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Magnetic resonance study of $M_3Fe_4V_6O_{24}$ (M = Mg, Zn, Mn, Cu, Co) compounds

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Multicomponent vanadates, $M_3Fe_4V_6O_{24}$ (M = Mg(II), Mn(II), Zn(II), Co(II) and Cu(II)), have been synthesized by the solid-state reaction method using a stoichiometric mixture of MO, Fe_2O_3, and V_2O_5 oxides. They crystallize in the triclinic space group $P\overline{1}$ and have a complicated structure with two metal ion subsystems. Electron paramagnetic resonance (EPR) measurements have been performed at room temperature and an intense, almost symmetric EPR lines were recorded for all investigated samples except $Co_3Fe_4V_6O_{24}$. The integral intensity and linewidth of this line essentially depends on the kind of M(II) metal ion in the crystalline matrix. The EPR line intensity for the sample $Co_3Fe_4V_6O_{24}$ is over one order of magnitude smaller than for all other investigated compounds, and the position of its resonance line is shifted towards lower magnetic fields. The difference in linewidths and intensities are due to the various magnetic interactions between magnetic ions in the lattice, especially for systems containing two different magnetic ions.

Key words: *electron paramagnetic resonance; vanadate*

1. Introduction

Multicomponent vanadate oxide systems attract a particular interest due to their interesting physical properties, especially site disorder and frustration phenomena [1–7]. The temperature dependences of the magnetic susceptibilities and electron paramagnetic resonance (EPR) spectrum of the $Zn_2FeV_3O_{11}$ compound have shown an

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inherent magnetic inhomogeneity in the iron(III) subsystem [5]. XRD and neutron diffraction studies of $M_2FeV_3O_{11}$ (M = Zn(II), Mg(II)) compounds showed that iron(III) and metal(II) ions were disordered in their corresponding subsystems, and the distributions on the octahedral and trigonal bipyramidal sites were non-statistical [3, 4, 6]. Novel $M_3Fe_4V_6O_{24}$ (M = Zn(II), Co(II), Mg(II)) compounds have been obtained as a product of the reaction between $FeVO_4$ and $M_3V_2O_8$ (M = Zn(II), Co(II), Mg(II)) and have been found to crystallize in the triclinic space group $P\overline{1}$ [6, 8, 9]. Neutron diffraction studies of the $Zn_3Fe_4V_6O_{24}$ compound have not shown any disorder in its corresponding subsystem of iron(III) and metal(II) ions [11].

This work presents the results of EPR measurements of $M_3Fe_4V_6O_{24}$ (M = Mg(II), Mn(II), Zn(II), Co(II) and Cu(II)) compounds, prepared as a product of the reaction between MO, Fe_2O_3, and V_2O_5, and discusses the reasons for the observed differences in the resonance fields, linewidths and integrated intensities of their EPR spectra recorded at room temperature.

2. Experimental

Polycrystalline $M_3Fe_4V_6O_{24}$ samples were prepared by the solid-state reaction method using a stoichiometric mixture of MO, V_2O_5, and Fe_2O_3 oxides or appropriate hydroxycarbonates, according to the following reaction [8, 9]:

$$3MO + 3V_2O_5 + 2Fe_2O_3 \rightarrow M_3Fe_4V_6O_{24}$$

The reactants were mixed, pressed into pellets and calcinated in air at a temperature range of 560–900 °C in 20 h stages. After each heating stage, the samples were slowly cooled down to room temperature, ground, and analysed by differential thermal analysis (DTA) and X-ray diffraction (XRD). Heating was continued until the formation of a single-phase sample could be confirmed. The obtained compounds crystallize in the triclinic space group $\mathrm{P}\overline{1}$, forming powders with a brown-olive colour, with a melting point in the range of 1100–1140 K. The $Zn_3Fe_4V_6O_{24}$ sample was prepared by two methods, differing in the starting reactants: the first method was based on the above described reaction, in the other the $FeVO_4$ and $Zn_3V_2O_8$ vanadates were synthesized separately and subsequently mixed according to the reaction:

$$4FeVO_4 + Zn_3V_2O_8 \rightarrow Zn_3Fe_4V_6O_{24}$$

The heating cycles were: 700 °C (24 h), 750 °C (24 h) and 800 °C (24h) [8].

EPR measurements were carried out with a conventional X-band (ν = 9.43 GHz) Bruker E 500 spectrometer, with 100 kHz magnetic field modulations. The samples, in the form of loose powder, containing about 30 mg of the material, were placed into 4 mm diameter quartz tubes.

3. Results and discussion

Table 1 presents the crystallographic parameters for the studied $M_3Fe_4V_6O_{24}$ compounds, and for comparison, also for an isomorphic $M_2FeV_3O_{11}$ system. The replacement of metal(II) ions in the structure introduces some differences in the crystallographic parameters.

Table 1. Structure parameters for the $M_2FeV_3O_{11}$ and $M_2Fe_4V_6O_{24}$ compounds

Compound	Crystallographic system	Lattice constants [nm]	Angles [°]	*Z*	Reference
$Mg_2FeV_3O_{11}$	triclinic	a = 0.64406(4)	α = 97.371(8)	2	[4]
		b = 0.68117(4)	β = 103.458(8)		
		c = 1.01057(7)	γ = 101.504(7)		
$Zn_2FeV_3O_{11}$	triclinic	a = 0.64538(5)	α = 97.556(9)	2	[5]
		b = 0.68393(4)	β = 102.650(8)		
		c = 0.9988(1)	γ = 101.308(8)		
$Mg_3Fe_4V_6O_{24}$	triclinic	a = 0.6678(5)	α =105.16(8)	1	[8]
		b = 0.8027(4)	β = 104.95(9)		
		c = 0.9759(7)	γ = 101.91(9)		
$Mn_3Fe_4V_6O_{24}$	triclinic	a = 0.67034(5)	α = 105.25(1)	1	[2]
		b = 0.81477(7)	β = 105.54(1)		
		c = 0.9808(8)	γ = 102.37(1)		
$Zn_3Fe_4V_6O_{24}$	triclinic	a = 0.66812(1)	α = 105.25(4)	1	[8]
		b = 0.8021(2)	β = 105.00(4)		
		c = 0.9778(4)	γ = 102.20(4)		
$Co_3Fe_4V_6O_{24}$	triclinic	a = 0.6685(2)	α = 105.30(9)	1	[9]
		b = 0.8003(5)	β = 105.21(6)		
		c = 0.9764(8)	γ = 101.83(7)		
$Cu_3Fe_4V_6O_{24}$	triclinic	a = 0.6600(3)	α = 106.08(3)	1	[10]
		b = 0.8048(4)	β = 103.72(3)		
		c = 0.9759(5)	γ = 102.28(2)		

The distances between magnetic iron(III) ions in the $M_3Fe_4V_6O_{24}$ compounds are given in Table 2. These values show a decreasing trend in both sublattices with iron(III) ions ($d_{\mathrm{Mg}} > d_{\mathrm{Mn}} > d_{\mathrm{Zn}} > d_{\mathrm{Cu}}$), while the differences $\Delta d = d_{\mathrm{Fe(1)–Fe(1)}} - d_{\mathrm{Fe(2)–Fe(2)}}$ are over twice as large for the sample with Mg(II) and almost the same for the other three compounds.

Table 2. The distances between magnetic ions in the $M_3Fe_4V_6O_{24}$ system

Compound	$d_{\mathrm{Fe(1)–Fe(1)}}$ [nm]	$d_{\mathrm{Fe(2)–Fe(2)}}$ [nm]	Δd [nm]	Reference
$Mg_3Fe_4V_6O_{24}$	0.3148	0.3330	–0.0182	
$Mn_3Fe_4V_6O_{24}$	0.3132	0.3212	–0.0080	[10]
$Zn_3Fe_4V_6O_{24}$	0.3117	0.3192	–0.0075	[11]
$Cu_3Fe_4V_6O_{24}$	0.3095	0.3152	–0.0057	[10]

Figure 1 shows the EPR spectra for all investigated $M_3Fe_4V_6O_{24}$ samples at room temperature. An intense, almost symmetric EPR line is recorded for all samples except for $Co_3Fe_4V_6O_{24}$. The lineshape of this EPR line has been fitted very well by using the Lorentzian-shape function. The obtained parameters of the EPR spectra for all six samples are given in Table 3. The resonance fields of five samples (excluding the sample with cobalt(II)) are basically the same, with $g = 2.00$, similarly as the EPR spectrum arising from the high spin ground state of the iron(III) ion. The peak-to-peak linewidth ΔH_{pp} and integrated intensity I, defined as the product of the signal amplitude and the square of the peak-to-peak linewidth, strongly depend on the kind of M(II) ion in the crystal matrix. An EPR study of the $M_2FeV_3O_{11}$ (M = Ni(II), Zn(II), Mg(II), Co(II)) system has shown that the coexistence of two different magnetic ions in the lattice (Ni(II)–Fe(III) or Co(II)–Fe(III)) induces the absence of an EPR signal in the high spin iron(III) ions [12]. For the $Co_2FeV_3O_{11}$ sample, no EPR signal was recorded, while for the $Ni_2FeV_3O_{11}$ compound the EPR spectrum was dominated by the exchange coupled vanadium(IV) ions [13]. The coexistence of magnetic iron(III) ions with nonmagnetic ions (Zn and Mg) in the above samples manifests itself in the EPR spectra through the variation of the integrated intensity (Table 3), while the disorder phenomena between magnetic and nonmagnetic ions take place. It has been suggested that the disorder processes of iron atoms with zinc atoms in the $Zn_2FeV_3O_{11}$ compound could be responsible for the significant differences observed in its physical properties, influenced by the method of sample preparation [2, 5, 6].

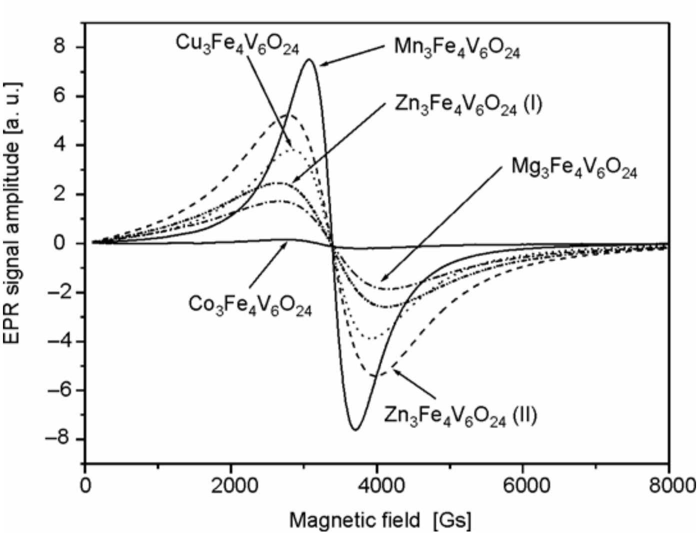

Fig. 1. The EPR spectra of all investigated samples at room temperature

Neutron diffraction of $Zn_2FeV_3O_{11}$ powder has shown that the iron(III) and zinc(II) ions are disordered in their corresponding sublattices, and that the distribution on the octahedral and the trigonal bipyramidal sites is non-statistical. A Mössbauer spectroscopy study has found that some cations are disordered between the octahedral iron and the fivefold coordinated copper site in the β-$Cu_3Fe_4V_6O_{24}$ compound [10]. In contrast, neutron diffraction analysis of the $Zn_3Fe_4V_6O_{24}$ system has shown that iron atoms are not disordered with zinc atoms on any sites in this material [11]. The simultaneous existence of magnetic dimers and of triangular cationic topology around some sites has incited us to explore the magnetic behaviour and possible frustration effects in these compounds. For the polycrystalline β-$Cu_3Fe_4V_6O_{24}$, the inverse magnetic susceptibility varies linearly with temperature in the 250–20 K range and has a negative Curie–Weiss temperature Θ (–80 K), which indicates the presence of antiferromagnetic interactions in this substance [10].

Table 3. EPR parameters at room temperature for some compounds of the multicomponent vanadate oxide system

Compound	Linewidth ΔH_{pp} [kGs]	Resonance field		Integrated intensity I [a. u.]
		H_r [kGs]	g	
$Mg_3Fe_4V_6O_{24}$	1.498(5)	3.382(4)	1.999(1)	91.5
$Mn_3Fe_4V_6O_{24}$	0.636(5)	3.386(4)	1.997(1)	69.2
$Zn_3Fe_4V_6O_{24}$ (I)	1.524(5)	3.362(4)	2.010(1)	133.1
$Zn_3Fe_4V_6O_{24}$ (II)	1.204(5)	3.376(4)	2.002(1)	174.9
$Co_3Fe_4V_6O_{24}$	1.052(5)	3.193(4)	2.117(1)	4.5
$Cu_3Fe_4V_6O_{24}$	1.094(5)	3.373(4)	2.005(1)	104.6
$Mg_2FeV_3O_{11}$	1.527(5)	3.380(1)	2.000(1)	–
$Zn_2FeV_3O_{11}$	1.449(5)	3.375(1)	2.004(1)	–

For the $Co_3Fe_4V_6O_{24}$ compound, a weak EPR line, shifted towards lower magnetic fields, is observed. This could be the result of interaction between iron(III) ions and highly magnetic cobalt(II) ions. A similar trend was observed for other samples with two different magnetic ions (Mn(II) and Cu(II)), in which the linewidths and intensities are influenced (Table 3).

The differences in the parameters of the EPR spectra for two samples of $Zn_3Fe_4V_6O_{24}$ prepared using different thermal annealing processes could arise from the inherent disorder or from presumed oxygen deficiency. The effects of disorder processes, seen by the EPR spectroscopy, could not be recorded by neutron diffraction measurements.

4. Conclusions

$M_3Fe_4V_6O_{24}$ compounds were synthesized from appropriate oxides and EPR measurements have been carried out at room temperature. An analysis of the EPR spectra was done using Lorentzian-type functions. The observed differences in the crystallographic parameters of these compounds did not have a major influence on the recorded EPR parameters. We observe that the coexistence of two different magnetic ions in the lattice has a strong influence on the EPR spectrum.

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