

Local structure and oxidation state of Ni impurity in SrTiO₃, BaTiO₃, and PbTiO₃

I. A. Sluchinskaya and A. I. Lebedev

Physics Department, Moscow State University, Moscow, 119991, Russia

In recent years, doped ferroelectric perovskite oxides have attracted attention because of developing a new type of solar energy converters based on the photovoltaic effect. Recent theoretical studies have shown that the substitution of Ti at the *B* site of PbTiO₃ by vacancy-compensated divalent impurities with the *d*⁸ electron configuration (Ni, Pd, Pt) reduces the band gap to the levels optimal for effective energy conversion [1]. As an 3*d* impurity may occupy different sites in SrTiO₃, BaTiO₃, and PbTiO₃ and have different oxidation states [2], the aim of this work was to use XAFS spectroscopy to determine the structural position and oxidation state of nickel in SrTiO₃, BaTiO₃, and PbTiO₃ and to compare the obtained results with results of first-principles calculations.

Samples of SrTiO₃, BaTiO₃, and PbTiO₃ with Ni concentration of 2–3% were prepared by the solid-state reaction method at 1100–1500°C. Since the doping with 3*d* elements results in the formation of the hexagonal phase of BaTiO₃, in addition to doped hexagonal samples of BaTiO₃, samples with the cubic structure obtained by substituting 20% of Ba atoms by Sr atoms were investigated. Doping was performed by adding nickel acetate in the case of SrTiO₃ and BaTiO₃ and by adding NiNb₂O₆ columbite phase in the case of PbTiO₃. The quality of the samples was controlled by X-ray diffraction. Spectra of fluorescent EXAFS and XANES were recorded at the KMC-2 station of the BESSY synchrotron radiation source at the Ni *K*-edge in the fluorescence mode at 300 K. The calculations were performed in the LDA+*U* approximation for supercells containing Ni atoms in the oxidation state determined from the XANES data.

All the samples were single-phase with the cubic, tetragonal, or hexagonal perovskite structures at 300 K. To determine the oxidation state of the Ni impurity, the position of the absorption edge in XANES spectra was compared with those of the reference compounds (Fig. 1). It is seen that in SrTiO₃ nickel is in the 4+ oxidation state [3], whereas in BaTiO₃, Ba_{0.8}Sr_{0.2}TiO₃, and PbTiO₃ it is in the 2+ oxidation state.

To determine the local structure of the Ni impurity, EXAFS spectra were analyzed. According to the EXAFS data, in SrTiO₃ the Ni⁴⁺ ions are located at the *B* sites and are on-center ($R_{\text{Ni-O}} = 1.925 \text{ \AA}$, $R_{\text{Ni-Sr}} = 3.36 \text{ \AA}$, $R_{\text{Ni-Ti}} = 3.89 \text{ \AA}$) [3]. The calculated distances for this structural model ($R_{\text{Ni-O}} = 1.923 \text{ \AA}$, $R_{\text{Ni-Sr}} = 3.376 \text{ \AA}$, $R_{\text{Ni-Ti}} = 3.935 \text{ \AA}$) were in good agreement with experiment.

For cubic Ba_{0.8}Sr_{0.2}TiO₃ the satisfactory agreement between the experimental and calculated spectra was obtained in the model in which the impurity atom forms the complex with the oxygen vacancy and is shifted from the Ti site ($R_{\text{Ni-O}} = 2.07 \text{ \AA}$). However, as was shown in the first-principles calculation for this impurity complex, the Ni²⁺ ion forms a typical square-planar coordination with the Ni-O distance of 1.940 Å which is 0.13 Å shorter than the experimental one. So, this model disagrees with the experimental data. In order to improve the agreement, other Ni impurity complexes were modeled and it was shown that to retain large Ni-O distance observed in the experiment, the local environment of Ni should be perfect (six oxygen atoms). So we think that the oxygen vacancy that compensate the ionic charge of Ni at the Ti site is distant from the impurity atom. For this models, we get the $R_{\text{Ni-O}}$ distance of 2.064–2.079 Å, close the experimental one.

For tetragonal PbTiO₃, the distances to the closest atoms determined from the EXAFS data analysis were $R_{\text{Ni-O}} = 2.04 \text{ \AA}$ and $R_{\text{Ni-Ti(Ni)}} = 2.95\text{--}2.99 \text{ \AA}$. To construct the structural model of the local environment of Ni atom in PbTiO₃, three first-principles models were analyzed. First, we used the model proposed in [1] in which the Ni²⁺ atom at the *B* site is surrounded by five oxygen atoms and one oxygen vacancy. Second, we analyzed the model with Ni²⁺ at the *B* site and a distant oxygen vacancy (two configurations). And the last, we analyzed the model with off-center Ni²⁺ ion at the *A* site. Unfortunately, none of these models agrees with

the experiment. The first and third models give the Ni^{2+} -O distance of 1.905 Å and 1.896 Å, respectively, which are typical of square-planar Ni coordination and are inconsistent with experiment. The Fourier transforms of the EXAFS spectra for all studied samples and NiTiO_3 reference compound are shown in Fig. 2. The most intriguing feature of the Fourier transforms for $\text{PbTiO}_3(\text{Ni})$ is the appearance of an extra peak corresponding to the light (Ti or Ni) atom in the second shell. This distance is absent in three above-mentioned models of $\text{PbTiO}_3(\text{Ni})$. We suppose that Ni atoms in PbTiO_3 form some complexes, whose structure is resembling the NiTiO_3 structure in which the octahedra are edge-sharing. At the same time, no traces of NiTiO_3 and NiNb_2O_6 phases are present in EXAFS and X-ray data.

It should be noted that the color of the samples depends on the local structure of the Ni impurity: the color is nearly black for SrTiO_3 and BaSrTiO_3 in which Ni is at the B site and dark-yellow for PbTiO_3 in which Ni forms a complex with a structure different from the perovskite structure.

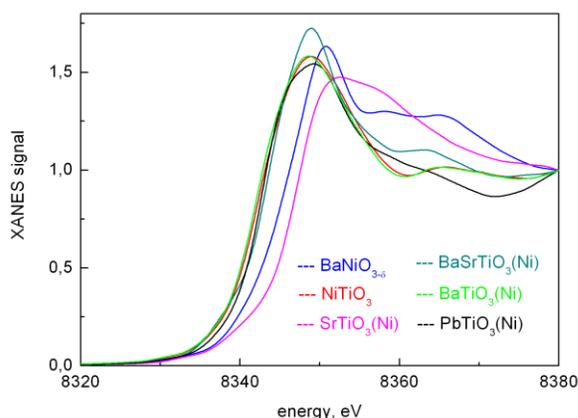


Fig. 1. XANES spectra of $\text{SrTiO}_3(\text{Ni})$, $\text{BaTiO}_3(\text{Ni})$, $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3(\text{Ni})$, and $\text{PbTiO}_3(\text{Ni})$ samples and of $\text{BaNiO}_{3-\delta}$ ($\delta \approx 0.4$) and NiTiO_3 reference compounds recorded at the Ni K-edge at 300 K.

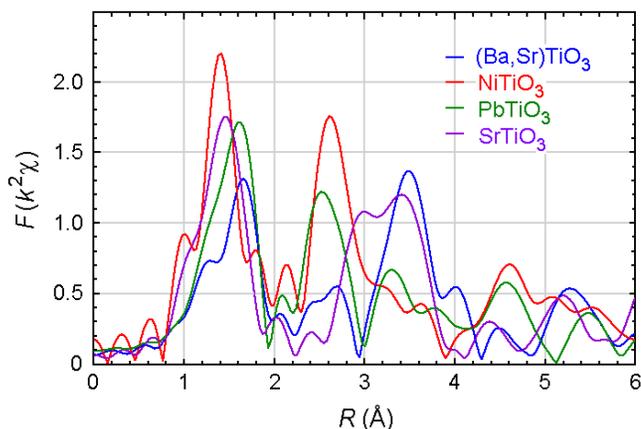


Fig. 2. Fourier transforms of the EXAFS spectra of $\text{SrTiO}_3(\text{Ni})$, $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3(\text{Ni})$, and $\text{PbTiO}_3(\text{Ni})$ samples and of NiTiO_3 reference compound.

Acknowledgment. This work was supported by RFBR Grant No. 13-02-00724. The authors are grateful to the Russian-German laboratory of BESSY for fruitful collaboration.

References

- [1] W. Bennett, I. Grinberg, A.M. Rappe. *J. Am. Chem. Soc.* **130**, 17409 (2008).
- [2] A.I. Lebedev, I.A. Sluchinskaya, A. Erko, V.F. Kozlovskii. *JETP Lett.* **89**, 457 (2009).
- [3] I.A. Sluchinskaya, A.I. Lebedev, A. Erko. *Phys. Solid State* **56**, 442 (2014).