Domain wall contributions in $Pb(Zr,Ti)O_3$ ceramics at morphotropic phase boundary: A study of dielectric dispersion

Li Jin (靳立),[a] Viktor Porokhonskyy, and Dragan Damjanovic
Ceramics Laboratory, Swiss Federal Institute of Technology (EPFL), Lausanne 1015, Switzerland

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The dielectric properties of undoped, Nb-, and Fe-doped $Pb(Zr,Ti)O_3$ ceramics with composition near morphotropic phase boundary were investigated in the frequency range from 1 MHz to 20.2 GHz at room temperature. Temperature dependences of dielectric permittivity ε' and loss ε'' are measured at 100 kHz from 50 to 300 K and around 13.4 GHz from 100 to 300 K. These measurements permit estimation of the upper limit of the intrinsic permittivity and lower limit of the extrinsic contributions to the permittivity as a function of temperature. The extrinsic contributions account for more than 50% of the quasistatic dielectric permittivity in studied samples. © *2010 American Institute of Physics*. [doi:10.1063/1.3455328]

Ferroelectric ceramics are the most widely used piezoelectric materials. The best properties are found in solid solutions exhibiting the morphotropic phase boundary (MPB).[1] The processes leading to the enhanced properties in the MPB region are of considerable technological and scientific interest. It is well known that in ferroelectric materials the motion of domain walls accounts for a large part of the experimentally observed piezoelectric and dielectric response.[2–6] In practice, the domain wall contributions are most often controlled by dopants, leading to electromechanically hard or soft materials.[1] In addition to dopants, domain wall contributions are dependent on microstructure and crystal structure of ceramics and, in general, it is found that the density of domain walls, domain structure, domain wall mobility, and the ceramics grain size are inter-related, and all depend on dopant concentration.[7–9] Within such a complex relationship among many parameters that influence properties, it is difficult to separate effects due to individual factors. It is advantageous when intrinsic properties are known either from a theory or direct measurements. This is unfortunately not the case for the most widely used piezoelectric material, $Pb(Zr,Ti)O_3$ (PZT), where single crystal data are not available and for which intrinsic (lattice) properties can be obtained only indirectly from the phenomenological Landau–Ginzburg–Devonshire (LGD) theory. One approach in separating lattice and domain wall contributions has been to measure properties of ceramics as a function of temperature and compare them with those obtained from the LGD theory.[10] The difference between thus obtained values is taken as an estimate of domain wall contributions. A good agreement between the dielectric properties measured in ceramics at low temperatures where domain walls are assumed to be frozen and values predicted from the LGD theory were taken as an indication that this method works well.[11] However, the recent discovery of a monoclinic phase in the MPB region of PZT (Ref. 12) has put some doubts in estimates derived from LGD approach based only on tetragonal and rhombohedral phases.

Another approach to estimate domain wall and lattice contributions is to examine properties of ferroelectric ceramics as a function of frequency. In many ferroelectric materials, a strong dispersion of permittivity accompanied by a loss peak is observed in the range from hundreds of megahertz to several gigahertz (sometimes named "microwave" region).[13–15] This dispersion is attributed to the motion of domain walls and it is thus reasonable to assume that above this dispersive region the properties approach their intrinsic values. Interestingly, while temperature dependent measurements performed in the conventional frequency range clearly indicated expected differences in domain wall contributions for soft (donor-doped) and hard (acceptor-doped) materials which disappeared at low temperatures,[10] it is not known whether such behavior is reflected in the microwave range.

In this study, we combine the microwave dielectric spectroscopy and low temperature dielectric measurements to study domain wall contributions to the dielectric properties of undoped, Nb-, and Fe-doped PZT with the same composition near MPB. The motivation is to see whether permittivity measured beyond the frequency range of the microwave dispersion is a good estimate of the intrinsic permittivity. If so, those measurements can be used to investigate extrinsic contributions to the permittivity as a function of temperature and can be compared with the existing estimates based on LGD theory. Furthermore, it is of interest to see whether dopants and domain configuration significantly affect the permittivity at frequencies above the microwave dispersion range.

Undoped, Nb-, and Fe-doped ceramics with Zr/Ti atomic percent ratio of 52/48 were synthesized by a conventional solid state process.[9] Concentration of Nb and Fe was 1 at. %. For the sake of convenience, the samples are labeled in the following manner: for example, PZT(52/48)Fe1.0 refers to the nominal formula $Pb(Zr_{0.52}Ti_{0.48})_{0.99}Fe_{0.01}O_3$, etc. Samples shaped into the form of small cylinders (5 mm long and 0.5 to 0.8 mm in diameter) were used for the dielectric characterization. The base surfaces were sputtered with Au electrodes. From 1 MHz to 1.8 GHz, a HP 4396A impedance analyzer was used to acquire the impedance spectra, and nonuniform fields distribution across the sample has been accounted for during permittivity calculation.[16] From 3.4 to 20.2 GHz, the sleeve resonator technique was employed.[17] Here we used it in a multimode regime, where TE_{011}-mode and its radial harmon-

[a]Electronic mail: li.jin@epfl.ch.

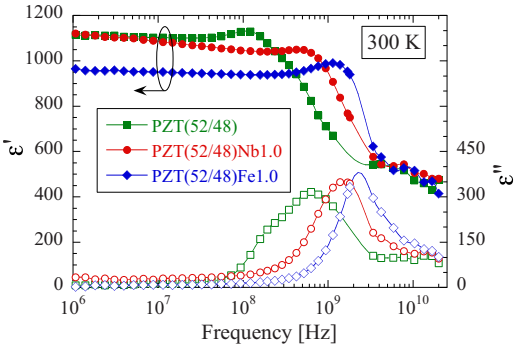

FIG. 1. (Color online) Permittivity ε' (full symbols) and loss ε'' (open symbols) spectra of studied PZT samples at room temperature. The thin lines are a guide to the eye. For a given composition, ε' and ε'' share the same color and symbol type.

ics (TE_{0m1}) were observed. The permittivity ε' and loss ε'' values were extracted from transmission spectra collected by means of a HP8722D network analyzer.

Figure 1 shows the ε' and ε'' spectra of studied PZT samples from 1 MHz to 20.2 GHz at room temperature. In each spectrum, we observed a good match between data sets corresponding to two aforementioned techniques. This observation speaks for reliability of our data. In agreement with earlier studies,[13,14] all samples exhibit steep dispersion of the permittivity. It sets in above 100 MHz and is accompanied by a pronounced loss maximum. Here we use the term "steep" to facilitate distinction from quasilinear dependence of ε' on $\log(f)$ associated with the nearly constant loss behavior ($1/f$-noise),[18] which is a much broader feature. The $1/f$-noise dispersion could be readily seen in Fig. 1 in the spectra of PZT(52/48)Nb1.0 below 100 MHz. Unlike $1/f$-noise, the steep dispersion is accompanied by a pronounced loss peak. The peak's position, f_m, is located around 0.68 and 1.49 GHz in PZT(52/48) and PZT(52/48)Nb1.0, respectively. The loss spectrum of PZT(52/48)Fe1.0 shows a monotonous increase toward 1.8 GHz and a monotonous decrease above 3.4 GHz, indicating that f_m is located between these two frequencies.

Compared to the high value of loss around the f_m, the loss usually falls to a relatively lower level far away below and above the f_m. In the case of materials studied here, all loss spectra in Fig. 1 tend to level off above 10 GHz at the value of about 100, which is roughly 20%–25% of the maximum value. This observation, in the first place, indicates a possible overlap with another process whose dispersion range centers above our upper frequency limit. We shall return to this observation later. Second, it is obvious that the major part of the steep dispersion is accomplished within the interval from 100 MHz to 10 GHz. Therefore, we can estimate the contribution of the steep dispersion, $\Delta\varepsilon'_{st}$, to the permittivity from the difference of the permittivity far away below and above f_m. For convenience and easier comparison with the data in the literature we choose these frequencies as 100 kHz and 13.4 GHz; therefore $\Delta\varepsilon'_{st}=\varepsilon'(100\ \text{kHz})-\varepsilon'(13.4\ \text{GHz})$. From earlier studies on PZT,[14] $(1-x)BiScO_3-xPbTiO_3$ (BSPT),[18] and $(K_{0.5}Na_{0.5})NbO_3$ (KNN),[16] it is known that the position of loss maximum f_m observed at "microwaves" reveals negligible temperature dependence. This result gives an opportunity to estimate the temperature dependence of $\Delta\varepsilon'_{st}$ from those of $\varepsilon'(100\ \text{kHz})$ and $\varepsilon'(13.4\ \text{GHz})$ shown in Fig. 2(a).

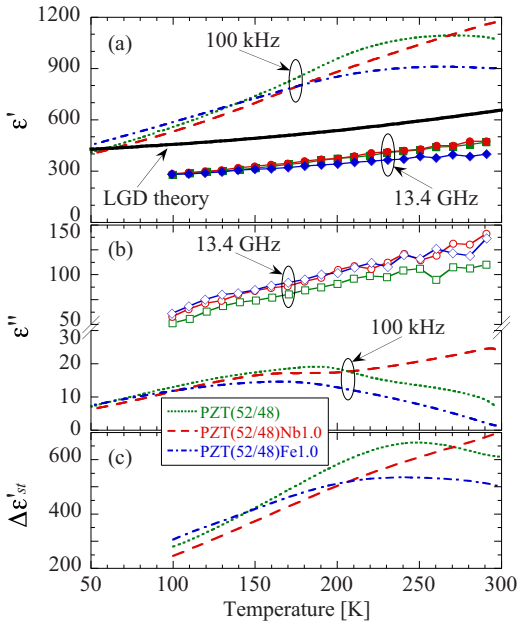

FIG. 2. (Color online) Permittivity ε' (a), loss ε'' (b), and dispersion strength $\Delta\varepsilon'_{st}$ (c) vs temperature. $\Delta\varepsilon'_{st}$ represents the difference between values measured at 100 kHz (color thin lines) and 13.4 GHz (symbols). The data corresponding to a given composition are shown in the same color. The estimation based on LGD theory (Ref. 11) is shown in a thick line in (a). Note the change in the vertical scale in (b).

The temperature dependence of $\varepsilon'(100\ \text{kHz})$ is similar to previously published results for MPB region.[10,19,20] The qualitative difference between hard and undoped on one and soft samples on the other side has been linked to the higher concentration of oxygen vacancies in the former samples; oxygen vacancies are associated with acceptor dopants and are known to control the mobility of domain walls.[21,22] Our measurements reveal much smaller variation between the hard, soft and undoped samples and weaker temperature dependence at 13.4 GHz than at 100 kHz. This gives further supports to the idea that the low frequency anomalies are indeed related to domain wall motion that becomes suppressed at higher frequencies.

We next compare the high frequency permittivity values with the prediction of LGD theory for polycrystalline samples.[11] The latter is shown as the full line in Fig. 2(a). At this point, it is important to understand all contributions to the $\varepsilon'(13.4\ \text{GHz})$. Besides intrinsic (lattice) contribution, $\varepsilon'(13.4\ \text{GHz})$ contains contribution from the dispersion process associated with the loss above 13.4 GHz mentioned earlier. Therefore, the value of $\varepsilon'(13.4\ \text{GHz})$ can only be regarded as the upper limit of the intrinsic contribution. Nevertheless, it shows considerably lower values compared to the theoretical prediction. A part of the discrepancy could be explained by the fact that the permittivity at 13.4 GHz should correspond to the clamped (constant strain) permittivity that is lower than the free (constant stress) permittivity calculated by the LGD (Ref. 11) and shown in Fig. 2(a). However, this difference is expected to be small in unpoled samples even if individual grains are partly piezoelectric and their electromechanical resonances contribute to microwave dispersion.[23] Note that extrapolation of $\varepsilon'(100\ \text{kHz})$ and $\varepsilon'(13.4\ \text{GHz})$ to 0 K leads to a good agreement between the two, as should be expected when all extrinsic contributions are frozen. Therefore, we conclude that over a broad tem-

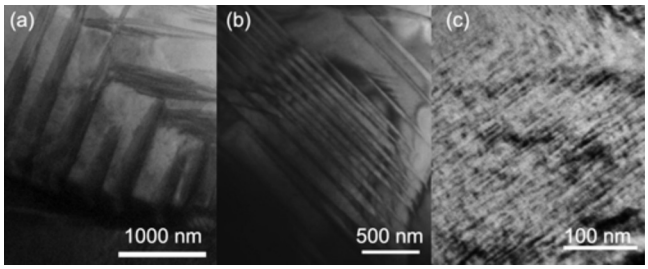

FIG. 3. Room temperature bright field TEM image of (a) PZT(52/48), (b) PZT(52/48)Nb1.0, and (c) PZT(52/48)Fe1.0 ceramics.

perature range the LGD theory predicts higher permittivity values than observed here at 13.4 GHz. Apart from possible question about averaging procedure used to calculate LGD values reported in Ref. 11, our data suggest a need for a revision of LGD analysis for compositions near MPB. Our conclusion is, therefore, that the microwave measurements can be used to estimate upper limit of the intrinsic contributions and are at present more reliable than theoretically derived values for MPB compositions.

At microwave frequencies, the loss ε'' monotonously increases with increasing temperature, Fig. 2(b), and is at least five times as high as ε'' probed at 100 kHz. Such behavior of loss is consistent with the temperature dependence of $\Delta\varepsilon'_{st}$ depicted in Fig. 2(c). The multifold decrease in $\Delta\varepsilon'_{st}$ toward low temperatures seen in Fig. 2(c) is also revealed by BSPT (Ref. 18) and KNN.[16] The temperature dependence of $\Delta\varepsilon'_{st}$ reflects freezing of extrinsic contributions at low temperatures further validating our procedure of estimation of extrinsic contributions.

As domain wall motion is intimately related to the steep dispersion in ferroelectrics,[13–15] an examination of domain morphology is of interest here. The TEM images presented in Fig. 3 provide such an opportunity. The representative domain patterns shown here clearly demonstrate progressive decrease in domain size as we move from PZT(52/48) through PZT(52/48)Nb1.0 to PZT(52/48)Fe1.0. Rough estimation of domain sizes along with the grain size $\bar{D}$ is summarized in Table I, where $\bar{D}$ is extracted from SEM images as described in Ref. 23. As it was already pointed out, very strong reduction in domain size observed in PZT(52/48)Fe1.0 cannot be accounted by the variation in the grain size alone,[9] where a square root of dependence ($\sim\sqrt{\bar{D}}$) is usually expected.[7,24] It is worth noting that the increase in the domain wall density does not lead to any enhancement of extrinsic response, as recently suggested for MPB compositions[8] of PZT and reported for piezoelectric properties of $BaTiO_3$;[25] other factors besides domain wall density must be taken into account. In addition, it appears that the domain wall density by itself has no impact whatsoever on dielectric properties above 13.4 GHz. The only enhancement of extrinsic contribution we observe in addition to microwave dispersion is due to the nearly constant loss behavior in PZT(52/48)Nb1.0. In PZT(52/48)Fe1.0, this polarization mechanism is most likely suppressed by the pinning centers associated with Fe^{3+}-ions.[26] As for the positive role of Nb^{5+}-ions, one option could be higher domain wall mobility promoted by the presence of Nb^{5+}-ions and associated defects disorder.[27] Interestingly, within resolution of our measurements, the dopants do not seem to affect the polarization response above the region of steep dispersion.

TABLE I. Average grain size $\bar{D}$ and domain size of studied PZT samples.

Composition	$\bar{D}$ (μm)	domain size (nm)
PZT(52/48)	7.92	100–1000
PZT(52/48)Nb1.0	2.91	20–300
PZT(52/48)Fe1.0	2.05	~10

In conclusion, the permittivity probed in the microwave range [in our case ε'(13.4 GHz)] can be used to estimate the upper limit of the intrinsic dielectric permittivity in PZT ceramics. The extrinsic contribution to the permittivity $\Delta\varepsilon'_{st}$ accounts for more than 50% of the quasistatic dielectric permittivity ε'(100 kHz) in all (undoped, soft, and hard) studied samples. Our results also suggest that the phenomenological LGD theory with presently available free-energy coefficients overestimates intrinsic permittivity for MPB compositions.

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