

EXAFS study of $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ system

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Abstract

The room-temperature EXAFS measurements have been made on FeBO_3 and VBO_3 , as well as on $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ series with concentration $x = 0.13, 0.3$, and 0.95 . The first-shell Me–O bond lengths deduced from EXAFS have shown a compositional independence. It has been found that $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ forms solid solutions with random distribution of Fe^{3+} and V^{3+} ions.

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The boron-oxides with chemical formula M^{3+}BO_3 , where $\text{M}^{3+} = \text{Ti}, \text{V}, \text{Cr}, \text{Fe}$, occupy a special place in condensed-matter physics. It is expected that oxygen 2p states are occupied and metal 3d states are partially occupied that makes the explanation of insulating properties difficult. The general understanding of issue is that these compounds belong to the systems with strong electron–electron correlations. The crystal lattice of M^{3+}BO_3 has rhombohedral symmetry with the space group $\text{R}\bar{3}\text{c}$ (D_{3d}^6) [1,2]. The unit cell contains two formula units. The metal ions are in oxygen octahedrons. The FeBO_3 crystal structure refinement has shown that the interatomic distances are $(\text{Fe}–\text{O}) = 2.028 \text{ \AA}$ and $(\text{Fe}–\text{Fe}) = 3.601 \text{ \AA}$, while the angles of the bonds $(\text{O}–\text{Fe}–\text{O})$ are 91.82° and 88.18° [3].

The magnetic coupling in the M^{3+}BO_3 compounds is caused by 90° superexchange $\text{M}–\text{O}–\text{M}$. In the ferric borate the weak ferromagnetic ordering is established below $T_N = 348 \text{ K}$ [4]. The VBO_3 vanadium borate is a ferromagnet with $T_C = 32.5 \text{ K}$ [5].

The M^{3+}BO_3 borates are in general insulating systems except for VBO_3 , that is semiconductor [6]. Electron band structures of FeBO_3 and VBO_3 have been studied [7,8]. It

has been shown that the former can be considered as a charge transfer insulator, while the latter belongs to Mott–Hubbard insulators.

Taking into account the difference in magnetic and electric properties of FeBO_3 and VBO_3 end members, we have synthesized the $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ system. The magnetic, optic and electric properties of these samples have been investigated in our previous work [6].

The mixed occupancy of a site by different ions, as in a solid solutions, is often accompanied by local distortions that are absent in the end members. The EXAFS spectroscopy data allow to characterize directly the local structure around a chosen element, as well as bond distances and local distortions [9]. The present work is devoted to the spectroscopic investigation of the $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ system.

Single crystal calcite-type $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ samples with $x = 0.0, 0.13, 0.3, 0.95$, and 1.0 have been grown using the solution melt technology [6]. The exact amounts of the elements have been determined by the energy-dispersive X-ray spectroscopy. X-ray diffraction study has been made with the D8ADVANCE type setup using CuK_α radiation ($\lambda = 1.5406 \text{ nm}$). The hexagonal indices for FeBO_3 ($a_H = 4.524 \text{ \AA}$, $c_H = 14.470 \text{ \AA}$) and for VBO_3 ($a_H = 4.621 \text{ \AA}$, $c_H = 14.518 \text{ \AA}$) are close to those reported earlier [1,2]. X-ray diffraction measurements carried out at

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77 and 300 K have revealed that mixed compositions have the same crystal lattice as the end members and experience no phase transition.

EXAFS measurements at the K-edge of Fe and V have been carried out. Measurements have been performed on single crystal powders. Data have been taken at room temperature using either the transmission or the fluorescence-yield technique depending on concentration. Synchrotron radiation of VEPP-3 storage ring has been monochromatized by the Si(111) channel-cut single-crystal monochromator. The energy resolution of monochromator has been estimated to be approximately 1 eV. The pre-edge background has been subtracted using Victorian fit and XAFS spectrum has been normalized to the edge jump of 1.0. All the Fourier transforms have been obtained using the VIPER EXAFS code within the k range of $2.5\text{--}12\text{ \AA}^{-1}$ with k^2 weighting of the fine oscillations.

Fig. 1 shows the k^2 weighted fine structures for $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ ($x = 0.0, 0.13, 0.3, 0.95, 1.0$) samples. The EXAFS oscillations for all compounds coincide well, demonstrating the similarity of iron (vanadium) local

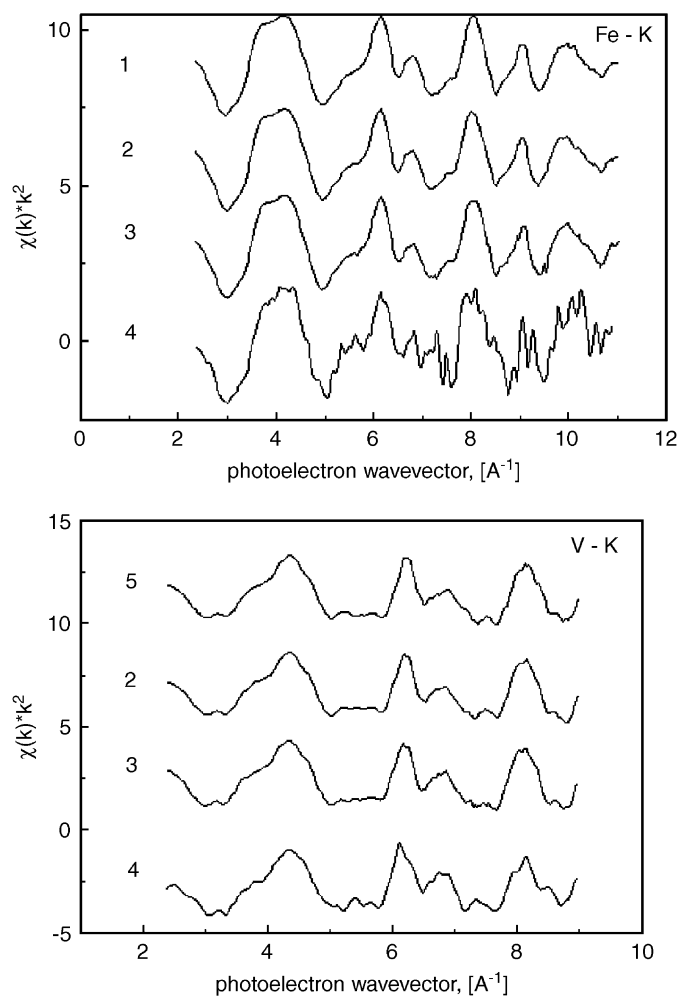


Fig. 1. $\chi^2 k^2$ for Fe and V K-edge for 1- FeBO_3 , 2- $\text{Fe}_{0.87}\text{V}_{0.13}\text{BO}_3$, 3- $\text{Fe}_{0.7}\text{V}_{0.3}\text{BO}_3$, 4- $\text{Fe}_{0.05}\text{V}_{0.95}\text{BO}_3$, 5- VBO_3 .

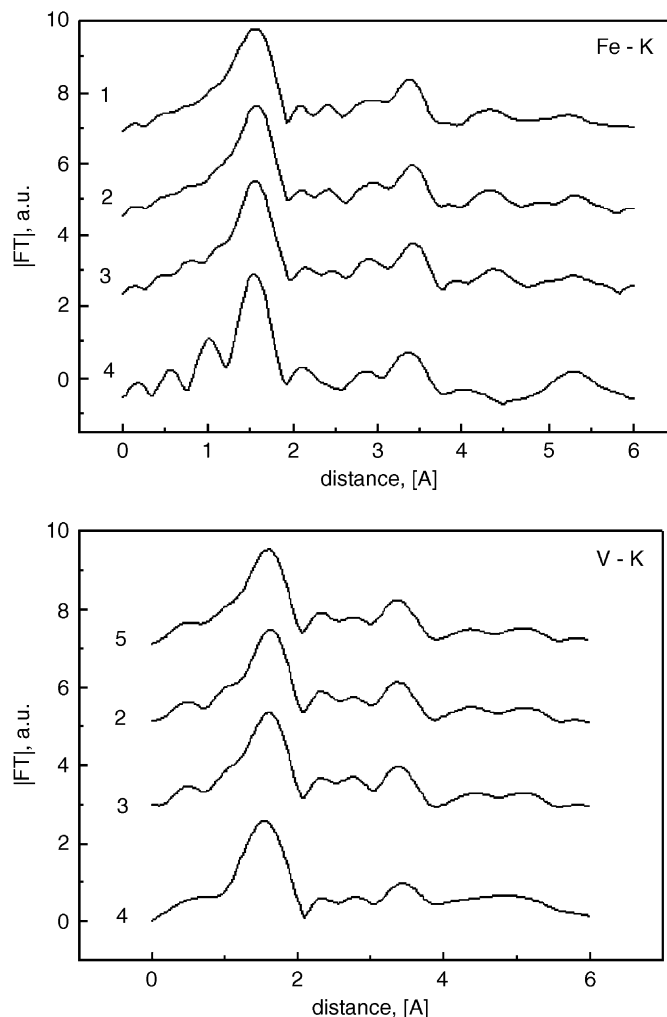


Fig. 2. FT for Fe and V K-edge for the same samples as in Fig. 1.

coordination. Slight discrepancy can be explained by glitches of the monochromator and experimental statistics. Fig. 2 shows the corresponding Fourier transforms of EXAFS spectra in the range of $0\text{--}6\text{ \AA}$. For both Fe-K and V-K edges in the Fourier transform the oxygen coordination shells give rise to the peak at 1.8 \AA . The second peak at 3.3 \AA corresponds to the Me-Me next-nearest neighbors.

There is some uncertainty connected with the discrepancy between the observed position of the main peak in the Fourier transform and X-ray diffraction data for FeBO_3 [3]. However, the EXAFS spectra modeling with the FEFF 7.02 code [10] has shown that this discrepancy is fairly explained by phase dependence on the photoelectrons energy.

Spectroscopic results have revealed that the first-neighbor Fe(V)-O bond lengths remain close to the distance in the pure end members. The second-neighbor cation-cation distances are also similar to those found for FeBO_3 and VBO_3 . Minor differences in the shape of peaks in the range of $3\text{--}4\text{ \AA}$ may be assigned to the

slight lattice distortion. Taking into account that the ionic radii of V^{3+} and Fe^{3+} ions are very close, the embedding of V in $FeBO_3$ causes no noticeable changes of the crystal structure.

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