

EPR STUDY OF THREE GADOLINIUM(III) TUNGSTATES

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Abstract. Three gadolinium(III) tungstates ($\text{II-Gd}_2\text{WO}_6$, $\text{CoGd}_4\text{W}_3\text{O}_{16}$, and $\text{ZnGd}_4\text{W}_3\text{O}_{16}$) have been prepared by the solid-state reaction method using stoichiometric mixtures of the WO_3 , Gd_2O_3 , CoWO_4 or ZnWO_4 . The EPR measurements have been done at room temperature for all three samples. A very intense asymmetric EPR line of gadolinium(III) ions has been recorded. The intensity and the linewidth essentially depended on the metal (M(II)=Co(II) and Zn(II)) ions in the crystalline matrix. The difference of the linewidth and intensities is arising from magnetic interactions between magnetic ions, especially for the system with coexisting two different magnetic ions. It was estimated that the exchange field in the $\text{II-Gd}_2\text{WO}_6$ and $\alpha\text{-Fe}_2\text{WO}_6$ systems is similar but differs significantly in its polymorphic modification. For new divalent metal and gadolinium(III) tungstates ($\text{CoGd}_4\text{W}_3\text{O}_{16}$ and $\text{ZnGd}_4\text{W}_3\text{O}_{16}$) the exchange field is modified by about 6% after substitution of metal(II) magnetic ions for a non magnetic ion.

1. INTRODUCTION

The tungstate oxide materials containing rare earth(III) ions have been studied very extensively due to their extraordinary optical properties [1-3]. Gd_2WO_6 could form two polymorphic modifications ($\text{II-Gd}_2\text{WO}_6$ and $\text{V-Gd}_2\text{WO}_6$) with different crystallographic structures (monoclinic and orthorhombic). There are problems in finding physical processes responsible for their behaviour [4]. Iron(III) tungstate oxide Fe_2WO_6 could form three different polymorphic modification with different lattice constants [5-7]. The main role in the crystallographic structure determination and existence of many physical modification is connected with replacement of metallic

ions(III) of iron(III) by rare earth(III). It is well known that the wave functions of rare earths are localised while for iron ion they are extended. The electron paramagnetic resonance (EPR) investigations of three modification of iron(III) tungstate oxide Fe_2WO_6 have shown a strong differences in the EPR spectra, mainly in the linewidth and intensity. These differences stems from essential modifications of magnetic interactions between them [6-9]. Due to their $^8\text{S}_{7/2}$ ground state with small orbital contribution from the excited state, gadolinium(III) ions are most suitable for EPR studies which can provide valuable information on the static and dynamic interaction among the gadolinium(III) and its host system.

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The aim of this paper is to report on preparation by using the solid-state reaction method of gadolinium(III) tungstate ($\text{II-Gd}_2\text{WO}_6$) and two new zinc (cobalt) gadolinium tungstates with the following formulas: $\text{CoGd}_4\text{W}_3\text{O}_{16}$, and $\text{ZnGd}_4\text{W}_3\text{O}_{16}$ as well as to study the magnetic interactions in these compounds by the EPR spectroscopy.

2. EXPERIMENTAL

Three samples of tungstates with gadolinium(III) ions, i.e. $\text{II-Gd}_2\text{WO}_6$, $\text{CoGd}_4\text{W}_3\text{O}_{16}$, and $\text{ZnGd}_4\text{W}_3\text{O}_{16}$ have been prepared by the solid-state reaction method using stoichiometric $\text{WO}_3/\text{Gd}_2\text{O}_3$, $\text{WO}_3/\text{Gd}_2\text{O}_3/\text{MWO}_4$ ($\text{M}=\text{Co}, \text{Zn}$) mixtures. Additionally, during thermal annealing process an equimolar mixture of $\text{CoGd}_4\text{W}_3\text{O}_{16}$ and $\text{Co}_2\text{Gd}_2\text{W}_3\text{O}_{14}$ (other compounds existing in $\text{CoWO}_4\text{-Gd}_2\text{WO}_6$ system) has been obtained. The gadolinium(III) tungstate ($\text{II-Gd}_2\text{WO}_6$) has been synthesised according to procedure described in [4]. It has been obtained by thermal annealing in air atmosphere of WO_3 and Gd_2O_3 oxides mixed at the molar ratio of 1:1, at the temperature of 1100°C during 24 hours. In this condition, $\text{II-Gd}_2\text{WO}_6$ compound was obtained by the following reaction: $\text{WO}_{3(s)} + \text{Gd}_2\text{O}_{3(s)} = \text{II-Gd}_2\text{WO}_{6(s)}$. This material could form two different polymorphic phases, one monoclinic (C2/c) with the lattice parameters: $a=16.38(2) \text{ \AA}$; $b=11.159(2) \text{ \AA}$; $c=5.42(2) \text{ \AA}$; $\beta=107.63(2)^\circ$; $Z=8$ and $d_{\text{rtg}}=8.362 \text{ g/cm}^3$ and the other orthorhombic ($\text{P2}_1\text{2}_1\text{2}_1$) with $a=5.278(1) \text{ \AA}$; $b=9.116(2) \text{ \AA}$; $c=10.012(3) \text{ \AA}$; $Z=4$ and $d_{\text{rtg}}=8.195 \text{ g/cm}^3$ [4].

$\text{II-Gd}_2\text{WO}_6$ has been used for preparation of new divalent metal and gadolinium(III) tungstates with the formula: $\text{MGd}_4\text{W}_3\text{O}_{16}$ ($\text{M}=\text{Zn}$ and Co). The synthesis of Co-contained compound has been carried out according to the reaction: $\text{CoWO}_{4(s)} + 2 \text{II-Gd}_2\text{WO}_{6(s)} \rightarrow \text{CoGd}_4\text{W}_3\text{O}_{16(s)}$. Thermal annealing was made in air atmosphere at the temperatures: 800°C for 12 hrs, 900°C for 12 hrs, 1000°C for 12 hrs, and 1100°C for twice 12 hrs.

For synthesis of the $\text{ZnGd}_4\text{W}_3\text{O}_{16}$ compound, the following procedure has been carried out: $\text{ZnWO}_4/2 \text{II-Gd}_2\text{WO}_6$ mixture was annealed in air atmosphere, at the temperatures: 800°C for 12 hrs, 900°C for 12 hrs, 1000°C for 12 hrs, and 1075°C for 12 hrs by using the following reaction: $\text{ZnWO}_{4(s)} + 2 \text{II-Gd}_2\text{WO}_{6(s)} = \text{ZnGd}_4\text{W}_3\text{O}_{16(s)}$. Indexing procedure of $\text{ZnGd}_4\text{W}_3\text{O}_{16}$ powder diffraction pattern has shown that it crystallizes in the orthorhombic system with the following lattice parameters: $a=17.5458(4) \text{ \AA}$; $b=7.3644(0) \text{ \AA}$; $c=7.2683(3) \text{ \AA}$, $Z=3$ and density $d_{\text{exp}}=7.97 \text{ g/cm}^3$ ($d_{\text{rtg}}=7.96 \text{ g/cm}^3$). On the basis of

XRD and IR studies it was found that $\text{ZnGd}_4\text{W}_3\text{O}_{16}$ and $\text{CoGd}_4\text{W}_3\text{O}_{16}$ are isostructural.

The EPR spectra were recorded using a conventional X-band spectrometer produced by the BRUKER type 500 E, with the magnetic field modulation of 100 kHz. The magnetic field was scaled with a usual NMR technique. The sample, containing 30 mg of substance in the form of fine powder without any cement-dielectric, was placed into a 2 mm diameter quartz tubes. The measurements were done at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 presents the EPR spectra of $\text{II-Gd}_2\text{WO}_6$, $\text{CoGd}_4\text{W}_3\text{O}_{16}$, $\text{ZnGd}_4\text{W}_3\text{O}_{16}$, and $\text{Co}_2\text{Gd}_2\text{W}_3\text{O}_{14}/\text{CoGd}_4\text{W}_3\text{O}_{16}$ mixture at room temperature. A very intense and broad EPR resonance line is observed with a strongly asymmetric lineshape for all investigated samples. Strongly asymmetric line is the result of specific broadening of the EPR spectrum. The main part of EPR spectrum is arising from the high-spin state ($S=7/2$) of gadolinium(III) ions with the ground state $^8S_{7/2}$. The derivative EPR spectra of all samples were fitted to a full Lorentzian line comprising the tail of the resonance absorption at negative field, a consequence of the linear polarised radio frequency field that is important when the width becomes comparable to the resonance field. The obtained EPR parameters (resonance field H_r , peak-to-peak linewidth ΔH_{pp} , signal amplitude I_{pp} , and the integrated intensity I_{in}) obtained from the least-squares fitting procedure are given in Table 1. For the mixture of $\text{Co}_2\text{Gd}_2\text{W}_3\text{O}_{14} + \text{CoGd}_4\text{W}_3\text{O}_{16}$ from EPR study it was estimated that this mixture is dominated by $\text{CoGd}_4\text{W}_3\text{O}_{16}$ compound in 89 %.

All EPR parameters of gadolinium(III) essentially depend on type of the matrix and on kind of replaced metal ion (M(II)). The g -value for an isolated (or doped) gadolinium(III) in the matrix is usually below $g < 2.000$, but for the powder and in the bulk state it becomes $g > 2.00$ [10]. Introduction of additional metal ions could make further increase of this value [11]. The polymorphic different phases of the magnetic S -state ions could provide for changing the strong g -value, e.g. high spin iron(III) ions (Table 1), where analytical relation is similar to $\text{II-Gd}_2\text{WO}_6$ (Fe_2WO_6). The wave function of the rare earth(III) ions is more localised than for iron(III) ions and thus the physical properties could be different, in particular magnetic interaction in the system could be modified significantly. The position of the resonance lines are similar in both systems with iron(III) and gadolinium(III).

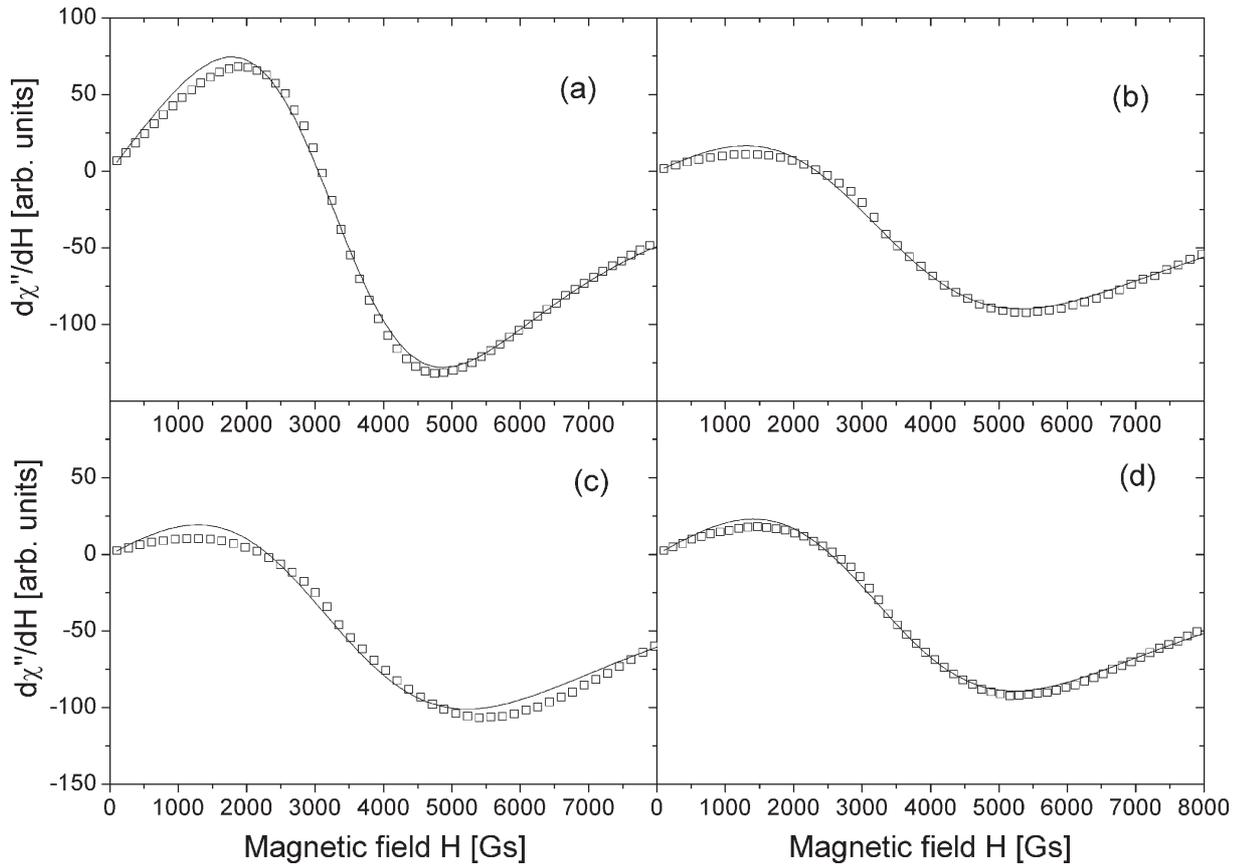


Fig. 1. The EPR spectra at room temperature for compounds: II-Gd₂WO₆ (a), CoGd₄W₃O₁₆ (b), ZnGd₄W₃O₁₆ (c), and 11%Co₂Gd₂W₃O₁₄+89%CoGd₄W₃O₁₆ (d). Empty squares – experimental points, solid line – fitted line.

Table 1. EPR parameters of tungstate compounds.

Compound	Resonance field		Linewidth ΔH_{pp} [Gs]	Intensity [arb. units]	
	H_r [Gs]	g_{eff}		I_{pp}	I_{in}
II-Gd ₂ WO ₆	3247(6)	2.008(5)	3380(7)	11.52	13.16
Co ₂ Gd ₂ W ₃ O ₁₄ +	3151(7)	2.069(7)	4591(9)	7.40	15.60
CoGd ₄ W ₃ O ₁₆					
CoGd ₄ W ₃ O ₁₆	3131(7)	2.082(6)	4815(9)	7.25	16.81
ZnGd ₄ W ₃ O ₁₆	3082(8)	2.116(5)	4791(9)	8.20	18.82
α -Fe ₂ WO ₆	3260(9)	2.000(1)	2000(10)	12.51	5.00 [3]
β -Fe ₂ WO ₆	3161(9)	2.111(1)	4100(10)	3.91	6.57 [2]

Strong differences are observed in values of other EPR parameters (linewidth and intensities). The EPR signal amplitude I_{pp} has decreased strongly with changing of matrix from a Gd₂WO₆ system to MGd₄W₃O₁₆ system, while the integrated intensity, $I_{in} = I_{pp}(\Delta H_{pp})^2$, which is proportional to the static magnetic susceptibility, has behaved oppositely and increased essentially (Table 1). For the mixture system, 11%Co₂Gd₂W₃O₁₄+89%CoGd₄W₃O₁₆, which

is dominated by the CoGd₄W₃O₁₆ compound, the position of resonance line and intensity I_{pp} is almost similar as for the bulk compound (Table 1).

The linewidth ΔH_{pp} was 1.3-15 times greater for the system MGd₄W₃O₁₆ than the system II-Gd₂WO₆ what suggests stronger magnetic interactions. Only small differences are recorded for the MGd₄W₃O₁₆ system, where the magnetic cobalt(II) ion is replaced by diamagnetic zinc(II) ion.

The presence of dipolar and isotropic exchange interactions results in an exchange narrowed resonance line with Lorentzian lineshape in the center of the line [10,11]. The peak-to-peak width of the resonance line would be approximately given by relation: $\Delta H_{pp} = 2 M_{2d}/\sqrt{3} H_{ex}$, where M_{2d} is the contribution of dipole interaction to the second moment of resonance line from the truncated dipolar hamiltonian and H_{ex} is the exchange field. Taking the power average, the second moment of resonance line could be written as: $M_{2d} = 3/4 S(S+1)g^4 \mu_B^4 \sum_j 1/r_{jk}^6$, where r_{jk} is the distance between the j and k spins and the S is spin ($S=5/2$ for iron(III) ions and $S=7/2$ for gadolinium(III) ions). The ratio of values of the linewidth for $\alpha\text{-Fe}_2\text{WO}_6$ and $\text{II-Gd}_2\text{WO}_6$ compounds is 1.7 and it is in good agreement with the ratio $[S_{Gd}(S_{Gd}+1)]/[S_{Fe}(S_{Fe}+1)]=1.8$ where g and $\sum_j 1/r_{jk}^6$ parameters are almost similar. Thus the differences of the exchange fields between these two systems will be about 6%. For two different phases $\beta\text{-Fe}_2\text{WO}_6$ and $\alpha\text{-Fe}_2\text{WO}_6$ the ratio of linewidth ΔH_{pp} is 2.05 while the ratio of g^4 factor is 1.3 and the effect of the exchange field is greater. Using the above relation for estimation of magnetic interaction for the $\text{MGd}_4\text{W}_3\text{O}_{16}$ system the following value for $(\Delta H_{ppCo}/\Delta H_{ppZn})/(g_{Zn}^4/g_{Co}^4)\sim 0.94$ is obtained and thus the exchange field for the sample with cobalt(II) changed by about 6%.

4. CONCLUSIONS

It was estimated that the tungstates with gadolinium(III) and iron(III) ions in their polymorphic modifications, $\text{II-Gd}_2\text{WO}_6$ and $\beta\text{-Fe}_2\text{WO}_6$, have shown similar exchange field while in other polymorphic phases the substitution of Gd for Fe could have a strong influence on magnetic interactions. The new $\text{CoGd}_4\text{W}_3\text{O}_{16}$ and $\text{ZnGd}_4\text{W}_3\text{O}_{16}$ compounds with magnetic and non-magnetic metal(II) ions have shown differences in all EPR parameters. Substitution of Co for Zn have resulted in decreasing of magnetic interactions by about 6%.

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