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Local Environment and Oxidation State of a Mn Impurity in $SrTiO_3$ Determined from XAFS Data

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Abstract—The local environment and oxidation state of a Mn impurity in strontium titanate doped with 3% Mn were studied by X-ray absorption fine structure spectroscopy. The effect of the synthesis conditions on the incorporation of the impurity into *A* and *B* sites was studied. It was established that Mn ions substituting for Ti are in the Mn^{4+} oxidation state and are on-center. Mn ions substituting for Sr are in the Mn^{2+} oxidation state and off-center, and are displaced from the lattice site by 0.32 Å. It is shown that studies of the X-ray absorption near the edge structure can be used to determine the ratio of Mn atoms incorporated into *A* and *B* sites in the lattice.

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INTRODUCTION

It was long considered that upon the doping of $SrTiO_3$ with manganese, the impurity atoms substitute for the Ti atoms and are in the Mn^{4+} oxidation state [1]. Annealing of samples in a reduction atmosphere can move the Mn ions to a lower valence state [2]. Recently, Lemanov et al. [3, 4] found strong dielectric relaxation in $SrTiO_3$(Mn) at $T < 77$ K. They explained the observed phenomena as reorientation of the dipoles of the "polaron" defects and dipole moments of off-center Mn_{Ti}^{4+} ions; however, they did not relate them to the appearance of ferroelectricity in the crystal. Tkach et al. [5] later found the conditions for impurity Mn atoms to substitute for Sr atoms in the Mn^{2+} oxidation state. Unusual dielectric phenomena were observed in all such samples. In samples where the Mn atoms were found in Ti sites, these effects were absent. To explain the dielectric properties of samples doped with Mn, the authors assumed that Mn^{2+} ions are off-center when substituting for the Sr sites and the observed relaxation phenomena are due to the slowing down of the jumps between potential minima upon a decrease in temperature [6]. This assumption was confirmed by analyzing the EPR spectrum in [7].

This aim of this work was the X-ray absorption fine structure (XAFS) determination of the structural position and oxidation state of impurity Mn atoms in $SrTiO_3$ samples prepared in different ways.

EXPERIMENTAL

The studied samples had nominal composition $(Sr_{0.97}Mn_{0.03})TiO_3$ and $Sr(Ti_{0.97}Mn_{0.03})O_3$, and were prepared by solid-phase synthesis. The initial components were $SrCO_3$, nanocrystalline TiO_2 obtained by hydrolysis of tetrapropylortotitanate and dried at 500°C, and $Mn(CH_3COO)_2 \cdot 4H_2O$. The components were weighed in the required proportions, ground in an acetone layer until the mixture was completely dry, and annealed in air at 1100°C for 8 h. The obtained powders were once again ground 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 the use of the soluble manganese salt and its impregnation in the mixture of $SrCO_3$ and mamocrystalline TiO_2 led to the partial interaction of the salt with $SrCO_3$ and the adsorption of the manganese and strontium acetates on the developed surface of the TiO_2 nanoparticles. In the end, this ensured the 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 by X-ray fluorescence on the KMC-2 station of the BESSY synchrotron radiation source in the vicinity of the *K*-edge of Mn absorption (6.539 keV) at 300 K. EXAFS spectra were processed conventionally. The experimental methods are described in more detail in [8].

EXAFS spectra are shown in Fig. 1 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. An analysis of the EXAFS spectra for the $Sr(Ti_{0.97}Mn_{0.03})O_3$ sample shows that the spectra correspond completely to the model in which the Mn atoms substitute for the Ti atoms and are on-center (see table). For the $(Sr_{0.97}Mn_{0.03})TiO_3$ sample, good agreement of the experimental and calculated EXAFS spectra (Fig. 1b)

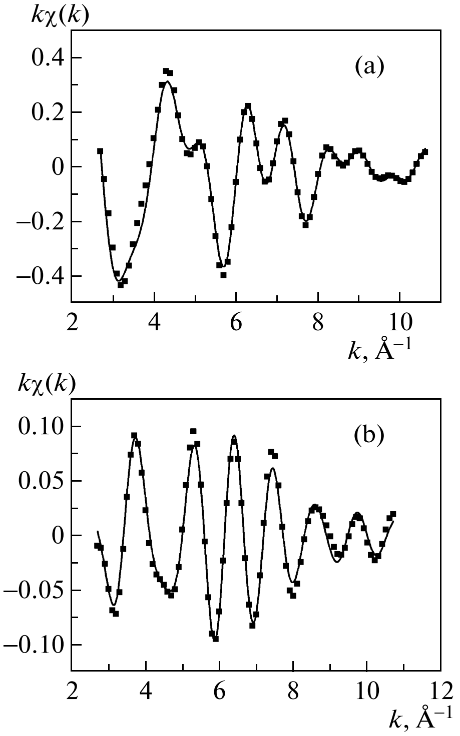

Fig. 1. EXAFS spectra of two $SrTiO_3$(Mn) samples recorded at the *K*-edge of Mn absorption: (a) $Sr(Ti_{0.97}Mn_{0.03})O_3$ sample annealed at 1100°C; (b) $(Sr_{0.97}Mn_{0.03})TiO_3$ sample annealed at 1500°C. The points represent the experimental data; the lines represent their best theoretical approximation.

is obtained only in the model with the off-center shift of the Mn atom from the Sr site. This is revealed as two Mn–Ti distances (3.095 and 3.467 Å, see table). The shift of the Mn atom from the *A* site was estimated from the Mn–Ti distances (~0.32 Å). Our data on the on-center position of the Mn^{4+} ion upon its substituting for titanium and the off-center position of the Mn^{2+} ion upon its substituting for strontium agree with the results from the theoretical calculations of Kvyatkovskii [9].

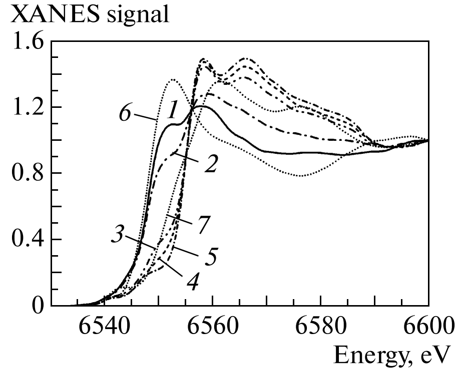

Fig. 2. XANES spectra of the $SrTiO_3$(Mn) samples and reference compounds of two- and four-valence manganese: (*1*) $(Sr_{0.97}Mn_{0.03})TiO_3$ sample annealed at 1500°C; (*2*) $(Sr_{0.97}Mn_{0.03})TiO_3$ sample annealed at 1350°C; (*3*) $(Sr_{0.97}Mn_{0.03})TiO_3$ sample annealed at 1100°C; (*4*) $Sr(Ti_{0.97}Mn_{0.03})O_3$ sample annealed at 1100°C; (*5*) $Sr(Ti_{0.97}Mn_{0.03})O_3$ sample annealed at 1500°C; (*6*) $Mn(CH_3COO)_2 \cdot 4H_2O$, (*7*) MnO_2.

The XANES spectra for five $SrTiO_3$(Mn) samples and two reference samples ($Mn(CH_3COO)_2 \cdot 4H_2O$ and MnO_2) are shown in Fig. 2. A comparison of them shows that the edges of absorption 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 displaced with respect to one another by about ~7 eV. It is conventionally thought that the oxidation state of an atom in the crystal can be determined from the position of the steepest region on the edge of absorption of the atom in the XANES spectra, and the shift of the edge of the absorption therefore directly indicates that in the above two samples the Mn atoms, being located (according to the EXAFS data) in two different sites in the lattice, are in two different oxidation states. By comparing our spectra with those of the reference samples, we may conclude that the Mn ions in $SrTiO_3$ located in the *A* site are in oxidation state +2, and the Mn ions located in the *B* site are in oxidation state +4. The difference in the form of the

Structural parameters obtained from processing EXAFS spectra of the two studied samples (R_i is the distance to the *i*th coordination sphere, and σ_i^2 is the sphere's Debye-Waller coefficient)

Sample	Coordination sphere	R_i, Å	σ_i^2, Å^2	Atom
$Sr(Ti_{0.97}Mn_{0.03})O_3$, annealing 1100°C	1	1.914	0.0012	O
	2	3.328	0.0015	Sr
	3	3.895*	0.0061*	Ti
$(Sr_{0.97}Mn_{0.03})TiO_3$, annealing 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 given value is for the channel of single scattering with account of the focal effects (two- and threefold scattering).

edge of the absorption in the studied samples, in which the Mn ions are in oxidation state +4, and that of the MnO_2 sample is due to the position and the form of the edge of the absorption in XANES spectra being determined not only by the oxidation state of the atom, but also by the band and crystalline structure of the studied object. At room temperature, MnO_2 is a metal with rutile structure, while the studied samples are dielectrics with a cubic lattice of the perovskite type. The weak near-edge structure observed in all of the samples is due to forbidden transitions from the 1*s* level of the Mn atom to the conductivity band (i.e., it is also determined by the band structure).

From a comparison of the XANES spectra for the samples of nominal composition $(Sr_{0.97}Mn_{0.03})TiO_3$ annealed at 1350°C (curve *2* in Fig. 2) and 1100°C (curve *3* in Fig. 2) with the spectra of samples for which the EXAFS analysis was performed (curves *1* and *4* in Fig. 2), it follows that spectra *2* and *3* are a superposition of spectra *1* and *4*. This means that in these samples, Mn is in both lattice sites and in both oxidation states. It follows from these data that in the sample with a deliberate shift away from Sr/Ti stoichiometry to the deficiency in Sr (the $(Sr_{0.97}Mn_{0.03})TiO_3$)-type sample), an increase in the temperature of the final annealing leads to a systematic increase in the concentration of manganese in oxidation state +2 in the *A* sites. In the sample annealed at 1100°C (curve *3* in Fig. 2), a large number of the Mn atoms are in the *B* sites, despite the composition's deliberate shift away from stoichiometry in order to introduce the admixture in the *A* site. Thermal treatment of sample *3* 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 the deliberate shift from stoichiometry to the deficiency in Ti (the $Sr(Ti_{0.97}Mn_{0.03})O_3$)–type samples), an increase in the temperature of the final annealing also leads to increase in the concentration of manganese in oxidation state +4 located in the *B* site (curves *4* and *5*).

CONCLUSIONS

Our studies of the XANES and EXAFS spectra in $SrTiO_3$(Mn) show that, depending on the preparation conditions, Mn atoms can be incorporated into the *A* and *B* sites of the perovskite lattice and remain there in different oxidation states. The redistribution of the impurity atoms between two sites can be controlled by changing the annealing temperature and creating a deliberate shift away from stoichiometry in the composition of the crystal. It was established that the impurity Mn atoms substituting for Ti atoms occupy the on-center position in the lattice and are in oxidation state +4, while the Mn atoms substituting for Sr atoms are off-center, displaced from the lattice sites by a distance of about ~0.32 Å, and in oxidation state +2. Our direct data confirm the assumption of the authors [5, 6] about the possibility of incorporating impurity manganese into the *A* sites. It has been shown that XANES studies of the edge structure can be used to determine the ratio of the manganese atoms occupying different crystallographic positions in the lattice.

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