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Journal of the European Ceramic Society 24 (2004) 1545–1549

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Broad-band dielectric response of doped incipient ferroelectrics

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Abstract

Broad-band dielectric responses (10^2–10^{14} Hz) of $Sr_{1\text{-}1.5x}Bi_xTiO_3$ ($x=0.0067\div0.133$) ceramics and $K_{1\text{-}x}Li_xTaO_3$ ($x=0.050\div14$) single crystals are analysed and compared. The common features are emphasized: softening of the polar phonon is suppressed by the doping, dielectric dispersion takes place in a wide frequency range below polar phonon modes, multiple relaxation regions and distribution of relaxation times occurs. Mechanisms of the main contributions to the dielectric permittivity and temperature evolution of their characteristic frequencies in doped incipient ferroelectrics are discussed. Dynamics of the soft phonon, off-centred ions and polar clusters, induced by the off-centred ions interacting via crystal lattice, is considered to be responsible for the observed dielectric response. Dielectric response of doped incipient ferroelectrics is compared with that of model relaxor ferroelectrics.

Keywords: Dielectric properties; Ferroelectric properties; Incipient ferroelectrics; Perovskites; Spectroscopy

1. Introduction

Doped incipient ferroelectrics $SrTiO_3$ (ST) and $KTaO_3$ (KT) were broadly investigated, including their dielectric properties. In the case of $Sr_{1\text{-}1.5x}Bi_xTiO_3$ (SBiT-x) and $K_{1\text{-}x}Li_xTaO_3$ (KLT-x), the impurity ions Bi and Li take off-centred positions, form reorienting dipole system and consequently provide significant dielectric relaxation in a wide frequency range.[1–7] Interaction of the off-centred ions with (and via) highly polarisable crystal lattice of ST and KT results both in hardening of the crystal lattice[2–6] and in formation of polar nano-clusters, which freeze at low temperatures (at T_C) in a multi-scale dipole ordered states, depending on the Li/Bi concentration.[2–7] That is why dielectric response of SBiT and KLT is very complicated and to some extent similar to that of relaxor ferroelectrics.[8–10] The aim of our study is to determine the main polarisation mechanisms contributing to the dielectric response of SBiT and KLT and to build up a general structure of the dielectric spectrum of moderately doped incipient ferroelectrics, as it has been done for the relaxor ferroelectrics.[9,10]

Dielectric data in a wide range, from low to infrared frequencies, are required for our analysis. Our recent study of SBiT ($x=0.0067\div0.133$) ceramics[2] provides the full dielectric response from 10^2 to 10^{14} Hz. We also combine results of systematic low-frequency study of KLT ($x=0\div0.3$)[3,4] and high-frequency/microwave study of KLT ($x=0.05\div0.14$) single crystals[5–7] with new data of infrared (IR) and sub-mm experiment, performed on crystals of the same origin (Ioffe Physical-Technical Institute, St. Petersburg). These results are used here as basic experimental data for our analysis. In the case of KLT, “x” denotes the impurity concentration in the melt, to avoid uncertainty in a value of impurity concentration inside the crystals.[3] For instance, $x=0.1$ in our paper corresponds to concentration inside the crystal $x_{in}=0.043$.[3]

Two relaxation processes attributed to the thermal motion of off-centred Li/Bi ions[2–7] are observed in KLT and SBiT in a wide range of impurity concentration (see two maxima in the dielectric loss $\epsilon''(T)$, **I** and **II**, Fig. 1). The first process dominates at lower concentrations, while the second one prevails at higher concentrations. For KLT-0.1 and SBiT-0.0267 both processes are well resolved and provide comparable contributions to

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doi:10.1016/S0955-2219(03)00530-2

dielectric loss and permittivity. Li/Bi doping results in significant stiffening of KT/ST crystal lattice[2–6] revealed in the hardening of the ferroelectric soft phonon. The total dielectric contribution of phonons at 20 K, estimated from IR and sub-mm data, reduces from ~8000 (ST) via 1000 (SBiT-0.0067) and 450 (SBiT-0.0267) to 170 (SBiT-0.133) for SBiT and consequently from ~4000 (KT) via 1350 (KLT-0.03) to 420 (KLT-0.1) for KLT. With increasing temperature, the phonon contribution of KLT-0.1 and SBiT-0.0267 linearly decreases down to 200 at 300 K (Fig. 2). In our opinion, KLT-0.1 and SBiT-0.0267 could be considered as compounds representing the moderately doped incipient ferroelectrics. Let us consider their dielectric properties more in details.

2. Broad-band dielectric response of KLT-0.1 and SBiT-0.0267

Dielectric spectra of KLT-0.1 and SBiT-0.0267 are generally similar to each other. Low frequency permittivity is characterised by a dominant maximum of $\epsilon'(T)$ which is much higher than phonon contribution and consists of superposition of two maxima, **I** and **II** (see Fig. 2 and ref. 2), corresponding to the two maxima of $\epsilon''(T)$. Relaxational dielectric dispersion takes place in the whole investigated frequency range. At low temperatures the dispersion begins at low frequencies and then shifts to the microwave and sub-mm wave range above 200 K. Two dispersion regions below phonon frequencies can be distinguished.[2,3,6,7] The higher-frequency dispersion (R-I) corresponds to the relaxation process **I**, the lower-frequency dispersion (R-II) corresponds to the relaxation process **II**. The relaxation time distribution of R-II is broader then that of R–I.[2,3,6,7] Detailed analysis of low-frequency dielectric spectra of KLT-0.1[3] revealed two contributions to the R-I. Besides the dominant contribution, attributed to the relaxation process **I** of Li ions, additional low-temperature relaxation, associated with Fe-related defects unavoidable in KT,[3,4] is present. In SBiT-0.0267 additional high-temperature relaxation, related to oxygen vacancies, was observed.[1,2] In our analysis we do not take into account these additional relaxations and focus on the relaxation processes **I** and **II**, caused by the off-centre Li/Bi ions.

Temperature dependences of characteristic frequencies of the main processes, contributing to the dielectric response of KLT-0.1 and SBiT-0.0267 (i.e., phonon dynamics, relaxation processes **I** and **II**), are

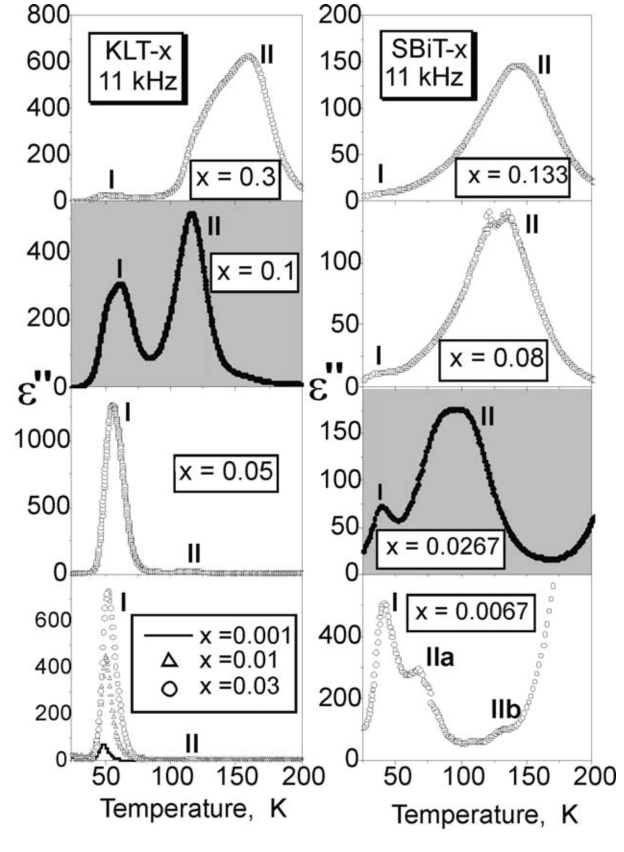

Fig. 1. Temperature dependences of dielectric loss (ϵ'') of KLT-x single crystals and SBiT-x ceramics at 11 kHz. Markers **I** and **II** denote maxima corresponding to the relaxation processes caused by off-centred Li/Bi ions.

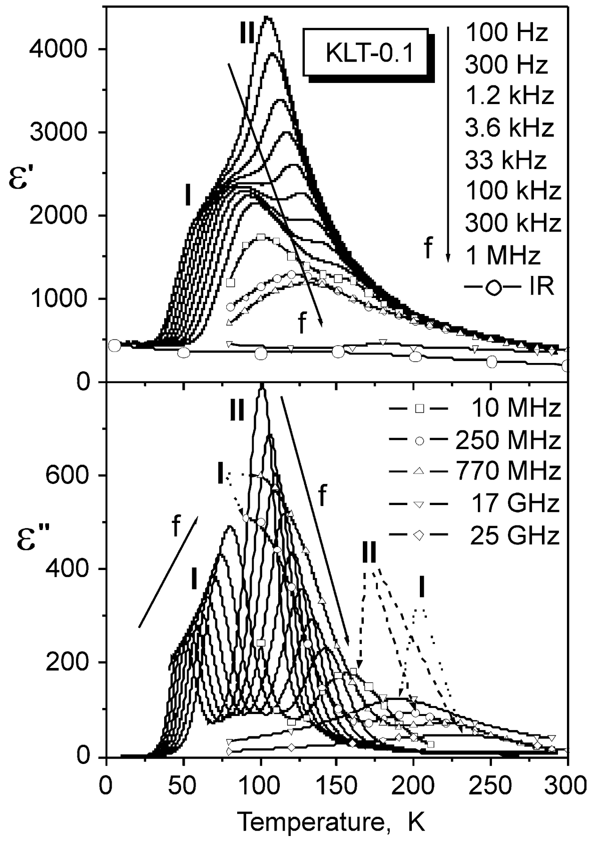

Fig. 2. Temperature dependences of dielectric permittivity (ϵ') and loss (ϵ'') of KLT-0.1 single crystals at various frequencies. Markers **I** and **II** denote maxima corresponding to the relaxation processes caused by off-centred Li ions.

presented in Fig. 3 and show the similarity of the dielectric responses. The mean relaxation time (τ) of R-I obeys the Arrhenius law with parameters: $\tau_0 = 2.1 \times 10^{-13}$s, E = 1100 K for KLT-0.1[3] and $\tau_0 \approx 2 \times 10^{-13}$ s, E≈700 K for SBiT-0.0267.[2] These parameters were estimated on the basis of low-frequency data, but are also in a good agreement with high-frequency, microwave and sub-mm data. Temperature dependence of the mean relaxation time of R-II does not fit well to the Arrhenius law with physically reasonable parameters for both KLT-0.1[3,6,7] and SBiT-0.0267. It can be explained by a presence of two contributions to the R-II,[2,3] which should be analysed separately. The detailed analysis of R–II is still in progress. Preliminary we can suppose that τ(T) of one of the contributions to the R-II probably obeys the Vogel–Fulcher law.

The R-I dispersion in KLT-0.1, corresponding to the relaxation process **I**, is certainly attributed to a 90° reorientation of individual Li dipoles,[3–7] while the nature of R-II dispersion corresponding to the relaxation processes **II**, in is still a subject of discussion. At least three possible origins of R-II could be listed: 180° reorientation of individual Li dipoles;[3,4] relaxation of pairs of Li dipoles reorienting as single unit;[3,4] relaxation of dynamic polar nano-clusters, created by the off-centred Li ions interacting via crystal lattice, i.e., correlated motion of the off-centred Li ions.[3–7] We support the last idea, which can explain all experimentally observed features, including: higher activation energy, higher mean relaxation time and broader distribution of relaxation times, comparatively to R-I; presence of two dielectric contributions; deviation of τ(T) from the Arrhenius law, etc. In the same way, we attribute the R-I dispersion and relaxation processes **I** in SBiT-0.0267 to the relaxation of individual Bi ions, while the R-II dispersion and relaxation processes **II** are attributed to the relaxation of dynamic polar nano-clusters, created by the off-centred Bi ions interacting via crystal lattice.[2] The presence of polar clusters in SBiT was proved by our micro-Raman study.[2]

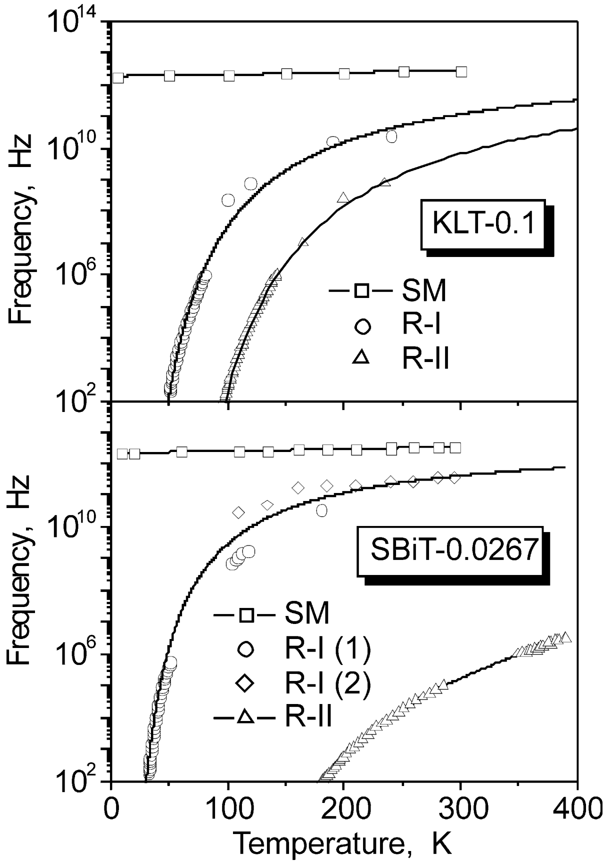

Fig. 3. Temperature dependences of characteristic frequencies of the main processes, contributing to the dielectric response of KLT-0.1 and SBiT-0.0267. Markers denote frequencies of: SM - soft phonon mode, R-I and R-II- relaxation processes **I** and **II**. Points R-I(1) correspond to low-, high-frequency and microwave dielectric experiment, while points R-I(2) are results of sub-mm data fit.

3. General structure of the dielectric spectrum of moderately doped incipient ferroelectrics

We expand the common approach to the analysis of dielectric spectra of KLT-0.1 and SBiT-0.0267 to construct a scheme of the dielectric behaviour of moderately doped incipient ferroelectrics. Dynamics of the soft phonon, off-centred ions and polar clusters, induced by the off-centred ions interacting via crystal lattice, is considered to be responsible for the observed dielectric response. Soft mode behaviour, characteristic for KT and ST, is suppressed by the interaction with off-centred ions and polar clusters. Consequently, the phonon contribution to the dielectric permittivity is not a dominant and much lower than in KT or ST. The higher concentration of the off-centred ions results in the lower and less temperature dependent phonon contribution. The relaxation (hopping) of individual off-centred ions takes place in a wide temperature interval and provides dielectric contribution with a maximum at low temperatures. The dynamics of polar clusters generally includes two processes: dipole reversal (flipping) of polar clusters and fluctuations (breathing) of polar cluster boundaries, similar to relaxor ferroelectrics.[8,10] These processes provide two dielectric contributions with a single unresolved maximum, situated at higher temperature than the maximum of the individual ions contribution. A general structure of the dielectric spectra (Fig. 4a) shows a dominant role of the contributions of individual ions (2) and polar clusters (3) and (4). The contribution (2) dominates at lower concentrations of the off-centred ions, while the contributions (3) and (4) prevail at the higher concentrations. Below T_C, where flipping of polar clusters (i.e., correlated hopping of the off-centred ions) is frozen-out, the individual ion hopping (2) and cluster boundaries breathing (3) are the leading mechanisms. Only near helium temperatures, where all relaxation processes are effectively frozen, the phonon contribution (1) becomes dominant.

With increasing frequency, the contributions to static permittivity will switch off in the sequence: polar clusters reversal, breathing of cluster boundaries, individual ion hopping and phonon contribution. Temperature evolution of characteristic frequencies of the main dielectric contributions is schematically presented in Fig. 5a: f_{SM} weakly decrease with lowering temperature, $f_{IH}(T)$ and $f_B(T)$ obey the Arrhenius law, while $f_{CL}(T)$ obeys the Vogel–Fulcher law with a freezing temperature T_C. Both polarisation mechanisms, related to the cluster dynamics, are characterised by broad distributions of the relaxation times/frequencies. That is why the contributions of polar clusters reversal and breathing of cluster boundaries are not well resolved in the frequency domain and form a single range of relaxational dispersion, limited by the upper f_2 and lower f_1 relaxation frequencies. $f_2(T)$ obeys the Arrhenius law and is close or equal to the f_{IH}, while $f_1(T)$ obeys the Vogel–Fulcher law with the same freezing temperature T_C as $f_{CL}(T)$. Consequently, the grey region in Fig. 5a between $f_2(T)$ and $f_1(T)$ denotes the frequency-temperature range of the relaxation processes caused by the off-centred ions.

Comparing the scheme of dielectric response of doped incipient ferroelectrics (Figs. 4a and 5a) and relaxor ferroelectrics (Figs. 4b and 5b), one can see the common features, caused by the important role of the polar cluster dynamics and soft mode hardening. The main difference consist in presence of the individual ions hopping mechanism (2) and absence of a specific temperature, below which the polar clusters appear (Burns

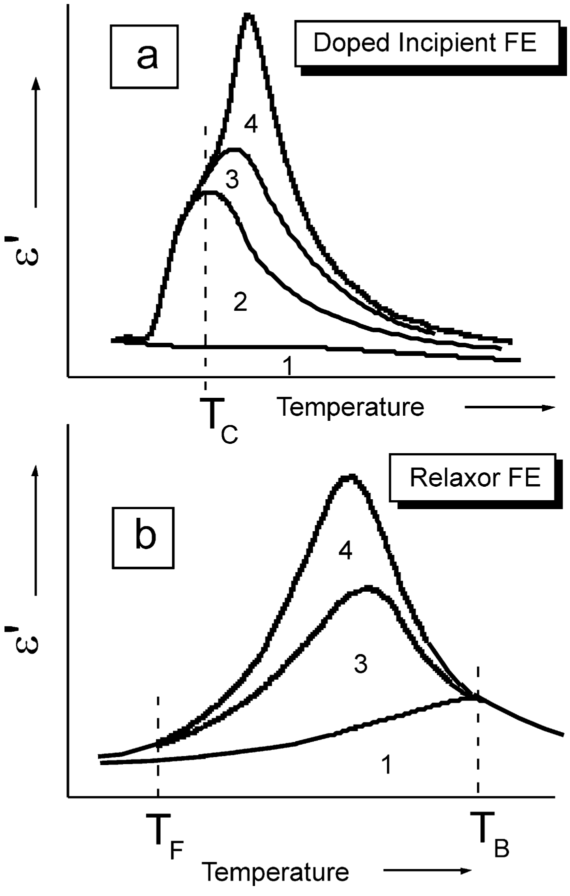

Fig. 4. Structure of dielectric spectra of (a) moderately doped incipient ferroelectrics and (b) relaxor ferroelectrics. The main dielectric contributions are caused by: 1—phonon polarisation mechanism (including small contribution of optical polarisation mechanism, see ref. 9,10); 2—hopping of individual off-centred ions; 3—fluctuations (breathing) of polar cluster boundaries; 4—polar cluster reversal. Markers denote specific temperatures, corresponding to: T_C—phase transition (freezing) to multi-scale dipole-ordered states, T_F—freezing of polar clusters, T_B—Burns temperature.

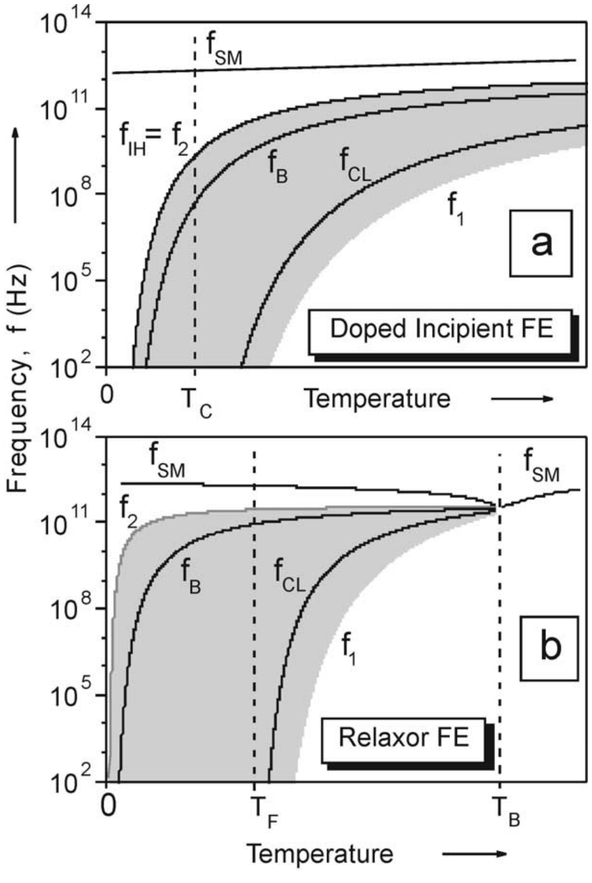

Fig. 5. Temperature evolution of the characteristic frequencies of main dielectric contributions of (a) moderately doped incipient ferroelectrics and (b) relaxor ferroelectrics. Bold curves correspond to: f_{SM}—soft phonon mode frequency, f_{IH}—mean relaxation frequency of individual off-centred ions, f_B —mean relaxation frequency of polar cluster boundaries, f_{CL}—mean relaxation frequency of polar clusters reversal. Curves f_1 and f_2 correspond to lower and upper limits of distribution of relaxation frequencies of polar clusters reversal and of cluster boundaries breathing. The grey region between f_1 and f_2 curves denotes the frequency-temperature range of the relaxation processes caused by the off-centred ions (a) or the frequency-temperature range of relaxor behaviour (b).

temperatures[10]), in the doped incipient ferroelectrics compared to the relaxor ferroelectrics. Also, the range of relaxation time distribution seems to be wider in the case of relaxor ferroelectrics, probably because of the dominant role of the polar clusters. We should note that very slow relaxation processes and dielectric response below 100 Hz are outside of our consideration.

Acknowledgements

The work was supported by the Grant Agency of the Czech Republic (projects No 202/98/1282, 202/02/0238/A) and the Grant Agency of the Academy of Science of the Czech Republic (project No A1010828).

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