Comparative study of structural, optical and magnetic properties of Fe–Pt, Fe–Cu and Fe–Pd-codoped WO₃ nanocrystalline ceramics: effect of annealing in hydrogen atmosphere

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Abstract. Tungsten oxide (W-oxide) nanoparticles doped and codoped with different transition-metal (TM) ions (Fe, Pt, Cu and Pd) were synthesized by hydrochloric acid-assisted precipitation. The synthesized powders were characterized by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) and magnetic characterization methods. The room temperature (RT) monoclinic (P21/n) structure founded for pristine WO₃ nanopowder was converted into orthorhombic (Pbam) structure by Fe-doping, while codoping, (Fe–Pt) and (Fe–Cu) preserved the P21/n space group (SG) structure. It was found that the hydrogenation of the synthesized doped-samples corroded the crystallites without changing the crystalline SG structure. Moreover, controllable room temperature ferromagnetic (RT-FM) properties were created by hydrogenation of the codoped W-oxide samples. The oxygen vacancies-mediated ferromagnetic (FM) interaction could be responsible for the observed FM. The relative highest RT-FM energy was created with hydrogenated Fe–Pd codoped W-oxide. Therefore, Fe–Pd-codoped W-oxide nanopowder could be considered as a potential candidate for many applications involving partial FM properties, such as catalysts and optical phosphors.

Keywords. TM-doped WO₃; created ferromagnetism; hydrogen treatment.

1. Introduction

Among metal oxides, tungsten oxide (W-oxide) has exceptionally great crystal-structural properties of many different polymorphs depending on the synthesis conditions, which control the oxygen stoichiometry content in the oxide. Thus, multiple crystalline structures called as Magneli structures (i.e., phases contain structural O-vacancies) of type WO_x ($x = 2.625\text{--}2.92$) as well as to standard WO₃ were synthesized [1–3].

The polymorphs in W-oxide were observed not only with the different stoichiometric compositions, but also with temperature range of the sample, such as by heating of W-oxide, triclinic (P-1), monoclinic (P21/n), orthorhombic (Pbcn), etc. could be obtained depending on the temperature range [1]. Through controlling the physical properties of W-oxide ceramic by its crystalline structure, one can expect multiple diverse applications in different fields, like optoelectronic, photocatalytic, photoluminescence, electrochromic, gasochromic, gas-sensing technology, etc. [4–10]. Hence, method of synthesis of pristine and doped W-oxide powder is considered very important in the fields of applications. Therefore, many methods of synthesis of powder W-oxide ceramic like sol–gel, hydrothermal; acidification, etc. were utilized [11–15].

To create different exotic properties like stable room temperature ferromagnetic (RT-FM), doping of W-oxide with different magnetic metallic ions under different synthetic conditions was conducted. In addition, create RT-FM properties in W-oxide ceramic includes a suitable control on the crystalline electronic medium (CEM) of the W-oxide crystal, through which spin–spin (S–S) exchange interaction between dopant magnetic ions could take place. Creation of oxygen (O) vacancies (V_O) in W-oxide crystalline medium is considered as one of the ways necessary to keep up the magnetic role in CEM for superexchange interactions. According to the bound magnetic polarons (BMP) theory [16,17], the O-vacancies bound some polarons as tools for the S–S superexchange coupling of the dopant ions producing FM ordering. Those structural O-vacancies could be created by annealing of W-oxide in H₂ gas (hydrogenation) atmosphere under some chosen circumstances, including temperature, duration and type/amount of dopant-catalyst ions necessary to dissociate hydrogen molecules (H₂) into atoms/ions [18,19]. The dissociation stimulates interaction of H-atoms/ions with the structural oxygen of W-oxide creating O-vacancies. Some of the transition metal (TM) ions are known to have a catalytic effect for hydrogen dissociation [10–21]. Therefore, Pt, Cu and Pd ions were used, in the present work, as dopants in synthesized W-oxide nanopowder for hydrogen dissociation,

while Fe ions were used on all the samples as FM sources. It is worth mentioning that almost similar work on WO_3 nanoparticles doped with Mn ions was recently published in ref. [22], which showed that dopant Mn^{2+} could not convert the original monoclinic (P21/n) structure of WO_3 into one of its Magneli phases.

2. Synthesis of samples and experimental procedure

W-oxide nanoparticles doped with impurities of Fe ions (referred as $\text{WO}_3\text{:Fe}$) and codoped with Fe–Pt ions ($\text{WO}_3\text{:Fe:Pt}$), Fe–Cu ions ($\text{WO}_3\text{:Fe:Cu}$), and Fe–Pd ions ($\text{WO}_3\text{:Fe:Pd}$) were synthesized by hydrochloric acid-assisted precipitation method, followed by thermal calcinations. The starting material of synthesis of W-oxide powder was pure sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) powder. The starting materials supplying dopant ions were of analytical grade fine powders of iron(III) hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Pt(IV) oxide hydrate ($\text{PtO}_2 \cdot \text{H}_2\text{O}$), Copper(II) acetylacetonate (abb. $\text{Cu}(\text{acac})_2$) and Pd dimethylglyoxime (abb. $\text{Pd}(\text{dmg})_2$) (from Sigma-Aldrich). Analytical grade methanol and hydrochloric acid (HCl) were also used in the following synthesis procedure. A certain controlled amount of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ fine powder was dissolved in ~ 20 ml of dilute HCl ($\sim 3\%$) acid in a ceramic bowl with continuous magnetic stirring, forming solution 1. A certain fixed amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ fine powder was totally dissolved in some small amount of methanol to get a yellow solution 2, which was added to solution 1 with continuous stirring forming solution 12. To synthesize $\text{WO}_3\text{:Fe}$, the magnetic stirring at room temperature (RT) continued for ~ 50 h and finally, the formed precipitate was collected by filtering and washed 3–4 times by double de-ionized distilled water. To synthesize the codoped W-oxide (i.e., $\text{WO}_3\text{:Fe:Pd}$ and $\text{WO}_3\text{:Fe:Cu}$), a controlled amount of each $\text{Pd}(\text{dmg})_2$ and $\text{Cu}(\text{acac})_2$ was totally dissolved in small amount of methanol and then, added to solution 12 with continuous stirring. However, to synthesize $\text{WO}_3\text{:Fe:Pt}$, a controlled amount of a very fine $\text{PtO}_2 \cdot \text{H}_2\text{O}$ powder was dissolved in small amount of concentric HCl acid with the help of ultrasonic vibration (using a Chromtech ultrasonic cleaner) and then, added to solution 12 with continuous magnetic stirring at room temperature. In all the cases of codoping of W-oxide, the magnetic stirring prolonged for ~ 50 h at RT, however, the temperature was raised up to $\sim 70^\circ\text{C}$ during the last 2 h. Finally, the formed precipitate was collected by filtering and washed 3–4 times with double de-ionized distilled water. The last amorphous precipitated paste was flash-calcined in a closed oven at 500°C for 2 h, followed by natural cooling to RT. For synthesis of a reference pristine WO_3 , only solution 1 was used. The calculation shows that the molar ratio of Fe/W was ~ 7.6 at% for all the samples and the molar ratios of each Pt/W, Pd/W and Cu/W was ~ 0.2 at%. Part of each synthesized powders was hydrogenated at 400°C for 30 min to induce oxygen O-vacancies for magnetic studies.

The X-ray diffraction (XRD) method was used to investigate the crystalline structures of the synthesized powders by using a Rigaku Ultima-VI diffractometer with $\text{CuK}\alpha$ radiation and a step size of 0.02° . The structural analyses, including lattice parameters and crystallite size (CS) were carried out with built-in PDXL software by Rietveld refinement and Williamson–Hall methods, respectively. The UV–Vis optical properties of the prepared powders in the range of 200–700 nm were studied by diffuse reflectance spectroscopy (DRS) with a Shimadzu UV-3600 double beam spectrophotometer equipped with an integrating sphere. The magnetic properties at RT were measured by a vibrating sample magnetometer (VSM) type Micro-Mag Model 3900 of sensitivity of $0.5 \mu\text{emu}$ on a 1 s averaging time scale.

3. Results and discussion

3.1 Structural characterization

Figure 1a presents the XRD patterns of the as-synthesized M-doped W-oxide samples (where M stands for Fe–, Fe–Pt, Fe–Cu and Fe–Pd) with reference pristine WO_3 powder synthesized by the same procedure. The structural analyses, including lattice parameters and crystallite size (CS) were obtained by the Rietveld refinement method and Williamson–Hall method, respectively (table 1). The refinement parameters (R_{wp} (%); R_{p} (%); R_{e} (%); and $S = R_{\text{wp}}/R_{\text{e}}$) given in table 1a show high, but reasonable fittings [23].

The lattice parameters of pristine WO_3 sample are very close to those previously known at RT of monoclinic ($\text{P}2_1/\text{n}(14)$) structure; $a = 0.730$ nm, $b = 0.753$ nm, $c = 0.768$ nm and $\beta = 90^\circ 54'$ [24]. The smallest fitting value of goodness-of-fit parameter, S (1.62) refers to the formation of a single pristine WO_3 phase. The characteristic main peaks in the monoclinic ($\text{P}2_1/\text{n}$) phase that ascribed to Miller indices (002), (020) and (200) lay in the angular range $2\theta = 23\text{--}24^\circ$.

The results of the present work show that the qualitative variation in the crystalline structure to one of Magneli forms [3] could be induced by Fe-doping or by codoping with Fe/Pd. By using the built-in PDXL software, that Magneli phase was identified to be mainly close to $\text{W}_{32}\text{O}_{84}$ ($\text{WO}_{2.625}$) orthorhombic phase (Pbam (55)).

Therefore, two types of crystalline structures were formed. Pristine WO_3 , $\text{WO}_3\text{:Fe:Pt}$ and $\text{WO}_3\text{:Fe:Cu}$ samples have quasi-cubic monoclinic ($\text{P}2_1/\text{n}$) structure (JCPDS 83-0950: $a = 7.3008 \text{ \AA}$, $b = 7.5389 \text{ \AA}$, $c = 7.6896 \text{ \AA}$, $\beta = 90.892^\circ$, space group (SG): $\text{P}2_1/\text{n}$ [25]). While $\text{WO}_3\text{:Fe}$ and $\text{WO}_3\text{:Fe:Pd}$ samples were crystallized in orthorhombic structure ($\text{W}_{32}\text{O}_{84}$ structure of $a = 21.431(9) \text{ \AA}$, $b = 17.766(7) \text{ \AA}$, $c = 3.783(2) \text{ \AA}$, SG = Pbam [26]). This phenomenon can be explained as follows; it is known that the crystalline structure and the SG of W-oxide sensitive to the abundance of structural O-vacancies. Therefore, in the present case, the total oxidized tungsten oxide (WO_3) of monoclinic ($\text{P}2_1/\text{n}$) structure could be transformed into orthorhombic (Pbam) structure of

Figure 1. XRD of the (a) as-synthesized and (b) hydrogenated pristine and doped WO_3 samples. (c) Fitting Rietveld plot of $\text{WO}_3\text{:Fe}$ sample.

Table 1. Structural analyses: **(a)** Crystallite size (CS), band gap (E_g) and Rietveld refinement quality parameters (R_{wp} , R_p , R_e and S). **(b)** Major SG, lattice parameters (a , b , c in Å, and α , β , γ in deg.) and unit cell volume (V_{cell} in Å³).

(a)						
Sample	CS (nm)	E_g (eV)	Refinement parameters			
			R_{wp} (%)	R_p (%)	R_e (%)	S
WO ₃	9.4	3.1	26.19	21.18	16.13	1.6241
WO ₃ :Fe	17.1	2.6	32.36	25.59	12.63	2.561
WO ₃ :Fe:Pt	11.4	3.0	29.21	24.01	10.49	2.785
WO ₃ :Fe:Cu	15.8	2.8	23.3	18.81	10.16	2.2941
WO ₃ :Fe:Pd	15.3	2.5	34.65	27.88	12.16	2.8485
<i>Hydrogenated samples</i>						
WO ₃ -H	11.9	2.92	25.39	20.37	15.18	1.6726
WO ₃ :Fe-H	11.5	3.0	27.74	21.7	11.45	2.4227
WO ₃ :Fe:Pt-H	7.0	3.2	19.8	15.88	10.5	1.8862
WO ₃ :Fe:Cu-H	9.1	3.16	19.12	15.39	12.82	1.4917
WO ₃ :Fe:Pd-H	10.7	3.14	33.51	26.91	10.74	3.1192

(b)								
Sample	Major-SG	Lattice parameters						V_{cell}
		a	b	c	α	β	γ	
WO ₃	P21/n	7.311(3)	7.518(3)	7.676(3)	90	90.801(19)	90	421.8(3)
WO ₃ :Fe	Pbam	20.27(5)	16.79(3)	3.831(4)	90	90	90	1304(4)
WO ₃ :Fe:Pt	P21/n	7.300(5)	7.480(5)	7.641(5)	90	90.60(5)	90	417.2(5)
WO ₃ :Fe:Cu	P21/n	7.323(2)	7.520(2)	7.682(2)	90	90.74(2)	90	423.0(2)
WO ₃ :Fe:Pd	Pbam	19.95(4)	17.24(3)	3.854(6)	90	90	90	1325(4)
<i>Hydrogenated samples</i>								
WO ₃ -H	P21/n	7.315(3)	7.497(3)	7.667(3)	90	90.76(2)	90	420.4(3)
WO ₃ :Fe-H	Pbam	20.23(7)	17.09(6)	3.861(7)	90	90	90	1335(7)
WO ₃ :Fe:Pt-H	P21/n	7.596(12)	7.692(13)	7.648(10)	90	89.49(14)	90	446.9(12)
WO ₃ :Fe:Cu-H	P21/n	7.330(3)	7.516(3)	7.684(3)	90	90.80(3)	90	423.3(3)
WO ₃ :Fe:Pd-H	Pbam	20.85(4)	17.22(2)	3.809(4)	90	90	90	1368(3)

chemical formula W₃₂O₈₄ or WO_{2.625} by creation of O-vacancies, which happened in the case of Fe and Pd dopants (figure 1). The S-values obtained for the incorporated W-oxide (table 1a) were about 2–3, referring to the crystallization in non-pure Magneli phase in addition to the effects of nanograin size, point-defect vacancies and crystallite boundaries. Moreover, values of parameters R_{wp} and R_p are of the order 0.2–0.3, which are reasonably comparable to those data of single WO₃ phase. As an example, figure 1c shows one of the Rietveld plots for WO₃:Fe sample. In general, it was concluded that the transformation of natural monoclinic crystalline structure of WO₃ to orthorhombic (W₃₂O₈₄) phase structure depends on all doping details accompanied with Fe³⁺ ions doping, as presented in table 1b.

The hydrogenation in the present conditions could not change the SG of the crystalline structure. Therefore, the increase in concentration of O-vacancies by hydrogenation was not much enough to change the SG, however, it could create/enhance the ferromagnetic properties of hydrogenated samples (later sections).

The calculated lattice parameters of monoclinic (P21/n) structures as given in table 1b are about the known parameters of pristine WO₃. However, the hydrogenation increases the unit cell volume due to creation of O-vacancies.

As given in table 1a, the effective nanocrystallite sizes (CS) of the synthesized host W-oxide samples were ~10–17 nm. The CS of host W-oxide slightly increased with doping, while it was slightly decreased by hydrogenation (corrosion of crystallites).

Finally, it is necessary to emphasize that the lack of peaks associated to dopant Fe, Pt, Cu and Pd-related phases confirms that the synthesized powders were mono-phase materials, as shown in figure 1. This observation along with other observations related to CS and SG suggest that the incorporated ions were dissolved in host W-oxide lattice or accumulated on crystallite boundaries (CBs) and thus, did not form isolated nanograins revealing the form of single phase.

As the common incorporated Fe³⁺ ion has a radius (0.064 nm) close to that of W⁶⁺ in WO₃ (0.06 nm [27]), dopant Fe³⁺ ions could substitute for W⁶⁺ ions in W-oxide

without large distortion in the crystalline structure and, thus, forming a substitutional solid solution (SSS). The crystalline structure of the formed SSS was orthorhombic (Pbam) of formula WO_{3-x} ($x = 0.375$) due to creation of abundance of O-vacancies for the charge electrostatic neutrality of the unit cell. As, other dopant ions Pt^{2+} (0.08 nm), Cu^{2+} (0.073 nm), and Pd^{2+} (0.086 nm) have a larger size than that of W^{6+} , then, the nature of the most probable incorporation is the occupation positions on CBs and slightly occupying interstitial place, but they could not form SSS by geometrical reason, as stated by Hume-Rothery rules [28]. The present results show that the co-presence of dopant Pt or Cu ions with Fe ions resists formation of orthorhombic ($\text{WFeO}_{2.625}$) SSS phase and therefore, the sample crystallizes in WO_3 monoclinic structure as shown in figure 1.

3.2 Optical characterization

The optical properties of the synthesized powders were investigated by the DRS technique. The spectral DR is related to the sample absorption coefficient (α) through Kubelka–Munk (K–M) equation [29]:

$$\frac{\alpha(\lambda)}{S} = F(\lambda) = \frac{[1 - R_\infty(\lambda)]^2}{2R_\infty(\lambda)}, \quad (1)$$

where S is the scattering coefficient, $R_\infty(\lambda)$ the measured spectral DR for a thick powder sample, and $F(\lambda)$ the K–M absorption function. The coefficient S is considered almost constant, therefore, $F(\lambda) \sim \alpha(\lambda)$. The spectral absorption $F(\lambda)$ of the as-synthesised samples in the range of 200–700 nm, are shown in figure 2a. The samples are transparent for $\lambda > 400$ nm. However, great changes in the spectral absorption $F(\lambda)$ were happening with hydrogenation as shown in figure 2b. The absorption spectrum $F(\lambda)$ was strongly enhanced in the Vis–NIR spectral regions, especially for W-oxide samples incorporated by Fe, (Fe–Pt) and (Fe–Pd) ions. This can be attributed to the formation of O-vacancies behaving as scattering/absorption point defects; similar results obtained by ref. [30]. Also, it was observed [31] that WO_3 samples prepared under lower oxygen pressure exhibit an increase in their absorbance, like in figure 2b, comparing with those samples prepared under higher oxygen pressure. Thus, the created O-vacancies energetically can be described by energy levels formed in the band gap of host W-oxide [32]. This situation totally changed the absorption spectrum $F(\lambda)$ as shown in figure 2b.

The optical transitions in monoclinic $\gamma\text{-WO}_3$ were measured and calculated by Johansson *et al* in ref. [33] to be mainly direct, therefore, the following Tauc equation can be used to estimate the direct band gap (E_g) of the host W-oxides [34]:

$$(F(\lambda) \cdot E)^2 = A_{\text{op}}(E - E_g), \quad (2)$$

Figure 2. Spectral diffuse absorption coefficient ($F(\lambda)$) of the (a) as-synthesized and (b) hydrogenated pristine and doped WO_3 samples.

where A_{op} is the sample constant and $E = h\nu$ the photon energy. Thus, the extrapolation of the straight-line portion of $(F(\lambda) \cdot E)^2$ vs. E plot to the line of the axis $F(\lambda) = 0$ gives the value of E_g as shown in figure 3a and table 1a. The inset of figure 3a shows the Tauc plot for the band gap of un-doped WO_3 . The obtained band gap of un-doped WO_3 (3.1 eV) agrees well with known values for pristine WO_3 powder synthesized by different methods [35].

The variation in energy band structure (EBS) due to Fe-doping was calculated by density-functional theory (DFT) [36]. Thus, it was established red shift of the band gap as a result of the slight shift of valence band maximum (VBM) to higher energy and significant lowering of the conduction band minimum (CBM) by formation of Fe-impurity band as an extension to CBM in the band gap, thereby, reducing the band gap energy. The band gap of WO_3 doped with $\sim 7.6\%$ Fe was 2.6 eV in the present work (table 1a) is very close to that value (2.67 eV) obtained in ref. [36].

Figure 3. Tauc plot for the (a) as-synthesized and (b) hydrogenated pristine (inset) and doped WO_3 samples.

In the present work, it is observed that with Fe-doping and codoping, the band gap of the host W-oxide was red-shifted of value depends on the dopant type. In summary, the band gap red shift is attributed to variation in the EBS by Fe-impurity doping as well as creation of structural point defects (including O-vacancies) during the doping process. The O-vacancies are considered energetically as trap levels in the band gap. The reduction of the band gap depends on the type and concentration of the dopant ions. The present experimental data show that doping with Pd create relatively higher concentration of O-vacancies that partially and strongly reduced E_g to 2.5 eV (table 1a).

Figure 2b shows that it is not possible to use the usual Tauc technique to determine the band gaps, especially for samples doped with Fe, (Fe–Pt) and (Fe–Pd). Therefore, the threshold of absorption $F(\lambda)$ shown in figure 3b is considered to be the band gap.

The main effect of hydrogenation of oxides containing TM dopant ions is the formation of V_O . The TM dopant ions behave as a catalyst for the dissociation of H_2 molecules forming H atoms/ions, which react with the structural oxygen ions, removing them and forming O-vacancies [19]. The hydrogenation of all doped SSS blue-shifted the band gaps by a value depending on the dopant ion type, so that the largest shift was happening with Pd^{2+} dopant due to the strong activity of Pd ions in H_2 dissociation and, therefore, creation of O-vacancies. However, the hydrogenation increases the concentration of created O-vacancies and generating more conduction electrons; the first effect red shifts E_g even for un-doped WO_3 and the second effect blue shifts E_g by Moss–Burstein (B–M) model [15] as tabulated in table 1a. Those two opposite-effect factors related to each other, so that the increase in free-electron concentration is mainly accompanied by increasing the point defects (oxygen vacancies) concentration [37,38]. The increase in carrier concentration (N_el) would increase the absorption, $F(\lambda)$, in the transparent region (gasochromic response) as shown in figure 3b when compared with figure 3a.

3.3 Magnetic properties

The measurement of magnetic properties of the synthesized pristine WO_3 ceramic shows diamagnetic (DM) behaviour, which confirms the previous known results [39]. DM behaviour of WO_3 did not change with hydrogenation. However, with Fe-doping, the host WO_3 transforms into PM defeating its natural DM behaviour. The magnetic susceptibility (χ) is given in table 2. The PM behaviour can be analysed with a Curie equation for magnetic volume susceptibility:

$$\chi(\text{vol}) = n_\text{Fe} \mu^2 / 3k_\text{B} T, \quad (1)$$

where n_Fe is the concentration of doped Fe ions, μ_Fe the magnetic moment per dopant Fe ion, k_B the Boltzmann constant and T the working temperature. The calculation gave the effective value of μ_Fe to be $4.04 \mu_\text{B}$ for sample $\text{WO}_3:\text{Fe}$. However, the previous observed values of μ_Fe were $(1.8\text{--}2.1 \mu_\text{B})$ for low spin Fe^{3+} ions and $(5.1\text{--}5.7 \mu_\text{B})$ for high spin Fe^{2+} ions [40]. If we consider the measured value as a statistical average value, then it is possible to estimate a contribution of $\sim 32\%$ for low-spin ions Fe^{3+} and $\sim 68\%$ for high-spin Fe^{2+} ions. The coexistence of both types of Fe ions was previously observed and verified in Fe-doped ZnO [41] and Fe-doped TiO_2 [42] by XPS measurements. According to the present analysis of data of table 2, the effective magnetic moment of Fe ions slightly increased by hydrogenation of $\text{WO}_3:\text{Fe}$ sample to $4.34 \mu_\text{B}$ due to the increase in high-spin ions contribution up to $\sim 77\%$. A partial FM behaviour could not be observed even with the present codoping (Fe–Pt), (Fe–Cu) and (Fe–Pd), except a small super paramagnetic (super PM) overlapped with major PM behaviour in (Fe–Pt) codoped WO_3 .

Table 2. Magnetic behaviour and FM parameters (coercivity (H_c), remanence (M_r), saturation magnetization (M_s), energy product (U_m) and PM susceptibility (χ)).

Sample	Major behaviour	H_c (Oe)	M_r (m emu g ⁻¹)	M_s (m emu g ⁻¹)	$U_m = H_c M_r$ (m erg g ⁻¹)	χ (cgs g ⁻¹)
WO ₃	DM	—	—	—	—	—
WO ₃ :Fe	PM	—	—	—	—	2.289×10^{-6}
WO ₃ :Fe:Pt	PM + Super PM	~0	~0	1.58	—	—
WO ₃ :Fe:Cu	DM	—	—	—	—	—
WO ₃ :Fe:Pd	PM	—	—	—	—	2.03×10^{-6}
<i>Hydrogenated samples</i>						
WO ₃ -H	DM	—	—	—	—	—
WO ₃ :Fe-H	PM	—	—	—	—	2.637×10^{-6}
WO ₃ :Fe:Pt-H	DM + FM	139.57	0.371	2.59	51.78	—
WO ₃ :Fe:Cu-H	DM + FM	252.4	0.77	2.63	194.3	—
WO ₃ :Fe:Pd-H	PM + FM	227.9	5.36	23.91	1221.54	—

Figure 4. Developing $M(H)$ behaviour of WO₃:Fe:Cu sample from (1) DM behaviour for as-synthesized to the (2) overlapped DM + FM behaviours for hydrogenated sample.

The hydrogenation could not create partial FM in pristine WO₃ as well as Fe-doped WO₃. However, the creation of FM properties was observed with all hydrogenated codoped samples. Thus, the creation of FM needs both the dopant magnetic ions (Fe²⁺) as well as oxygen vacancies, which support and boost the oxide crystalline medium to carry the S–S exchange interaction between Fe²⁺-dopant magnetic ions. The Pt, Cu or Pd codopant ions behave as catalysts for the dissociation of H₂ molecules into O ions/atoms, which in turn create O-vacancies.

Figure 4 shows the magnetic behaviour of WO₃:Fe:Cu sample, as an example; the DM behaviour (1) for the as-synthesized sample that transformed into the behaviour (2), which shows overlapped DM with the created FM behaviours for the same sample after hydrogenation. The behaviour (3)

Figure 5. $M(H)$ hysteresis behaviour of all hydrogenated codoped WO₃ samples. The inset shows the amplified low-field behaviour.

shows the extracted FM behaviour of WO₃:Fe:Cu sample. Figure 5 and table 2 demonstrate the magnetic properties of all codoped hydrogenated samples plotted with the linear PM behaviour of Fe-doped WO₃ for comparison. The inset of figure 5 shows magnified FM regions of the magnetization curves at low-field region.

The results demonstrate the key role of creation of partial FM properties. This refers to the essential rule of the crystalline electronic medium (CEM) of WO₃ crystal, through which the S–S exchange interactions between dopant magnetic ions take place, so that doping with a small amount of magnetic ions cannot guarantee the creation of FM properties of the host ceramic unless an action should be applied on CEM, which was hydrogenation process in the present work.

Thus, the two factors which decide the creation of FM properties in the present WO₃:Fe SSS are the average inter Fe²⁺ ionic distances (R) and the properties of CEM. The value

of R can be estimated by considering it as the radius of a sphere around each dopant Fe^{2+} ion. Thus, for approximately uniform distribution of Fe^{2+} dopants within the host WO_3 ceramic, R could be estimated through $n_{\text{Fe}}V = 1$, where n_{Fe} is the dopant Fe^{2+} concentration and $V = (4/3)\pi R^3$. Thus, the value of R was ~ 0.52 nm, which is larger than the Fe^{2+} – Fe^{2+} ionic distance in pure iron or oxides (~ 0.2 nm). Therefore, it is not expected to obtain RT-FM properties in the present $\text{WO}_3\text{:Fe}$ sample as shown in table 2.

Therefore, to control the magnetic properties of $\text{WO}_3\text{:Fe}$ solid solution, an action that affects the electric and magnetic properties of CEM should be applied. The applied action, in the present work, was the codoping by (Fe–Pt), (Fe–Cu) and (Fe–Pd) ions in addition to the hydrogenation at 400°C .

In case of codoping, data in table 2 show that the codoping could not help to create FM properties. Therefore, a hydrogenation route was applied to create RT-FM properties. Data of table 2 show that the highest created magnetic energy of ~ 1.22 erg g^{-1} was obtained in the presence of Pd^{2+} doping. This can be attributed to the magnetically improving of CEM by the creation of O-vacancies by hydrogenation. These oxygen vacancies catch polarons, which support the Heisenberg exchange interaction through superexchange interaction. As a practical rule, higher the concentration of the O-vacancies, the stronger the FM properties could be generated. This was happened in the presence of dopant Pd^{2+} ions, which are known as an effective catalyst for H_2 -molecule dissociation into H atoms/ions (for un-doped WO_3 such dissociations are excluded) [20,21]. The formed H atoms/ions could adsorb through grain and crystallite surfaces and other defects and then interacted and removed the structural oxygen of WO_3 crystal, generating O-vacancies and, thus, transformed its SG from P21/n to Pbam.

4. Conclusions

Fe-, Fe/Pt-, Fe/Cu- and Fe/Pd-codoped W-oxide nanoparticles were successfully synthesized by a simple unique HCl-assisted precipitation. Structural studies revealed the form of two SGs: P21/n or Pbam depending on dopant impurity type. It was established that the optical band gap of the host W-oxide was redshifted depending on the dopant impurity ionic type and attaining 2.5 eV with Fe/Pd co-dopants.

The hydrogenation corroded the nanocrystallites without changing the crystalline SG structure in spite the production of O-vacancies. However, the hydrogenation strongly changed the optical properties through gasochromic response and blue-shifted the band gaps.

Magnetic measurements have established that the common dopant iron ions could be simultaneously present in two oxidation numbers, Fe^{2+} and Fe^{3+} ions. However, the present work doping could not create RT-FM properties in host WO_3 . But, after hydrogenation, RT-FM properties were generated in only codoped W-oxide that was explained by

V_O -mediated ferromagnetic interaction. The relative highest RT-FM energy was created with hydrogenated Fe/Pd-codoped W-oxide nanopowder, which could be used as a potential candidate for many applications involving partial FM properties such as catalysts and optical phosphors.

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