Direct Evidence for Off-Centering of Mn Impurity in SrTiO₃

A. I. Lebedev[a],*, I. A. Sluchinskaya[a], A. Erko[b], and V. F. Kozlovskii[c]

[a] Faculty of Physics, Moscow State University, Moscow, 119991 Russia
* e-mail: swan@scon155.phys.msu.ru
[b] BESSY GmbH, 12489 Berlin, Germany
[c] Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia
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Mn-doped SrTiO₃ samples (3% Mn) with different deviations from stoichiometry have been investigated using XAFS spectroscopy. It was shown the under various preparation conditions manganese atoms can substitute A and B sites of the perovskite structure and are in them in different charge states. Impurity Mn^{4+} ions that substitute Ti sites occupy on-center position in the lattice, whereas Mn^{2+} ions that substitute Sr sites are off-center and are displaced from the lattice sites by a distance of 0.32 Å.

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It has been commonly accepted for a long time that manganese atoms in doped strontium titanate replace titanium atoms and are in the Mn^{4+} charge state [1]. The electron spin resonance (ESR) studies of the samples annealed in a reducing atmosphere revealed several new paramagnetic centers, which were attributed to the Mn^{2+} and Mn^{3+} ions located in titanium sites and their complexes with oxygen vacancies [2].

Recently, Lemanov et al. [3] observed strong dielectric relaxations at $T \leq 77$ K and the displacement of the maximum of the dielectric constant from 4.2 K to ~40 K in SrTiO₃(Mn). The authors explained the observed relaxation by the reorientation of dipoles associated with "polaron" defects of the $\{Mn_{Ti}^{2+}-O^-\}$ and $\{O^--Mn_{Ti}^{2+}-O^-\}$ types [3, 4] and the reorientation of the dipole moments of off-center Mn_{Ti}^{4+} ions [4]. The authors believe that the observed phenomena are not attributed to the appearance of ferroelectricity in crystals.

More recently, Tkach et al. [5−9] investigated the effect of the intentional deviation of the composition from stoichiometry, as well as the change in the temperature of annealing and the atmosphere in which it was performed, on the properties of the SrTiO₃(Mn) samples. The results were explained by the possibility of the appearance of Mn impurity atoms both at Sr (A) sites and Ti (B) sites under various preparation conditions. The samples in which, in the author's opinion, Mn is located at Sr sites and is in the Mn^{2+} charge state exhibited all unusual dielectric phenomena observed in [3, 4]. In the samples in which Mn atoms replace Ti atoms, dielectric relaxation is absent and the maximum dielectric constant (at 4.2 K) decreases with an increasing manganese concentration [5]. To explain dielectric relaxations in SrTiO₃(Mn), Tkach et al. [7] proposed a new hypothesis that the Mn^{2+} ions at Sr sites are off-center. The freezing of hopping of these impurity ions between the potential minima at low temperatures is the cause of relaxation phenomena. The observation of dielectric loops at low temperatures [7] made it possible to assume that a relaxor-type ferroelectric phase transition occurs in crystals, in which manganese atoms occupy the A sites. The effect of the annealing atmosphere on the dielectric properties and ESR spectra was analyzed in [8], where a correlation was found between the dielectric relaxation magnitude and the concentration of the paramagnetic centers with $g = 2.004$ attributed to the Mn_{Sr}^{2+} ions.

The strong broadening of the ESR lines of the Mn_{Sr}^{2+} ions with decreasing temperature from 300 to 120 K was considered as an evidence for the off-centering of these ions [10].

Interpreting the results of their investigations of the temperature dependence of the intensity of ESR lines in SrTiO₃(Mn) [11], the third group of the authors attributed the strong weakening of these lines with decreasing temperature to a transition of the second-phase nanoprecipitates of MnO or MnO_2 in these samples to a magnetically ordered state. Discussing the results of the investigations of dielectric relaxations in ceramic samples and single crystals of SrTiO₃(Mn) [12], the authors agreed with the interpretation proposed in [3] for relaxations in lightly doped (~0.1% Mn) samples and attributed relaxations in heavily doped (1−3% Mn) samples to various manifestations of inhomogeneity.
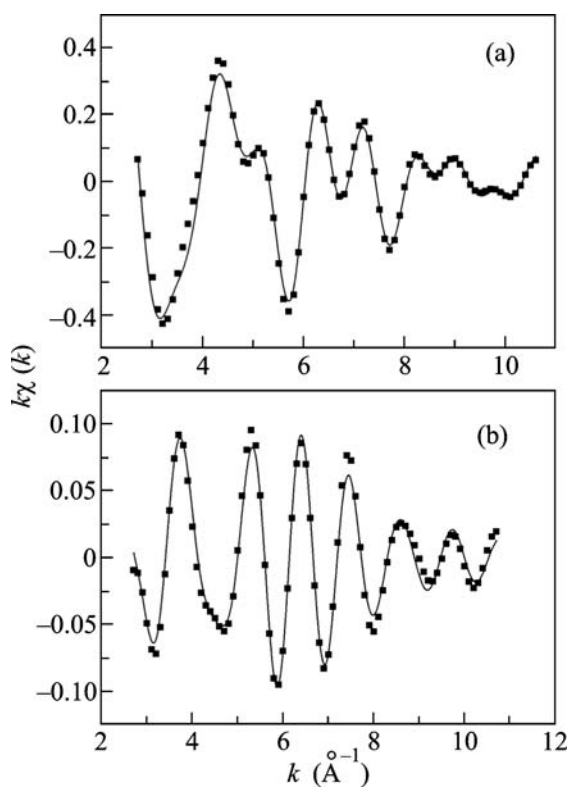
Fig. 1. EXAFS spectra recorded at the Mn K absorption edge for (a) the $Sr(Ti_{0.97}Mn_{0.03})O_3$ sample annealed at 1100°C and (b) the $(Sr_{0.97}Mn_{0.03})TiO_3$ sample annealed at 1500°C. The lines are the best theoretical approximations of the experimental data shown by points.

The impossibility of unambiguous determination of the structural position and charge state of the Mn impurity from ESR data and the inconsistency of the results and interpretations of dielectric anomalies in $SrTiO_3(Mn)$ stimulated us to use direct methods of the local structure analysis. To determine the structural position of the Mn impurity and its charge state directly, the XAFS spectroscopy method was used in this work. This method is a powerful modern method providing detailed information on the local structure in perovskite crystals (see [13] and references cited therein).

The samples with nominal compositions of $(Sr_{0.97}Mn_{0.03})TiO_3$ and $Sr(Ti_{0.97}Mn_{0.03})O_3$ were prepared by the solid-state synthesis method. The starting components were $SrCO_3$, nanocrystalline TiO_2 that was obtained by hydrolysis of tetrapropyl orthotitanate and was dried at 500°C, and $Mn(CH_3COO)_2 \cdot 4H_2O$. The components were weighted in proper proportions, grinded in acetone, and annealed in air at 1100°C for 8 h. The resulting powders were repeatedly grinded and annealed under the same conditions. Some samples were additionally annealed in air at 1500°C for 1 h.

The extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectra were recorded in the fluorescence mode on KMS-2 station of the BESSY synchrotron radiation source (an electron energy of 1.7 GeV, a maximum current of 290 mA) at the Mn K absorption edge (6.539 keV) at 300 K. The radiation was monochromatized by a double-crystal $Si_{1-x}Ge_x$ monochromator with a (111) orientation. The intensity of the radiation incident on a sample was measured by an ionization chamber and the intensity of the fluorescence radiation was measured by a RÖNTEC silicon drift detector operating in the energy dispersion regime. Five or six spectra were recorded for each sample. Then, these spectra were independently processed and the resulting fine-structure spectra were averaged. The EXAFS spectra were processed in the conventional way [14] using the models with the on-center and off-center positions of an Mn impurity at A and B sites.

Figure 1 shows the EXAFS spectra for the $Sr(Ti_{0.97}Mn_{0.03})O_3$ sample annealed at 1100°C and the $(Sr_{0.97}Mn_{0.03})TiO_3$ sample annealed at 1500°C. These samples were taken to investigate the local environment of the Mn impurity because their preparation method chosen according to the data reported in [6] implies that the manganese impurity atoms in these samples occupy different sites of the $SrTiO_3$ lattice and are in different charge states at these sites.

The data analysis shows that the EXAFS spectra for the $Sr(Ti_{0.97}Mn_{0.03})O_3$ sample annealed at 1100°C completely correspond to the model in which manganese atoms replace titanium atoms and are in on-center positions (see the table). To obtain a good agreement between the experimental and calculated spectra (see Fig. 1a), it is necessary to take into account two multiple-scattering paths: Mn–O–O–Mn and Mn–Ti–O–Mn.

Analysis of the EXAFS spectra for the $(Sr_{0.97}Mn_{0.03})TiO_3$ sample annealed at 1500°C is more complicated. The experimental spectra cannot be described in both the model with a Mn atom at a titanium site and the model with a Mn atom at a strontium site. Good agreement between the experimental and calculated EXAFS spectra (see Fig. 1b) was obtained only in the model with the off-center displacement of the Mn atom from the Sr site. Since the main contribution to the EXAFS signal in this sample comes from the atoms in the second shell, the off-centering of the atom is manifested in the form of two strongly different Mn–Ti distances (3.095 and 3.467 Å, see table). The contribution from the oxygen atoms in the first shell is characterized by a large Debye–Waller factor, which indicates a large dispersion of Mn–O distances in this shell. Note that the same manifestations of the off-centering were also observed for Pb atoms in $SrTiO_3$ and $BaTiO_3$ [13].

Structure parameters obtained from the processing of the EXAFS spectra of two investigated samples (R_i is the distance to the ith coordination sphere and σ_i^2 is the Debye–Waller factor for this sphere)

Sample	Shell	R_i, Å	σ_i^2, Å^2	Scattering atom
Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ annealed at 1100°C	1	1.916	0.0016	O
	2	3.313	0.0005	Sr
	3	3.67; 3.875*	−0.006; 0.014*	Ti
(Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ annealed at 1500°C	1	2.32; 2.86	0.040; 0.021	O
	2	3.095; 3.467	0.007; 0.008	Ti
	3	3.84	0.014	Sr

* The first value corresponds to the single scattering channel and the second value corresponds to the strongest multiple scattering channel.

From two Mn–Ti distances obtained from the analysis of the EXAFS data, the displacement of the Mn atom from the A site and the "local" lattice parameter were determined. Under the assumption that the Mn atom of the lattice is shifted along the tetragonal axis and that the other atoms remain at their places, the displacement of the Mn atom from the A lattice site was estimated to be ~0.32 Å. A small deviation of the local lattice parameter (3.78 Å) from the actual parameter (3.90 Å) obtained from the X-ray diffraction can be explained by the relaxation of the lattice around impurity manganese atoms whose ion radius is ~0.35 Å smaller than that of substituting strontium atoms.

Our data are in agreement with the theoretical calculations by Kvyatkovskii [15], who predicted the off-centering of the Mn^{2+} ion at the A sites with a displacement of ~0.4 Å and the stable on-center position of the Mn^{4+} ion at the B sites.

The XANES spectra for three samples are shown in Fig. 2. Their comparison shows that the absorption edges in the spectra of the (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample annealed at 1500°C and the Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ sample annealed at 1100°C are shifted from each other by ~7 eV. This directly indicates that in these two samples the Mn atoms, which occupy two different sites of the lattice, are in two different charge states. The absorption edge for the sample with the impurity at the A site (according to the EXAFS data) is lower in energy than the absorption edge for the sample in which the impurity is at the B site. This relation indicates that the charge state of the atom at the A site is lower. A comparison of our spectra with the spectra reported in [16] for the Mn^{2+} ions in Mn(CH$_3$COO)$_2$ and the Mn^{4+} ions in MnO$_2$ indicates that the Mn ions at the A and B sites in SrTiO$_3$ are in the charge states +2 and +4, respectively.

From the comparison of the XANES spectra for the (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample annealed at 1100°C (see line 3 in Fig. 2) with the spectra of the samples for which the EXAFS analysis was performed (see lines 1 and 2 in Fig. 2) it follows that spectrum 3 is the super-position of spectra 1 and 2. This means that Mn in this sample is present in both charge states. It is seen that most Mn atoms in this sample are at the B site despite the intentional deviation from stoichiometry in order to incorporate the impurity into the A site.

Our data on the relative fraction of Mn at the A and B sites in the (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample annealed at 1100°C are in agreement with the X-ray diffraction data. According to the XANES and EXAFS data,[1] the Mn atoms in this sample are predominantly at the B sites; therefore, an excess of titanium dioxide should appear in order to maintain stoichiometry in the sample. The TiO$_2$ phase precipitates are really observed in small amounts in X-ray diffraction patterns. The X-ray diffraction pattern of this sample changes strongly after its annealing at 1500°C: the second TiO$_2$ phase disappears completely and new weak lines of the second MnTiO$_3$ phase appear. This indicates that an increase in the annealing temperature leads to the transition of manganese impurity from the B site to the A site, which is confirmed by the EXAFS data. According to the X-ray data, the Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ sample annealed at 1100°C is single-phase; and so the annealing at this temperature is sufficient for the definite incorporation of the Mn impurity into the B site.

The precise measurement of the lattice parameter shows that the lattice parameter in the (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample annealed at 1500°C is 0.0008 Å larger than that in the sample of the same nominal composition annealed at 1100°C. This is in qualitative agreement with the data reported in [5] and our assumption of the transition of impurity atoms from the B site to the A site.

Note that a small amount of the second MnTiO$_3$ phase manifested in X-ray diffraction patterns does not affect the analysis of the EXAFS spectra, because their Fourier filtration did not reveal a noticeable peak

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[1] The data analysis of the EXAFS spectra for this sample requires a more complex model. Its analysis in the framework of simplified model gives the numerical parameters close to those obtained for the Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ sample annealed at 1100°C.
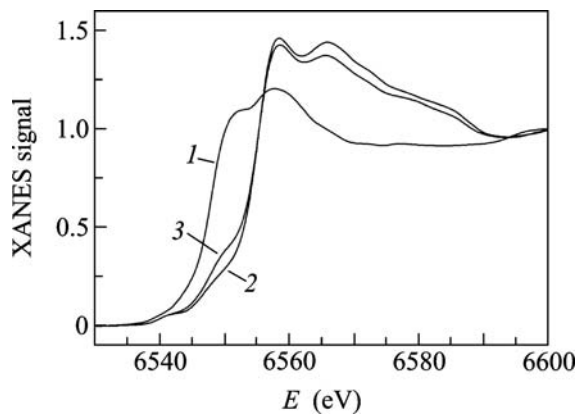
Fig. 2. XANES spectra for (*1*) the $(Sr_{0.97}Mn_{0.03})TiO_3$ sample annealed at 1500°C, (*2*) the $Sr(Ti_{0.97}Mn_{0.03})O_3$ sample annealed at 1100°C, and (*3*) the $(Sr_{0.97}Mn_{0.03})TiO_3$ sample annealed at 1100°C.

from Mn–O pairs with an interatomic distance of about 2 Å. The presence of the TiO_2 phase should not influence the EXAFS spectra recorded at the Mn absorption edge.

Our results contradict the hypothesis of the existence of MnO or MnO_2 precipitates in the $SrTiO_3(Mn)$ samples proposed in [11, 12]. Let this hypothesis be valid. Then, as follows from the almost complete weakening of the ESR line with $g = 2.004$ when cooling the samples (which was attributed by authors to the transition of the indicated phases into an antiferromagnetic state), manganese incorporated into the samples should be almost entirely in these precipitates. However, the EXAFS spectra for our similar ceramic samples are qualitatively different from the EXAFS spectra of MnO and MnO_2. In our opinion, Mn atoms in the $SrTiO_3(Mn)$ ceramic samples are inside the ceramic grains rather than in the precipitates at the grain boundaries.

Thus, the analysis of XANES and EXAFS spectra in $SrTiO_3(Mn)$ indicates that under different preparation conditions, Mn atoms can occupy the *A* and *B* sites of the perovskite lattice and are present in them in different charge states. The redistribution of impurity atoms between two sites can be controlled by varying the annealing temperature and creating the intentional deviation of the composition from stoichiometry. It has been shown that the impurity Mn atoms replacing Ti atoms are in the charge state +4 and occupy the site positions in the lattice, whereas the Mn atoms occupying Sr sites are in the charge state +2, are off-center, and are shifted from the lattice sites by a distance of about 0.32 Å. These results show that unusual phenomena in the $SrTiO_3(Mn)$ samples

should be analyzed using the model with the off-center Mn_{Sr}^{2+} ion. The off-center ions can lead either to the appearance of polar regions or to the appearance of the ferroelectric long-range order; both of these states can explain the strong decrease in the dielectric constant observed in the samples at 4.2 K. In addition, this work has demonstrated that analysis of the XANES structure can be used to quantitatively determine the fraction of manganese atoms occupying the *A* and *B* sites in the lattice.

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