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Dielectric permittivity and Cr^{3+} impurity ion probe luminescence in $SrTiO_3$ sol–gel ceramics

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Abstract

In order to inspect bulk properties of the $SrTiO_3$ ceramics grains, dielectric permittivity and temperature shift of a zero-phonon *R*-emission line of the Cr^{3+} impurity-ion probes were studied in sol–gel $SrTiO_3$:Cr ($3 \times 10^{-2}\%$) ceramics of the average grain size ~24 μm. We found that non-dispersive permittivity (100 Hz to 1 MHz) increases on cooling less steeply than in single crystals reaching ~5000 at 30 K. At lower temperatures the dispersion appears and the permittivity saturates at ~8 K ($\varepsilon' \approx 7000$, 400 Hz). However, the temperature shift of the *R*-line in ceramics remains practically identical to that for $SrTiO_3$ single crystals, in which *R*-line shifts with temperature is $\Delta\nu \sim 1/\varepsilon' \sim \omega^2_{TO1}$. This indicates that the bulk of the grains in ceramics exhibits properties inherent to $SrTiO_3$ quantum paraelectric, which agrees with the "generalized brick-wall" approach developed recently to describe polarization response of granular high permittivity materials.

Keywords: Spectroscopy; Composites; Ferroelectric properties

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1. Introduction

Dielectric permittivity of $SrTiO_3$ ceramics usually differs markedly from that of crystals. Single crystals typically exhibit non-dispersive permittivity (~300 at room temperature, RT),[1] which increases on cooling due to the TO1 mode softness saturating at ~4 K with values higher than 20 000[2] (~41 900)[3] because of quantum zero-point atomic motions. The dielectric permittivity of traditionally prepared dense ceramics is non-dispersive and reaches ~300 at RT, too. However, its rise upon cooling appears to be reduced. This effect increases strongly with the decreasing grain size. The nature of such discrepancy is typically ascribed to porosity, granularity and low-permittivity dead interface layers. A "generalized brick-wall" model (GBWM) developed recently appears to be able to describe main features of permittivity and TO1 mode behavior in ceramics (see Refs. 4–6, and references therein). This approach considers dead layers at polar grain boundaries with dipole moment penetrating into the bulk of the grains with polarization correlation length, or being temperature independent. Polar dead layers interact and diminish TO1 mode softness in the grain bulk, which was confirmed by Raman experiments and IR reflection,[4,6] demonstrating activation of the forbidden TO2 mode and strong stiffening of the TO1 mode in ceramics with grain size of 0.15 μm particularly, at lower temperatures. In accordance with GBWM, $SrTiO_3$ ceramics of grain size at least ≥1.5 μm reveal practically the same TO1 mode behavior as that in single crystal, with only modest stiffness below ~4 K.[4,6] So, GBWM and accompanied experiments[4–6] show identical properties of the bulk of the grains and single crystals for large enough grains size. However, determination of the soft mode parameters at low temperatures by the reflection technique with high accuracy is complicated and needs to be verified, because ω_{TO1} strongly decreases beyond the reliably measurable IR range and the reflectivity approaches unity. Besides, the penetration depth in the soft mode frequency range is less than 1 μm, so that the results are influenced by the surface layer whose properties are known to differ from those of the bulk. At the same time, information about TO1 mode behavior of the bulk of the ceramics grains can be obtained from impurity ion probes luminescence spectroscopy. As it was recognized

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in,[7] the zero-phonon *R* emission line ($^2E \rightarrow {}^4A_2$) of octahedral Cr^{3+} impurity center in $SrTiO_3$ shifts strongly to lower energies at cooling as $\Delta\nu \sim 1/\varepsilon' \sim \omega_0^2$, i.e., is controlled by TO1 mode[7,8] (*more exactly – due to interaction of the optical centre with the local soft mode, whose behavior depends strongly on TO1 lattice mode*).[9] Such Cr^{3+} impurity spectroscopy method have been successfully used by us for the studies of $KTaO_3$, $Sr_{1-x}Ca_xTiO_3$, and $SrTiO_3$:Mg crystals and ceramics.[8–12] In this work we applied this strategy for $SrTiO_3$ sol–gel ceramics of average grain size ~24 μm.

2. Experimental

$SrTiO_3$ ceramics with 0.03% of Cr was fabricated from stable stock solutions prepared by sol–gel method. The solutions with concentration of about 0.2 M were prepared using strontium acetate, tetra-*n*-butyl orthotitanate and chromium acetate. Acetic acid, 1,2-propanediol and absolute ethanol were used as solvents. Strontium acetate was initially dissolved into heated acetic acid followed by the addition of chromium acetate under constant stirring to form a transparent solution. After cooling to room temperature the former solution was diluted in 1,2-propanediol and titanium isopropoxide was added. Transparent solution was dried at 373 K about 24 h and calcined at 1223 K for 20 h. The calcined powders were milled again for 8 h. Pellets were uniaxially pressed at 100 MPa and then isostatically pressed at 200 MPa. Sintering was performed in air 5 h at 1823 K. The crystalline structure of samples was evaluated by X-ray diffraction analysis (XRD, Rigaku D/Max-B, Cu Kα). The observed X-ray diffraction lines are consistent with the cubic crystallographic structure of $SrTiO_3$ and no second phases were observed. The ceramics microstructure was examined by scanning electron microscopy (SEM, Hitachi S-4100). The density of the samples sintered was ~95% and average grain size appeared to be ~24 μm. It should be noted that $SrTiO_3$ ceramics sintered at the same conditions usually yield grain size approximately 10 times smaller. So we found that Cr doping leads to strong increasing of the sol–gel ceramic grain size. Permittivity measurements (100 Hz to 1 MHz) and luminescence spectroscopy techniques were described in Refs. 10–12. Photoluminescence of polished specimens was excited at $\lambda = 514$ nm.

3. Results

Fig. 1 represents the temperature dependence of the dielectric constant at several selected frequencies. A value of the non-dispersive permittivity is ~300 at RT and increases on cooling due to TO1 mode softness. At $T \sim 30$ K some dispersion appears and permittivity saturates at ~8 K, reaching ~7000 (400 Hz), which is much less than for single crystals and close to ~10 000 at 5 K in a more dense (98%) $SrTiO_3$ ceramics of ~1.5 μm grain size.[4] The inset in Fig. 1 represents the tan δ frequency–temperature behavior in the region of the dielectric dispersion, which reveals relaxation character of tan δ(*T*) maximum shifting to higher temperatures with frequency. We found that the relaxation obeys Arrhenius law, $\tau = \tau_0 \exp(U/kT)$ with $\tau_0 \approx 8 \times 10^{-12}$ s and $U \approx 245$ K (21 meV). This can be connected to the Cr^{3+} charge compensation mechanism. According to,[7,13] Cr^{3+} substitutes Ti^{4+} in $SrTiO_3$ with nonlocal charge compensation due to cubic symmetry of Cr^{3+} centers. As the compensation defect, we can consider oxygen vacancies V_0 and O^- bound hole polarons, whose movement can originate dielectric relaxation. Because the activation energy of V_0 reorientations is more large (~1 eV),[14] we believe that the observed relaxation can be caused by O^- polarons motion.

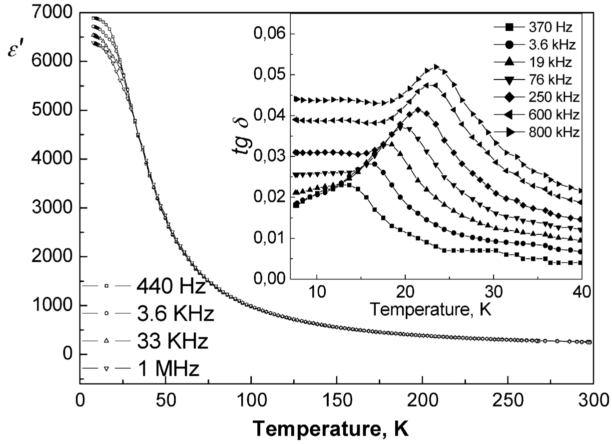

Fig. 1. Dielectric permittivity and tan δ of $SrTiO_3$:Cr (3×10^2%) sol–gel ceramics at several selected frequencies.

The emission spectrum of Cr^{3+} consists of barely resolved *R*-line doublet 12 599 and 12 601 cm^{-1} of total linewidth ~7 cm^{-1} at 10 K (inset to Fig. 2). This is very close to that for $SrTiO_3$ crystals (12597.5 and 12600.2, but with linewidth of ~1 cm^{-1}).[7,8] The *R*-line splitting originating from the splitting of the ^2E state of Cr^{3+} in the tetragonal field of antiferrodistorsive phase, is somewhat smaller than that in crystals. This implies that the tilt of the TiO_6 octahedra below the $O_h^1 - D_{4v}^{18}$ structural transition is slightly smaller in ceramics. The *R*-line broadening is obviously connected with the apparent inhomogeneity of ceramics. Shift of *R*-lines position to higher energies is also observed in $SrTiO_3$:Ca, where it increases with Ca concentration,[10] which was related to the system inhomogeneity, stresses, and reduction of TO1 mode effect on optical centre transitions.

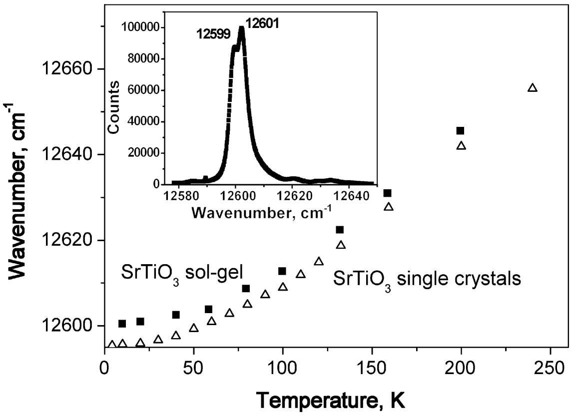

Fig. 2. The emission spectrum and average position of *R*-emission lines of Cr^{3+} in $SrTiO_3$ single crystals[1,2] and $SrTiO_3$:Cr (3×10^2%) sol–gel ceramics. Inset presents *R*-line of Cr^{3+} emission spectrum for $SrTiO_3$ sol–gel ceramics.

Fig. 2 shows the temperature dependencies of the average positions of the *R*-emission line of Cr^{3+} in $SrTiO_3$ single crystals[7,8] and sol–gel ceramics. We see that *R*-line shift in ceramics appears to be nearly the same as in crystals, both in character and magnitude (~45.3 cm^{-1} for crystals, 44.4 cm^{-1} for ceramics – from 20 to 200 K). Energy of the *R*-line increases as $\sim 1/\varepsilon'$ with rising temperature.[7,8] Since the Lyddane–Sachs–Teller relation $\varepsilon_0 \times \omega_0^2 \cong \text{const}$ is obeyed in $SrTiO_3$ crystals, we conclude that *R*-line shift of Cr^{3+} in ceramics is not proportional to the inverse effective permittivity of ceramics, but rather to that in crystals, where this shift is controlled by the TO1 mode behavior. This fact evidences that the grain bulk properties and TO1 mode behavior in $SrTiO_3$ ceramics with grain size ~24 μm are very close to those in $SrTiO_3$ quantum paraelectric crystals. This result, as well as a slightly smaller *R*-line temperature shift in ceramics, more noticeable at lowest measured temperatures, is consistent with the ideas[4–6] in which the effect of frozen grain boundary dipole moment on soft mode in the bulk of the grain bulk steeply increases on cooling. Experiments with ceramics of smaller grain size are in progress.

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