for 0.8PMN-0.2PT to 270°C for 0.5PMN-0.5PT), since there is competing influences of the intrinsic contribution of domains, mainly micro-domains, and the extrinsic contribution of re-polarization and growth of micro-polar regions, with opposite responses, the dielectric constant of these compositions becomes rather stable with increasing applied stress, as seen in Figure 2.

For the PMN-PZT system, the results for the case of PZT-rich compositions can easily be explained in the same way as in the BT-PZT system. Since PMN is a relaxor ferroelectric material, the situation is very different for PMN-rich compositions. The stress dependence of the dielectric constant of the compositions is attributed to competing influences of the domain contribution and the extrinsic contribution of re-polarization and growth of micro-polar regions (Zhao and Zhang, 1996; Zhang et al., 1997). Since the dielectric response of both contributions is affected by the applied stress in an opposite way, the behavior of the composites depends on the composition ratio between PMN and PZT. Since the measurements were carried out at room temperature (25°C), the nano-domains dominate the dielectric response of the composites (Zhang et al., 1997). Therefore, the dielectric constant of the PMN-rich compositions decreases with increasing applied stress, as seen in Figure 3.

These results clearly demonstrate that the contribution of nano-domains to the dielectric responses of the BT-PZT, PMN-PT and PMN-PZT ceramics depends on the compositions and temperature. The nano-domains impose significant influences on the dielectric response to the uniaxial stress in relaxor ferroelectric-based ceramics. More importantly, this study undoubtedly shows that the applied stress has significant influences on the dielectric properties of ferroelectric ceramics.

## CONCLUSIONS

In this study, the dielectric properties under the uniaxial compressive stress of the BT-PZT, PMN-PT and PMN-PZT ceramics are observed at stress levels up to 15, 22 and 5 MPa, respectively, using a uniaxial compressometer. The dielectric constant of the BT-PZT ceramics increases significantly with increasing applied stress. Larger changes in the dielectric constant with the applied stress are observed in the PZT-rich compositions. For PMN-PT system, the dielectric constant of 0.9PMN-0.1PT decreases significantly with the applied stress, while that of other compositions is rather stable. For PMN-PZT system, the dielectric constant of the PMN-rich compositions decreases, while that of the PZT-rich compositions increases slightly with increasing applied stress. The experimental results are explained in terms of domains, domain walls and de-aging mechanisms. The nano-domains are found to play an important role in the dielectric response under the applied stress in relaxor-based ferroelectrics, such as PMN-PT and PMN-PZT. Finally, this study undoubtedly shows that the applied stress has significant influences on the dielectric properties of the three ceramic systems.

## ACKNOWLEDGEMENTS

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