Impurity centers and host microstructure in weakly doped SrTiO$_3$:Mn crystals: New findings.

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Abstract. Electron paramagnetic resonance (EPR), optical absorption and low-frequency (100 Hz - 1 MHz) dielectric permittivity investigations on Verneuil as-grown and reduced SrTiO$_3$:Mn (0.1% at.) crystals were carried out to establish connection between the structure of Mn doping related centers and the SrTiO$_3$ dielectric properties. At room temperature the EPR spectrum of as-grown crystals evidences isotropic Mn$^{4+}$ and Mn$^{2+}$ centers. The Mn$^{2+}$/Mn$^{4+}$ ratio increases, according to the EPR spectra, by decreasing the temperature and the signals intensity of both centers strongly decreases approaching T~120 K. Such behavior is attributed to antiferromagnetic interaction in MnO and MnO$_2$ nano-clusters. Also the dielectric permittivity behavior evidences samples inhomogeneity as well as absence of pronounced dielectric relaxation in as grown crystals. In reduced crystals the Mn$^{2+}$ concentration increases and the dielectric relaxation emerges evidencing a polaronic-related nature of dipole reorientations.

1. Introduction.

The growing interest in the Mn doped SrTiO$_3$ (STO) is mainly caused by recently recognized effects achieved by Mn doping, which make this material a promising candidate for novel modern applications: e.g., the possibility of manipulation of the practical properties of ceramics STO by tailoring the grain boundaries (GB) through Mn$^{2+}$ acceptors embedding into the Ti site at the GB core was reported in [1,2]. Improved ferroelectric and pyroelectric properties of Mn-doped lead zirconate titanate thin films due to Mn$^{4+}$ ions annihilating the oxygen vacancies generated during repeated switching, forming Mn$^{4+}$ ions, were reported in [3]. Antiferromagnetic (AF) interaction in heavily Mn doped GB was observed in STO:Mn powder samples [4]. Near room temperature (RT) ferromagnetism was recently observed in Mn ion implanted STO crystals [5]. Intriguing low temperature dielectric relaxation accompanying Mn doping of STO was also found in [6]. The nature of this relaxation appears to be nowadays a subject of burning discussions: in ceramics STO grown with MnO and MnO$_2$ admixture and named STO:Mn$^{2+}$(0.1 – 5%) and STO:Mn$^{4+}$(0.1-1%) it obeys the Arrhenius law, $\tau = \tau_0 \exp(U/kT)$, with nearly the same relaxation parameters ($\tau_0 \sim 5 \times 10^{11}$s and $U \sim 30$ meV, at 350 K), which allowed to attribute it to reorientations of polaronic centers localized on defects of $\text{MnO}_2$ - $O$ type [6]. Later dielectric permittivity studies have been performed on Mn-doped ceramics STO grown with Sr deficiency with the ratio (Sr+Mn)/Ti=1 (Sr$_{1.3}$Mn$_x$TiO$_3$, SMT) and
with Ti deficiency, keeping the ratio (Ti+Mn)/Sr=1 (SrTi_{1-x}Mn_xO_3, STM) [7-9]. A pronounced relaxation-type dielectric dispersion in the temperature region 25 – 65 K and also a polar behavior were reported for SMT (x=0.005 – 0.02) ceramics. In contrast, in STM ceramics only a reduction of the dielectric permittivity, and no dielectric relaxation, was observed. Such behavior was attributed to the formation of electric dipoles and corresponding random fields due to the off-centre position of Mn^{2+} ions at the Sr^{2+} site (ionic radii 1.25Å and 1.44 Å respectively [10]) of highly polarized STO lattice.

The main goal of this work was to elucidate the connection between Mn centers, STO:Mn host structure, dielectric permittivity behavior and dielectric relaxation processes. In order to exclude effects connected with ceramic features, we performed electron paramagnetic resonance (EPR), dielectric permittivity and optical absorption studies on weakly doped as-grown and reduced STO:Mn crystals.

2. Experimental.
STO:Mn(0.1% at) brown sugar tinted crystals have been grown by Verneuil flame fusion technique with the addition of MnO to the melt. Both as-grown and reduced specimens (treated for 3 hours at 1450 K in Formier gas (94% N_2, 6% H_2) atmosphere and subsequently quenched to 300 K by dropping them into a batch of silicone oil) were analyzed. EPR measurements were carried out by using a Bruker spectrometer in the X- band (9.3 GHz) between 300 – 100 K. Dielectric permittivity was measured under ac field ~ 35 V/cm in the frequency region 100 Hz – 1 MHz with a 4192 LF Hewlett-Packard Impedance Analyzer. Thin polished <100> oriented condensers with evaporated Pt-Au electrodes were suspended in a He-flow cryostat allowing temperature cycling within 10- 300 K with a rate ± (10-50) mK/s. Optical absorption spectra measurements have been performed at 300K using conventional spectrophotometry method.

3. Results and discussion
Figure 1 presents the EPR spectrum of an as-grown STO:Mn crystal, collected at 300 K. This spectrum is practically identical to that already observed in STO:Mn crystals [11,12], containing sextets of narrow lines.

![Figure 1. EPR spectrum of as-grown SrTiO₃Mn(0.1%) crystal, collected at 300 K.](image-url)
Indeed, it exhibits the characteristic six main hyperfine lines arising from Mn$^{4+}$ (3d$^3$, S=3/2) isotropic centers with $g = 1.993 \pm 0.001$ and hyperfine constant $|A| = 73 \pm 1$ Gauss and a weaker spectrum arising from Mn$^{2+}$ (3d$^5$, S=5/2) isotropic centers with $|A| = 83 \pm 1$ Gauss and $g = 2.002 \pm 0.001$.

Figure 2 represents the temperature dependence of the EPR signal. The following feature has to be underlined: the intensity of EPR signals from both Mn$^{4+}$ and Mn$^{2+}$ centers strongly decreases and the Mn$^{2+}$/Mn$^{4+}$ ratio increases with decreasing the temperature down to $\sim 120$ K. No EPR signals have been found from anisotropic Mn centers.

Figure 3 shows the temperature dependence of the dielectric permittivity in as-grown STO:Mn(0.1%) crystals. At RT the non dispersive dielectric permittivity $\varepsilon' \sim 315$, that is practically the same as in nominally pure STO crystals (307) [13]. At 10 K, $\varepsilon'$ reaches a value of $\sim 3000$, in contrast to the value of $\sim 10 000$ observed for randomly oriented nominally pure STO crystalline samples [14]. Only at the lowest temperatures a relatively weak dielectric dispersion is observed. The inset of Fig.3 shows that the temperature dependence of the dielectric permittivity for these crystals well obeys the Barrett formula for incipient ferroelectrics [15]:

$$
\varepsilon' (T) \sim \frac{C}{T_s \coth(T_s / 2T) - \frac{T}{T_0}}.
$$

where quantum fluctuations strength $T_s = 47$ K, Curie-Weiss temperature $T_0 = 16.5$ K and $C = 91400$ K.

So, prima facie, the low-temperature dielectric permittivity in STO:Mn crystals, lower than that
observed in nominally pure STO, could be connected to a “departure” from the ferroelectric instability caused by Mn doping. But it is not our case. In agreement with [16], the reduced magnitude of $\varepsilon'$ at low temperatures can evidence system inhomogeneity, as it was considered for grainy materials (powders, ceramics, films, polycrystals, etc.) in [17].

Figure 3. Permittivity behavior in as-grown SrTiO$_3$:Mn(0.1%) crystals. The inset shows experimental points taken at 1.2 kHz and fitted by the Barrett formula with: $C = 91400$ K, $T_S = 47$ K, $T_0 = 16.5$ K.

Figure 4. Changes of EPR spectra of SrTiO$_3$:Mn(0.1%) due to reduction; $T = 300$ K.

Figure 4 shows the EPR spectra in as-grown STO:Mn crystals before and after reduction with subsequent quenching treatment. An increase of the Mn$^{2+}$ centers concentration and a decrease of Mn$^{4+}$ one are evidenced.
Figure 5. Optical density spectra for reduced (1) and as-grown (2) SrTiO$_3$:Mn(0.1\%) crystal; $T = 300\ K$.

Figure 5 presents optical absorption spectrum of an as-grown and reduced STO:Mn crystals.

The as-grown crystals evidence a pronounced absorption band at 556 nm (2.23 eV) which is known to be characteristic of the $^4A_2 \rightarrow ^4T_2$ transition of octahedral cubic Mn$^{4+}$ in STO crystals [12]. This
absorption band appears to be strongly depressed in reduced STO:Mn crystals for which, instead, an optical absorption band appears at 477 nm (2.6eV). This band has been previously observed in [12] and attributed to optical transitions of Mn$^{2+}$ - V$_0$ axial centers and/or to the $^5$E $\rightarrow$ $^5$T$_2$ transition of Mn$^{2+}$ octahedral cubic centers. Thus, also optical absorption experiments evidence that a Mn$^{4+}$ $\rightarrow$ Mn$^{2+}$ transformation takes place as due to the crystals reduction.

The real part of the dielectric permittivity doesn’t evidence strong changes with the temperature in reduced specimens. The dispersion appearing at the lowest temperatures (Fig. 6) can be mainly ascribable dielectric losses (Inset of Fig. 6).

\[
\tau_0 = 1.7 \times 10^{-12} \text{ s} \\
U = 37 \text{ meV (440 K)}
\]

Figure 7. Arrhenius plot for reduced SrTiO$_3$:Mn(0.1%) crystals.

This dispersion reveals clear characteristics of dielectric relaxation when positions of tan$\delta$(T) maximums shifts to higher temperatures with monitoring ac electric field frequency. Figure 7 reveals that temperature dependence of the relaxation time good obeys the Arrhenius law:

\[
\tau = \tau_0 \exp \left( \frac{U}{kT} \right)
\]

with magnitudes of reorientation barrier energy $U$ = 37 meV (440K) and high temperature relaxation time $\tau_0 = 1.7 \times 10^{-12}$ s ($\tau = \omega^{-1}$ at the temperature of tan$\delta$ temperature maximum at given $\omega$). Such magnitudes are close to that obtained in [6] evidencing rather polaronic related character of dielectric relaxation emerged in reduced weakly doped STO:Mn crystals.

Let us now discuss the main characteristics of the Mn centers, evidenced by EPR and optical absorption spectra. At first, at RT our STO:Mn crystals evidence Mn$^{4+}$ and Mn$^{2+}$ centers are both isotropic and substitute Ti in octahedral positions. This experimental evidence is not in contrast with the temperature behavior of the EPR signals for T >120 K, suggesting a Mn$^{4+}$ $\rightarrow$ Mn$^{2+}$ reduction.

But, the most intriguing feature observed in our crystals is the “non-paramagnetic” temperature behavior of the EPR spectra intensity. To our knowledge, the temperature dependence of the EPR spectra in STO:Mn compounds has been studied only on ceramic and powder specimens [4, 18, 19]. In [4], where EPR and static magnetization measurements have been performed on STO:Mn(1-3% mol.)
powders, it was found that the signal from octahedral Mn\textsuperscript{2+} (without V\textsubscript{0}) progressively decreases with decreasing the temperature and vanishes at ~ 120 K. Such behavior was connected with an inhomogeneous distribution of Mn centers and with the resulting presence of heavily doped GB so AF coupling between adjacent Mn\textsuperscript{2+} centers and a consequent AF ordering within heavily Mn doped GB develops approaching 120 K. What observed for our STO:Mn crystals is very near, at least for the Mn\textsuperscript{2+} ions behavior, to the EPR data reported in [4] and it is, instead, quite different from what obtained in [18,19]. Indeed, in [18], where polycrystalline STO:Mn(0.01%) ceramics with ~ 5 -10 µ of grain size have been investigated, the EPR spectra at RT evidenced the coexistence of Mn\textsuperscript{4+}, Mn\textsuperscript{3+}, Mn\textsuperscript{2+} and Mn\textsuperscript{2+}-V\textsubscript{0} centers. The temperature lowering was then accompanied by a slow enhancement of the Mn\textsuperscript{4+} signal and by a decrease and broadening of the Mn\textsuperscript{2+} EPR signal intensity. This last effect was attributed to Mn\textsuperscript{2+} → Mn\textsuperscript{3+} + e\textsuperscript{-} conversion when approaching the lattice antiferrodistorsive phase transition, at T\textsubscript{C} = 106 K. The nature of such conversion is still unclear. Only on the basis of the estimated value of the activation energy (U ~ 0.065 eV ), it was suggested that “this conversion has an activation energy corresponding to one of the TO soft modes” and that the charge redistribution among the Mn centers “is triggered by changes in soft phonon modes”. At last, let us consider the recent EPR investigations reported in [19] for STO: Mn ceramics prepared with a deficiency of Sr ions, i.e. Sr\textsubscript{x}Mn\textsubscript{1-x}TaO\textsubscript{3} with x = 0.005 and 0.02, for which a pronounced low-temperature dielectric relaxation was previously reported in [8]. The observed EPR spectrum, a sextet of hyperfine lines with spin Hamiltonian parameters \( g = 2.0032 \pm 0.0002 \) and \( A = 82.8 \pm 0.2 \), has been attributed to Mn\textsuperscript{2+} off-centers ions substituting in the Sr position. The unexpected broadening of these lines at T < 130 K was attributed to motional broadening due to Mn\textsuperscript{2+} off-centers jumping between equivalent off-center positions, with activation energy U = 86 meV (1000 K) and relaxation pre-factor \( \tau_0 = 1.0 \times 10^{-13} \) s and \( \tau_0 = 1.8 \times 10^{-14} \) s for x = 0.005 and 0.02 respectively.

4. Conclusions
EPR and optical absorption experiments performed on Verneuil grown weakly concentrated STO:Mn(0.1%) crystals have revealed only isotropic Mn\textsuperscript{4+} and Mn\textsuperscript{2+} octahedral centers. On the basis of the obtained g-factors, different from those reported in [19], no evidences of Mn\textsuperscript{2+} centers substituting in Sr sites have been observed. The most Mn impurity centers, both Mn\textsuperscript{4+}and Mn\textsuperscript{2+}, results to be inhomogeneously distributed in the crystal, forming Mn enriched regions containing MnO and MnO\textsubscript{2} clusters, with AF coupling between Mn centers as indeed suggested by the strong decrease of the EPR spectra intensity of both Mn\textsuperscript{4+} and Mn\textsuperscript{2+}, when cooling the crystal and approaching ~ 120 K (Neele temperature of MnO [21,21]). This is also associated to the Mn\textsuperscript{4+} → Mn\textsuperscript{2+} centers reduction. Opposite to the ceramics, the as-grown crystals have not evidenced any pronounced low temperature dielectric relaxation and neither the features reported in [7-9,18,19]. Dielectric relaxation only occurs in reduced and quenched specimens in which Mn\textsuperscript{2+} concentration is higher than in as-grown samples, as demonstrated by EPR and optical absorption experiments. Dielectric relaxation parameters appeared to be very close to that reported in [6], evidencing polaronic type reorientations. The obtained results are in good agreement with detailed dielectric permittivity, micro-Raman and IR reflectivity studies carried out on the same weakly concentrated STO:Mn crystals and on ceramics [16]. From these results [16], the size of Mn oxide clusters can be estimated as nanoscaled one.

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