Local environment and oxidation state of Mn impurity in SrTiO$_3$ determined from XAFS data

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The local environment and oxidation state of Mn impurity in strontium titanate doped with 3% Mn were studied by X-ray absorption fine structure spectroscopy. The influence of the preparation conditions on the incorporation of the impurity into the A and B sites was studied. It was established that Mn ions substituting for Ti are in the Mn$^{4+}$ oxidation state and on-center. Mn ions substituting for Sr are in the Mn$^{2+}$ oxidation state, are off-center and displaced from the lattice sites by $\sim$0.32 Å. It was demonstrated that studies of the X-ray absorption near-edge structure can be used to determine the concentration ratio of Mn atoms located at the A and B sites.

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It has long been considered that upon doping of SrTiO$_3$ with manganese, the impurity atoms substitute for Ti atoms and are in the Mn$^{4+}$ oxidation state. Annealing of the samples in a reducing atmosphere can convert the Mn ions to a lower oxidation state. Recently, Lemanov et al. revealed the strong dielectric relaxations in SrTiO$_3$ (Mn) at $T < 77$ K. They explained the observed phenomena by reorientation of the dipoles of “polaron” defects and off-center Mn$^{4+}$ ions; however, they did not associate these phenomena with the appearance of ferroelectricity in strontium titanate. Later, Tkach et al. found the preparation conditions in which the impurity Mn atoms can substitute for Sr atoms in the Mn$^{2+}$ oxidation state. Unusual dielectric phenomena were observed in all such samples. In contrast, in samples where the Mn atoms were at the Ti sites, these effects were absent. In order to explain the dielectric properties of Mn-doped samples, it was suggested that Mn$^{2+}$ ions are off-center when substituting for the Sr atoms, and the observed relaxation phenomena are due to the slowing down of their jumps between the potential minima when decreasing temperature. This supposition was confirmed by EPR studies in Ref. [6].

The aim of this work was to determine the structural position and oxidation state of the Mn impurity in SrTiO$_3$ samples prepared in various conditions using X-ray absorption fine structure (XAFS) spectroscopy.

The samples studied in this work had nominal compositions of (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ and Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ and were prepared by the solid-state synthesis method. The starting components were SrCO$_3$, nanocrystalline TiO$_2$ obtained by hydrolysis of tetraketylortititanate and dried at 500°C, and Mn(CH$_3$COO)$_2$·4H$_2$O. The components were weighed in the required proportions, ground in acetone until the mixture became completely dry, and annealed in air at 1100°C for 8 h. The obtained powders were ground once again and annealed under the same conditions. Some of the samples were additionally annealed in air at 1350°C for 2.5 h and at 1500°C for 1 h. It should be noted that a soluble manganese salt and its impregnation into a mixture of SrCO$_3$ and nanocrystalline TiO$_2$ results in a partial reaction of the salt with SrCO$_3$ and to the adsorption of the manganese and strontium acetates on the TiO$_2$ nanoparticles with a large surface area. Ultimately, this ensured a uniform distribution of the impurity in the obtained samples.

Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra were recorded in X-ray fluorescence mode on the KMC-2 station of the BESSY synchrotron radiation source in the vicinity of the Mn K-edge (6.539 keV) at 300 K. EXAFS spectra were processed in a conventional way. The details of the experiment can be found in Ref. [8].

The EXAFS spectra for two samples, Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ annealed at 1100°C and (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ annealed at 1500°C, are shown in Fig. [1]. An analysis of the EXAFS spectra for the Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ sample shows that the obtained spectra are completely consistent with the model in which the Mn atoms substitute for the Ti atoms and are on-center (see Table [9]). For the (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample, a good agreement between the experimental and calculated EXAFS spectra (Fig. [1]b)) can be obtained only in the model with an off-center Mn atom displaced from the Sr site, which manifests in the appearance of two Mn–Ti distances (3.095 and 3.467 Å, see Table [9]). The displacement of the Mn atom from the A site estimated from the obtained Mn–Ti distances is $\sim$0.32 Å. Our results on the on-center position of the Mn$^{4+}$ ion at the Ti site and the off-center position of the Mn$^{2+}$ ion at the Sr site agree with the results of the theoretical calculations by Kvyatkovskii.

The XANES spectra for five SrTiO$_3$(Mn) samples and two reference compounds (Mn(CH$_3$COO)$_2$·4H$_2$O and MnO$_2$) are shown in Fig. [2]. A comparison of them shows that the absorption edges in the spectra of the (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample annealed at 1500°C (curve 1) and Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ sample annealed at 1100°C (curve 4) are shifted with respect to one another by $\sim$7 eV. It is widely accepted that the oxidation state
TABLE I. Structural parameters obtained from the analysis of the EXAFS spectra of two studied samples ($R_i$ is the distance to the $i$th shell, and $\sigma^2_i$ is the Debye-Waller factor for this shell).

| Sample                                      | Shell | $R_i$ (Å) | $\sigma^2_i$ (Å²) | Atom       |
|---------------------------------------------|-------|-----------|-------------------|------------|
| Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$            | 1     | 1.914     | 0.0012            | O          |
| annealed at 1100 °C                         | 2     | 3.328     | 0.0015            | Sr         |
| (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$             | 3     | 3.895     | 0.0061*           | Ti         |
| annealed at 1100 °C                         | 1     | 2.32; 2.86| 0.040; 0.021      | O          |
| Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$             | 3     | 3.84      | 0.014             | Sr         |

Note: The values for a single channel that takes into account the focusing effect (double and triple scattering paths of multiple scattering).

FIG. 1. EXAFS spectra of two SrTiO$_3$(Mn) samples recorded at the Mn K-edge: (a) Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ sample annealed at 1100 °C; (b) (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample annealed at 1500 °C. The points represent the experimental data; the lines are their best theoretical fits.

FIG. 2. (Color online) XANES spectra of five SrTiO$_3$(Mn) samples and two reference compounds of divalent and tetravalent manganese: (1) (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample annealed at 1500 °C; (2) (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample annealed at 1350 °C; (3) (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ sample annealed at 1100 °C; (4) Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ sample annealed at 1100 °C; (5) Sr(Ti$_{0.97}$Mn$_{0.03}$)O$_3$ sample annealed at 1500 °C; (6) Mn(CH$_3$COO)$_2$·4H$_2$O; (7) MnO$_2$.

The position of an atom in a crystal can be determined from the position of the steepest region on the absorption edge of the atom in the XANES spectra, so the observed shift of the absorption edge directly indicates that in the above two samples the Mn atoms, located (according to the EXAFS data) at two different sites of the lattice, are in two different oxidation states. By comparing our spectra with those of the reference compounds, one may conclude that in SrTiO$_3$ the Mn ions located at the $A$ sites are in +2 oxidation state, and the Mn ions located at the $B$ sites are in +4 oxidation state. Some difference in the shape of the absorption edge of the samples, in which the Mn ions are in +4 oxidation state, and of the MnO$_2$ reference compound is due to the fact that the position and the shape of the absorption edge in XANES spectra are determined not only by the oxidation state of the atom, but also by the band structure and crystal structure of the sample under investigation. At room temperature, MnO$_2$ is a metal with the rutile structure, whereas the studied samples are dielectrics with the cubic perovskite structure. The weak pre-edge structure observed in all the samples is due to forbidden optical transitions from the 1$s$ level of the Mn atom to the conduction band (i.e., it is also determined by the band structure).

From a comparison of XANES spectra of the samples with a nominal composition of (Sr$_{0.97}$Mn$_{0.03}$)TiO$_3$ annealed at 1350 °C (curve 2 in Fig. 2) and 1100 °C (curve 3 in Fig. 2) and the spectra of the samples for which the EXAFS analysis was performed (curves 1 and 4 in Fig. 2), it follows that the spectra 2 and 3 can be regarded as
superposition the of spectra 1 and 4. This means that in these samples, Mn is at both lattice sites and in both oxidation states. From these data it follows that in the samples with a deliberate deviation from Sr/Ti stoichiometry toward the Sr deficit (the \((\text{Sr}_{0.97}\text{Mn}_{0.03})\text{TiO}_3\) nominal composition), an increase in the temperature of the final annealing results in a systematic increase in the concentration of manganese in +2 oxidation state at the \(A\) sites. Indeed, in the sample annealed at 1100°C (curve 3 in Fig. 2), the majority of Mn atoms are at the \(B\) sites despite the deliberate deviation of the sample composition from stoichiometry with the aim of incorporating the impurity into the \(A\) site. The thermal treatment of this sample at 1500°C transfers the impurity Mn atoms from the Ti sites to the Sr sites, in which their oxidation state is +2. As for the samples with a deliberate deviation from stoichiometry toward the Ti deficit (the \(\text{Sr(Ti}_{0.97}\text{Mn}_{0.03})\text{O}_3\) nominal composition), an increase in the temperature of the final annealing results in an increase in the Mn concentration at the \(B\) sites in +4 oxidation state (curves 4 and 5).

In summary, the studies of XANES and EXAFS spectra of SrTiO\(_3\)(Mn) have shown that, depending on the preparation conditions, Mn atoms can be incorporated into the \(A\) and \(B\) sites of the perovskite structure and stay in them in different oxidation states. The redistribution of the impurity atoms between two sites can be controlled by the annealing temperature and a deliberate deviation of the sample composition from stoichiometry. It was established that the impurity Mn atoms substituting for Ti atoms occupy the on-center positions in the lattice and are in +4 oxidation state, whereas the Mn atoms substituting for Sr atoms are off-center, displaced from the lattice sites by \(\sim 0.32\) Å, and are in +2 oxidation state. Our direct data confirm the supposition\(^5,6\) about the possible incorporation of the manganese impurity into the \(A\) sites. It was demonstrated that studies of the XANES structure can be used to determine the concentration ratio of Mn atoms occupying different crystallographic positions in the lattice.

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