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XPS study of $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ (M = Co, Fe) nanoscale oxides

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A strong correlation was found between the ionic state of magnetic Ti, V, Co and Fe ions in doped nanoscale titanium–vanadium oxides synthesized by a sol-gel method, the annealing conditions of the samples and the dopant ions.

The discovery of ferromagnetism in cobalt-doped anatase and rutile at room temperature fostered experimental and theoretical studies of these systems and related compounds with magnetic *d*-metal ions introduced into the TiO_2 lattice.[1] These materials are considered as diluted magnetic semiconductors (DMSs); they combine electron conduction, ferromagnetism, and optical transparency and thus open up fresh opportunities for modern microelectronics and spintronics. Usually, DMS materials are produced by different methods of physical or chemical vacuum deposition. The most promising method for obtaining DMS materials is a sol-gel technique[1] providing homogeneous distribution of magnetic *d*-metal ions in an oxide matrix.

The aim of this study was to examine the charge states of atoms, which determine the magnetic properties of $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ (M = Co, Fe) nanopowders obtained by the sol-gel technique, using XPS.

According to published data,[2] $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ is characterized by the presence of ion-exchange centers in its structure. This made it possible to obtain modified composites of titanium and vanadium oxides of the general formula $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ (M = Co, Fe).[†] According to chemical analysis, the doping ion concentration (*x*) per unit formula was 0.08 or 0.05, for Co or Fe ions, respectively. The as-prepared $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ (M = Co, Fe) samples are X-ray amorphous [Figure 1(*a*)]. The

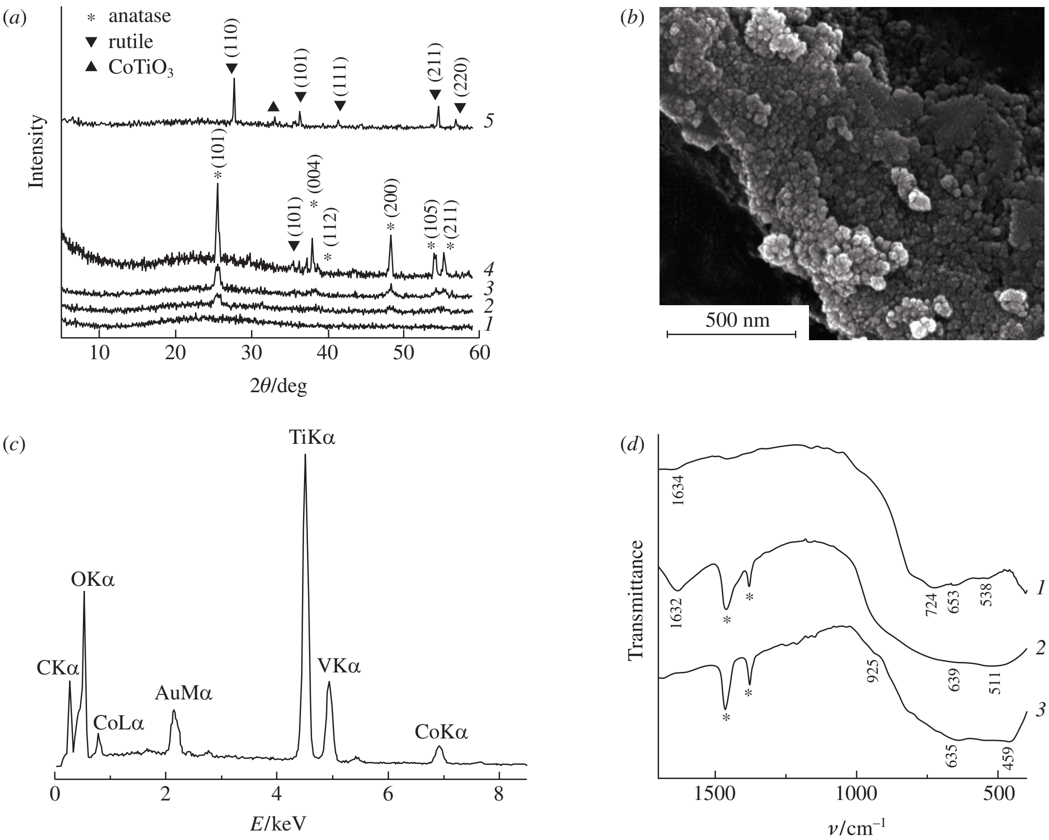

Figure 1 (*a*) XRD patterns of $Co_{0.08}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$: (*1*) air-dry and annealed at (*2*) 450, (*3*) 500, (*4*) 600 and (*5*) 700 °C, (*b*) SEM image, (*c*) EDX pattern, and (*d*) IR spectra of (*1*) $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$, (*2*) air-dry $Co_{0.08}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ and (*3*) annealed at 500 °C.

[†] The mixed oxide $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ obtained by the sol-gel method from $TiOSO_4\cdot 2H_2O$ and V_2O_5 taken in a V/Ti molar ratio of 0.10 and dissolved in water and hydrogen peroxide, respectively, served as an initial matrix for the synthesis of doped oxides. A stoichiometric amount of NH_4OH was added to form a gel, which was filtered off, washed with water and dried. $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ samples were prepared by exchanging protons of the titanium vanadium oxide in appropriate 0.1 M chloride solutions.

compounds annealed in air at 400–500 °C have a TiO_2 (A) type structure. The transition of anatase to rutile begins at 600 °C irrespective of the dopant cation. As reported earlier,[3] the ionic radii of Co^{2+} (79 pm) and Fe^{3+} (69 pm) are larger than that of Ti^{4+} (60.5 pm). Hence, the insertion of Co or Fe cations should increase the crystal lattice of $Ti_{0.91}V_{0.09}O_{2+\delta}$. However, doping with Co and Fe did not change considerably the lattice constants. These results are in good agreement with published data[4,5] showing that variations in the lattice parameters of doped compounds can be due to the location of Co ions in the interstitial sites or on the crystal surface.

The SEM study [Figure 1(*b*)] demonstrates that the $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ samples consist of agglomerated nanoparticles with average sizes from 20 to 30 nm. EDX analysis confirmed the purity of the synthesized products [Figure 1(*c*)].

The structural transformations were studied by IR spectroscopy using $Co_{0.08}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ as an example [Figure 1(*d*)]. A comparison of the IR spectra of $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ and $Co_{0.08}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ reveals shifts for all of the Ti–O and V–O modes to lower frequencies. This indicates that Co ions are well dispersed within $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$. The air-dry sample contained crystal water; the bending mode of the water was characterized by an intense broad band at 1632 cm^{-1}. A strong absorption band at 511 cm^{-1} corresponds to bond vibrations in a TiO_6 octahedron. The Ti–O stretching mode is characterized by a broad band near 653 cm^{-1}. Vibrations of the V–O–V bridges are detected at 884 cm^{-1}. The annealing of the samples is accompanied by the appearance of a peak near 925 cm^{-1}, which is indicative of the formation of typical Ti–O and V–O groups of the V_2O_5–TiO_2 solid solutions.

The valence state of ions in $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ nanopowders treated at different temperatures was examined by XPS (Figure 2).[‡] Vanadium in $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ has the oxidation state V^{5+} with a binding energy of 516.9 eV. It can be supposed that the introduction of V^{5+} into the Ti^{4+} positions in TiO_2(A) is accompanied by the formation of defects:

$$\tfrac{1}{2}O_2 + V_i^x \to O_i^x \to O_i'' + 2h^+,$$

where V_i^x and O_i^x is a vacancy and an oxygen atom, respectively, in an interstitial site with zero effective charge; O_i'' is an oxygen atom in an interstitial site with a negative effective charge; h^+ is a hole with an excess positive charge. The holes in the complex titanium oxide lattice are occupied by V^{5+} ions.

In $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ dried at 60 °C, the Ti 2*p* XPS spectra contain two components (Figure 3): the main band at 458.5 eV responsible for the Ti^{4+} state and an additional band at 456.8 eV attributed to Ti^{3+}.[6] Upon the annealing of $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ samples (M = Fe, Co) at 500 °C, the shape and position of the Ti 2*p* and V 2*p* spectra change drastically. The low-energy states typical of Ti^{3+} ions disappear, and only bands associated with Ti^{4+} remain. In the V 2*p* spectra, the chemical shift of doublet bands takes place in the direction of low binding energies. This shift is 0.8 or ~1.3 eV for the iron- or cobalt-doped compounds, respectively (Figures 2 and 4). The energy position of the V 2*p* bands for $Co_{0.08}Ti_{0.91}V_{0.09}O_{2+\delta}$ unambiguously points to the vanadium oxidation state V^{4+}. In case of $Fe_{0.05}Ti_{0.91}V_{0.09}O_{2+\delta}$, the V 2*p* spectrum contains the bands responsible for two chemical forms of vanadium: V^{4+} and V^{5+}.

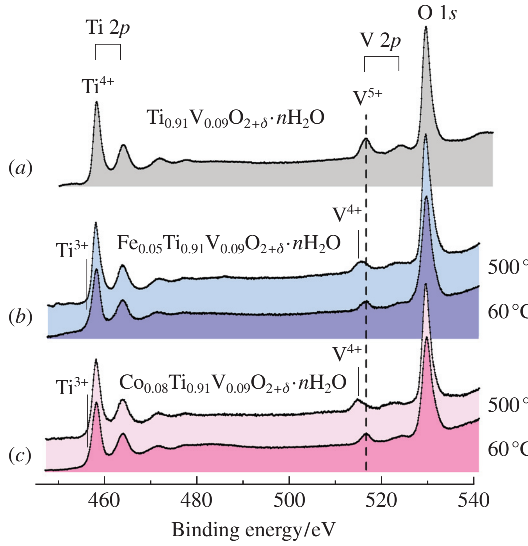

Figure 2 Ti 2*p*, V 2*p*, and O 1*s* XPS spectra of (*a*) $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$, (*b*) $Fe_{0.05}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$, and (*c*) $Co_{0.08}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ nanopowders after different annealing steps. At 500 °C, the O 1*s* spectrum shows peaks due to the ^-OH groups.

Figure 5 presents the Fe 2*p* and Co 2*p* photoelectron spectra of $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ (M = Fe, Co) upon drying at 60 °C and upon annealing in air at 500 °C. For the cobalt-containing sample, irrespective of the heat-treatment method, the Co 2*p* spectra represent a doublet with a $2p_{3/2}$ maximum of binding energy at 781.3 eV and a characteristic satellite S1 and S2 structure, which is ~6 eV away from the main maxima in the direction of high binding energies. According to the Co 2*p* spectrum, the cobalt oxidation state in these compounds is Co^{2+}.[7] A somewhat higher binding energy of the Co 2*p* levels in the test samples, as compared with CoO, is likely due to the arrangement of these cations in the anatase lattice of TiO_2.

The band shape of the Fe 2*p* spectra of $Fe_{0.05}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ nanopowders and the binding energies of the main maxima (710.9 eV for Fe $2p_{3/2}$) testify that the spectra contain contributions from Fe^{2+} and Fe^{3+} (Figure 5). Upon annealing at 500 °C in air, the Fe 2*p* spectra exhibit a small inflow from the

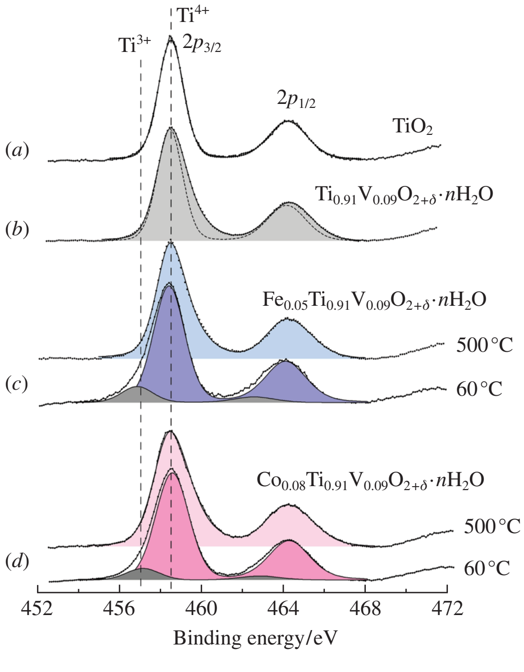

Figure 3 Ti 2*p* XPS spectra of (*a*) TiO_2, (*b*) $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$, (*c*) $Fe_{0.05}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$, and (*d*) $Co_{0.08}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$. At 500 °C, the Ti 2*p* peaks are asymmetrical owing to a change in the electronic density near the Fermi level.

[‡] XPS of the powders embedded into metal indium were examined on an ESCALAB MK II electron spectrometer in non-monochromatic MgKα radiation (1253.6 eV). It is difficult to analyze the V 2*p* spectra because of the overlap of the V $2p_{3/2}$ and V $2p_{1/2}$ lines with $K\alpha_{3,4}$ O 1*s* satellites. It is necessary to use a sample charge compensation system.

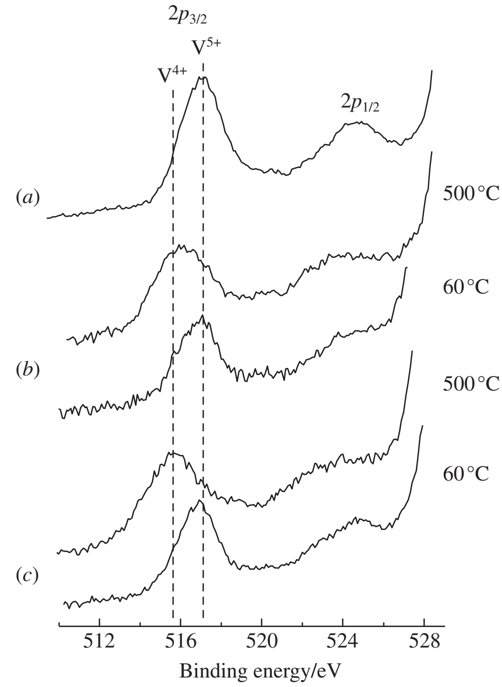

Figure 4 V 2*p* XPS spectra of (*a*) $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$, (*b*) $Fe_{0.05}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$, and (*c*) $Co_{0.08}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$.

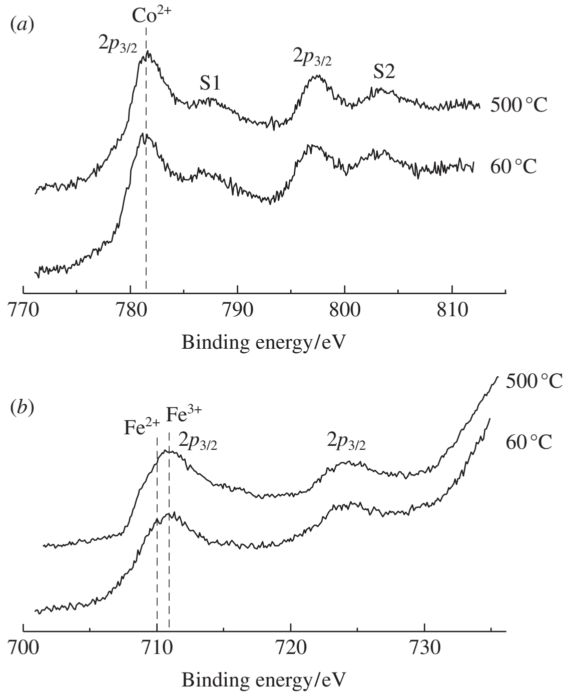

Figure 5 (*a*) Co 2*p* and (*b*) Fe 2*p* XPS spectra of $Co_{0.08}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ and $Fe_{0.05}Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$.

direction of low binding energies, which is indicative of an increased fraction of Fe^{2+} states, as compared with the air-dry sample.

Thus, the XPS spectra showed that the ionic state of magnetic ions in $M_xTi_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ nanopowders (M = Fe, Co) with the anatase structure obtained by the sol-gel method can be changed by varying the heat-treatment temperature of the sample and the type of the dopant ion.

The thermodynamic possibility of co-doping processes (*e.g.*, with Fe ions) can be evaluated from the standard redox potentials with the calculated emf value:[8]

$$V^{5+} + Ti^{3+} \rightarrow V^{4+} + Ti^{4+}, \quad E_0 = 1.06\ \text{V}, \qquad (1)$$

$$V^{5+} + Fe^{2+} \rightarrow V^{4+} + Fe^{3+}, \quad E_0 = 0.25\ \text{V}, \qquad (2)$$

$$Fe^{3+} + Ti^{3+} \rightarrow Fe^{2+} + Ti^{4+}, \quad E_0 = 0.81\ \text{V}. \qquad (3)$$

Among these redox reactions, reactions (1) and (3) are thermodynamically more probable. Therefore, the co-doping of $Ti_{0.91}V_{0.09}O_{2+\delta}\cdot nH_2O$ nanopowder with iron ions and its subsequent high-temperature annealing are described by reactions (1) and (3). The process is accompanied by an increase in the concentration of Fe^{2+} ions and by the complete oxidation of titanium ions to a tetravalent state, which is in good agreement with XPS data for iron-containing compounds.

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