Multiple relaxation and characteristic temperatures in PbMg$_{1/3}$Nb$_{2/3}$O$_3$:La relaxor ferroelectric crystals

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Unusual relaxation is a basic property of relaxor ferroelectrics which distinguish them from other ferroic materials. Several relaxation processes typically contribute to the dielectric spectra of a relaxor and their deconvolution is always a challenging task. The distribution of relaxation times function is used to adequately describe the entire spectrum, which provides restricted opportunities to determine the parameters of the constituent relaxation processes. A remarkable feature of relaxors is that different relaxation contributions to the dielectric response can appear or disappear at specific temperatures not related to structural phase transitions. It is known, in particular, that a high-frequency relaxation (central mode) emerges upon cooling at the Burns temperature, T_B and the characteristic relaxation time of the low-frequency part of the spectrum diverges at the freezing temperature $T_f \ll T_B$. However, at another characteristic temperature known as T^* ($T_f < T^* < T_B$), no evident anomalies have been observed in dielectric relaxation spectra.

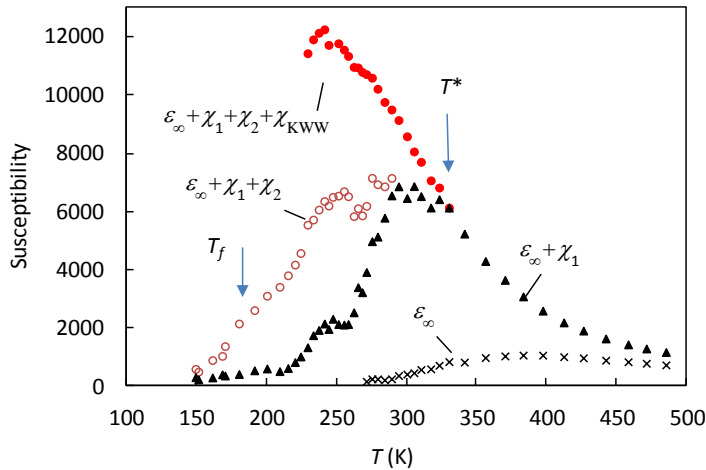In this work we analyze the dielectric relaxation spectra of PbMg$_{1/3}$Nb$_{2/3}$O$_3$ relaxor ferroelectric crystals doped with ~2 at.% La^{+3} (PMNL) in a wide frequency range between 10^{-2} Hz and 5×10^{10} Hz. These crystals are characterized by the enhanced degree of compositional order as compared to pure PMN. Previous investigations of relaxation in these crystals by means of dielectric spectroscopy at low-frequencies $f < 1$ MHz[1] and Brillouin scattering[2] showed that La impurity influences little the relaxation times and the width of the relaxation spectrum, but decreases significantly the magnitude of dielectric constant facilitating the measurements in the microwave range.

Our results indicate that two low-frequency relaxation processes which are usually believed to be related to flipping and "breathing" of polar nanoregions (PNRs), respectively, actually appear only below the T^*, but not below T_B, as believed earlier.[3] An additional strong relaxation process is discovered which provides the main contribution to the dielectric response at $T \sim T^*$. It was confirmed that the dielectric spectra of pure and La-doped crystals are qualitatively similar.
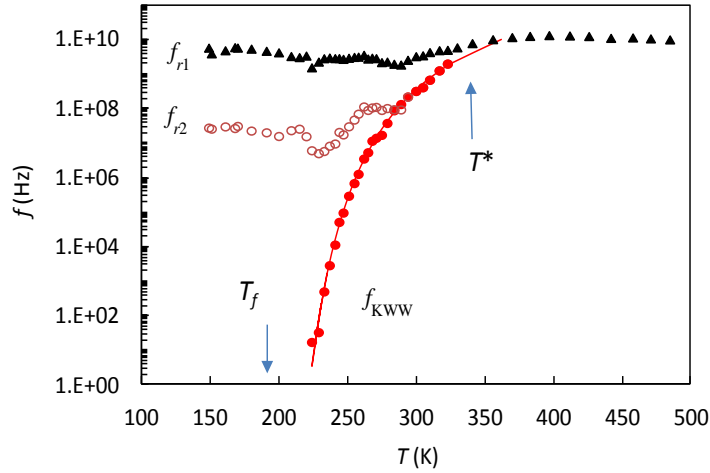
To determine the parameters of different relaxations the spectra were least-squares fitted to a multi-relaxation model in which the complex dielectric permittivity was represented as a sum of susceptibilities related to different polarization mechanisms: $\varepsilon^*(f) = \varepsilon_\infty + \sum \chi_k^*(f)$, where the susceptibilities χ_1^* and χ_2^* are represented by the Cole-Cole relaxation function, $\chi_3^* \equiv \chi_{KWW}^*$ is

Figure 1 Structure of the dielectric spectrum in PMNL crystal. Static susceptibilities associated with different contributions to the dielectric response are shown as a function of temperature.

represented by the Kohlrausch-Williams-Watts (KWW) relaxation function, $\chi_4^* \sim f^{\,n-1}$ is the "universal" relaxation which appeared in the low-frequency part of the spectrum due to the mobile charge carriers and the constant ε_∞ describes the contributions of electrons, phonons and the fast component of central mode which is known to exist in PMN and PMNL in the THz frequency range.[2,3.]

Figure 2 Temperature dependencies of characteristic relaxation frequencies of three relaxation processes observed in PMNL crystal. Solid line is the fit to Vogel-Fulcher law.

The temperature dependences of selected relaxation parameters extracted from the fitting model are shown in Figs. 1 and 2. At temperatures above $T^* \approx 340$ K only one relaxation process is resolved, which fits the Debye function (the Cole-Cole parameter $\alpha \approx 0$) whose relaxation frequency, f_{r1}, is practically temperature-independent. The relaxation strength of this process, χ_1, peaks at ~ 300 K and decreases upon further cooling. At $T<T^*$ a new relaxation contribution appears whose relaxation spectrum fits the KWW pattern, the characteristic relaxation frequency obeys the Vogel-Fulcher law, $f_{KWW} = f_0 \exp[-E_a/(T-T_f)]$ with $T_f = 185$ K, $E_a = 1100$ K and $f_0 = 4.8 \times 10^{12}$ Hz, while the shape parameter follows the similar law $\beta = \beta_0 \exp[-E_\beta/(T-T_f)]$. This dielectric contribution is usually believed to result from thermally-activated reorientations of PNRs.[3] The last relaxation mechanism with the intermediate relaxation frequency f_{r1} is developed at comparatively low temperatures. Its relaxation time distribution increases dramatically (i.e. α increases) on cooling, resulting in frequency–independent loss at $T< T_f$. This mechanism is presumably attributed to the motion of PNRs boundaries (breathing).[3]

References

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