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Electronic properties of $M_2InV_3O_{11}$ (M(II) = Zn(II) and Co(II)) compounds*

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The electronic properties of multicomponent vanadate oxides $M_2InV_3O_{11}$ (M(II) = Zn(II) and Co(II)) were investigated by electrical resistivity and electron paramagnetic resonance (EPR) measurements. Replacement of non-magnetic Zn(II) cations with magnetic Co(II) ions resulted in a significant drop in the electrical conductivity and an increase in the activation energy. The EPR spectroscopy revealed the presence of VO^{2+} vanadyl ions in both compounds, while the presence of divalent cobalt ions was identified in the $Co_2InV_3O_{11}$ oxide at low temperatures. The concentration of VO^{2+} vanadyl ions was found to be about one order higher for the vanadate oxide without magnetic ions. It is suggested that the increased concentration of VO^{2+} ions could be responsible for the enhanced conductivity of $Zn_2InV_3O_{11}$.

Keywords: *EPR; magnetic properties, conductivity*

1. Introduction

Indium oxide is one of the most important compounds for applications in optoelectronic technology [1, 2] due to its high electrical conductivity [3]. Both the structural defects caused by oxygen deficiency and intentional doping play a very important role in the transport properties of these oxides. Other compounds containing indium exhibit very interesting electronic properties, *e.g.* InN that has been found to be an *n*-type semiconductor with electron concentrations in the range of 10^{17}–10^{21} cm^{-1} and a small band gap value of about 0.7 eV [4–6]. Recently, some new multicomponent vanadate oxide indium materials with vanadium ions have been prepared and investigated by electron paramagnetic resonance (EPR), where vanadium ions at the lower oxidation state have been identified [7–9]. The EPR spectra of ionic V(IV) defects in multicomponent vanadates $Me_2InV_3O_{11}$ (Me(II) = Mg(II) and Zn(II) at room temperature have been recorded and reported in [7]. In $Me_2InV_3O_{11}$ of nominal stoichiometry all the ions can be diamagnetic but the temperature dependence of the EPR spectra has shown a rich variety of paramagnetic centers involving predominantly monomeric and dimeric V(IV) ions and their complexes in both cases [8, 9]. Additional magnetic clusters have appeared for a vanadate with Zn(II) [9]. Moreover, mixed vanadate oxides are very interesting for their catalytic properties, especially ortho- and divanadate (V) compounds [10], while M-Fe-V-O multi-component vanadates possess very interesting structural and magnetic properties [11–13]. However, little is known about their conductivity properties.

The aim of this work is the preparation of new mixed indium-vanadium oxides $M_2InV_3O_{11}$, M(II) = Zn(II) and Co(II)) with magnetic (Co) and non-magnetic (Zn) ions in the cation position and the study of concomitant variations in their electronic properties by means of EPR spectroscopy and DC resistivity measurements.

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2. Experimental

Polycrystalline samples of $M_2InV_3O_{11}$, M(II) = Zn(II) and Co(II) were prepared by the solid state reaction method [14, 15]:

$$4Zn(II)O + 3V_2O_5 + In(II)_2O_3 = 2Zn(II)_2InV_3O_{11} \quad (1)$$

$$4Co(II)CO_2 + 2V_2O_5 + In(II)_2O_3 = 2Co(II)_2InV_3O_{11} + 4CO \quad (2)$$

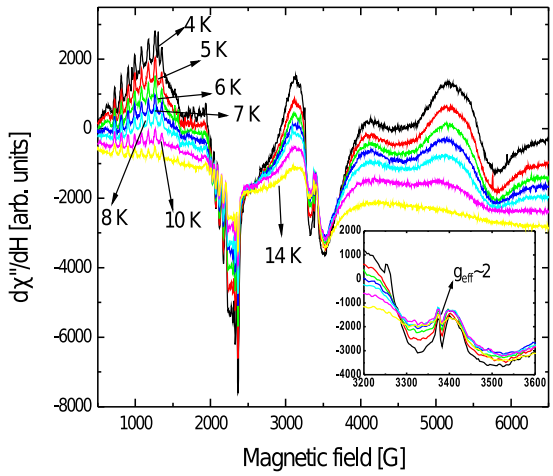
The samples $Zn_2InV_3O_{11}$ and $Co_2InV_3O_{11}$ are yellow and black, respectively and have been found to crystallize in the triclinic system [16].

The EPR spectra were recorded using a standard Bruker E500 X-band spectrometer (ν = 9.455 GHz) with the magnetic field modulation of 100 kHz. The magnetic field was scaled with an NMR magnetometer. The samples, containing 30 mg of the substance in the form of fine powder, without any cement-dielectric, were sealed into quartz tubes 4 mm in diameter. The measurements were performed in the temperature range of 4 to 290 K using an Oxford nitrogen flow cryostat and a standard hot air flow system.

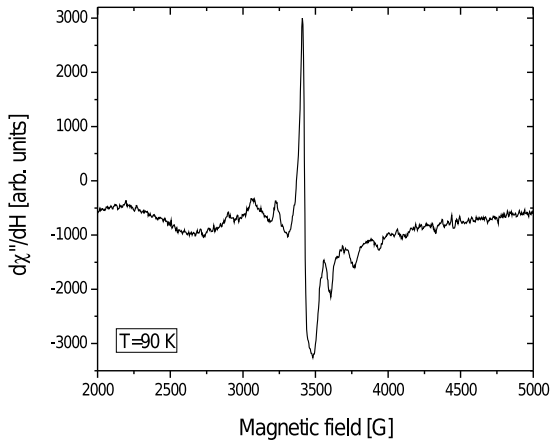
The DC electrical resistivity measurements were performed in the temperature range of 90–320 K for small pellets (about 6 mm in diameter, with a thickness of 3–4 mm) prepared under pressure of 0.7–0.8 MPa using special dielectric glue. The resistance was measured with a Keithley 181 electrometer according to the two-point geometry, with the highest limit of $2 \times 10\ \Omega$ for the circuitry of the experiment.

3. Experimental results

Fig. 1 compares the EPR spectra of the multicomponent vanadates $Co_2InV_3O_{11-\delta}$ and $Zn_2InV_3O_{11-\delta}$. Detailed EPR measurements as a function of temperature have been recently reported for the latter compound [8, 9]. The EPR spectra of $Co_2InV_3O_{11-\delta}$ have revealed an additional resonance line arising from high spin Co^{2+} ions in orthorhombic crystal field symmetry [17, 18]. The concentration of vanadium ions at the lower oxidation decreased significantly (about one order of magnitude), especially the VO^{2+} vanadyl ions for the sample with magnetic ions (Fig. 1).



(a)



(b)

Fig. 1. EPR spectra of (a) $Co_2InV_3O_{11}$ and (b) $Zn_2InV_3O_{11}$ compounds.

The temperature dependence of the EPR spectra of $Zn_2InV_3O_{11-\delta}$ and $Mg_2InV_3O_{11-\delta}$ has shown the presence of a complex of vanadium ions with lower valence, while the resonance lines at the lower magnetic field have been attributed to complex divalent cobalt ions [8, 9, 19, 20] and some additional lines could arise from trivalent indium ions [21]. A recent study of the temperature dependence of the EPR spectra of $Zn_2InV_3O_{11}$ has revealed the presence of monomeric and dimeric vanadium complexes. The EPR spectra have been described by the hyperfine interaction of VO^{2+} centers in axial symmetry. The latter component consists of two sets

of eight partially overlapping lines and it is due to the interaction of the 3d electron spins (S = 1/2) with the ^{51}V nuclei (I = 7/2, abundance 99.75 %). This EPR spectrum can be described by an axial spin-Hamiltonian of the form:

$$H = \mu_B\left[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)\right] + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (3)$$

with the parameters: $g_{\parallel}$ = 1.93, $g_{\perp}$ = 1.94 and $A_{\parallel} = 180 \times 10^{-4}$ cm^{-1}, $A_{\perp} = 50 \times 10^{-4}$ cm^{-1}. The appearance of another paramagnetic center at the lower magnetic field with g = 2.953(1) and ΔH = 700(3) *Gs* at room temperature has been reported for $Mg_2InV_3O_{11-\delta}$. This line could be connected with the formation of correlated spin system producing a ferromagnetic resonance signal (FMR). The second type of paramagnetic centers could be formed through replacement of magnesium(II) and indium(II) ions [14]. The EPR spectrum of this centers is strongly temperature dependent. It is only the intensity that increases with the decreasing temperature for the former EPR spectrum, while considerable shifts of the resonance lines are recorded in the latter case. A comparison with the $CuSO_4$ reference sample allowed estimating that about 0.017 % of the total vanadium ions were EPR active. Oxygen deficiency has been reported to vary essentially depending on the preparation conditions of these systems, whose physical properties could change strongly [23]. The EPR line that is centered at $g_{eff} \sim 2$ could arise from VO^{2+} vanadyl ions and is one order lower at liquid helium temperature [8, 9]. EPR measurements of In_2O_3 have shown three different paramagnetic centers [21]. The EPR spectra exhibit two broad asymmetric signals characterized by axial symmetry, poorly resolved hyperfine splitting and a sharp isotropic line. It has been proposed that indium(II) ions correspond to the electron configuration ($4d^{10}5s^1$ or $4d^95s^2$) with axial symmetry in an octahedral crystalline field. The hyperfine nuclear interaction with the nearest-neighbor ^{113}In or ^{115}In nuclei (I = 9/2) is also detectable and can be resolved into 10·(2I + 1) components. For $Co_2InV_3O_{11}$ EPR spectra characteristic for complexes of divalent cobalt ions have been recorded (Fig. 1a) [19, 20].

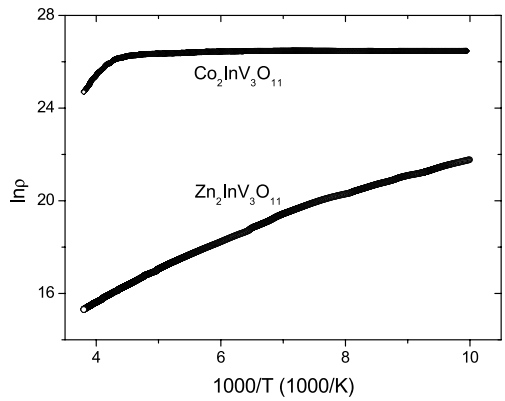


Fig. 2. Temperature dependence of resistivity for $Zn_2InV_3O_{11}$ and $Co_2InV_3O_{11}$ vanadate oxides.

Fig. 2 shows the temperature dependence of resistivity as $\ln\rho$ *vs* 1000/T for the two multicomponent vanadate oxide compounds $Zn_2InV_3O_{11}$ and $Co_2InV_3O_{11}$. Replacement of the non-magnetic Zn(II) cations with magnetic Co(II) ions resulted in a marked drop in the electrical conductivity, over three orders of magnitude, together with a significant variation of the activation energy. For $Zn_2InV_3O_{11}$, the variable activation energy E_a ($\rho = \rho_0 \exp(E_a/k_BT)$ was determined, ranging from E_a = 0.06(1) eV at low temperatures to E_a = 0.11(1) eV at higher temperatures. The observed increase in the activation energy at higher temperatures is most likely related to the compensation effects between various types of donor and acceptor impurity levels that effectively vary the activation energy. In the case of $Co_2InV_3O_{11}$, the resistivity exhibited even weaker temperature dependence at T < 200 K and activated behavior at higher temperatures with higher activation E_a = 0.19(1) eV. This behavior suggests that the concentration of charge carriers changed substantially upon replacement of Co(II) with Zn(II) ions, correlating with an increase in vanadium ions at the lower oxidation state derived by the EPR analysis. It is well known that a very good insulator with the energy gap of 7.6 eV becomes semiconducting after introducing a low concentration of trivalent ions [23]. Indium oxide has been found to be an *n*-type semiconductor over a wide temperature range, while its electrical resistivity at room temperature is of the order of ρ = 10 Ωcm with the activation energy of 1.55 eV [24].

The electrical properties of In_2O_3 have been found to vary strongly with molybdenum doping, where the resistivity could decrease down to 2×10^{-4} Ωcm [25]. The carrier concentration increases with increasing molybdenum doping to a maximum value of $6.6 \cdot 10^{20}$ cm^{-3}.

Previous conductivity measurements of the homologous compounds $Zn_kIn_2O_{k+3}$ (k = 3, 4, 5, 6, 7, 9, 11, 13, and 15) [26] have shown that the conductivity increases as k decreases due to an increase in both the carrier concentration and mobility. The lowest value of resistivity at room-temperature has been reported for sample $Zn_3In_2O_6$ ($\rho = 2.7 \times 10^{-3}$ Ω cm). In the case of the $M_2InV_3O_{11}$ oxides the replacement of Zn(II) with the magnetic Co(II) ions results in a marked decrease in the electrical conductivity most probably due to a decrease in the extrinsic charge carriers or compensation effects of both acceptor and donor impurities. This behavior may correlate with the accompanying decrease in the VO^{2+} defect concentration for $Co_2InV_3O_{11}$ quantified by EPR spectroscopy.

4. Conclusions

Combined EPR and resistivity measurements were employed to investigate the electronic properties of two multicomponent vanadate oxides $M_2InV_3O_{11}$ (M(II) = Zn(II) and Co(II)). Replacement of Zn(II) with the magnetic Co(II) ions resulted in a drastic reduction in the electrical conductivity over three orders of magnitude, accompanied by a significant increase in the concentration of VO^{2+} vanadyl defects and divalent cobalt ions, probed by EPR. It is thus suggested a change in the oxygen defect structure of the vanadate oxides by replacing a diamagnetic cation (Zn(II)) with a magnetic one (Co(II) to modify the extrinsic charge carrier concentration and electrical conduction in these complex systems.

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