Defect-induced ferromagnetic properties of Tb-doped CdO synthesized via Cd Hydroxychloride: Effect of hydrogen post treatment

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Cadmium oxide powder doped with Tb ions was synthesised by thermal decomposition of cadmium Hydroxychloride Cd(OH)Cl. The molar content of Tb is 2.6%. The purpose of the present study is to tailoring room-temperature ferromagnetic (RT-FM) properties to CdO in order to use it in the field of dilute magnetic semiconductors (DMS). The samples characterised by X-ray fluorescence (XRF) and X-ray diffraction (XRD). The optical band gap of the prepared powders was determined by diffuse reflection spectroscopy (DRS). Terbium ions doped in CdO are employed as source of FM properties. The electronic medium of Spin-Spin interaction in host CdO is studied by annealing in hydrogen atmosphere. Magnetic measurements reveal that Tb-doped CdO powder behaves as paramagnet defeating the intrinsic diamagnetic behaviour of CdO. However, after annealing in hydrogen atmosphere, RT-FM properties were created. Thus, it was proved that magnetic properties could be tailored by doping and post treatment under H₂ atmosphere.

Keywords: Tb-doped CdO, Room-temperature ferromagnetism, Hydrogen treatment

1. Introduction

Cadmium oxide is one of transparent conducting oxides (TCO) that have many applications in optoelectronic fields. The optoelectronic properties of CdO could be controlled by controlling its natural point defects, through doping with foreign metallic ions. It was established that doping of CdO with metallic ions of valency more than that of Cd²⁺ increases the concentration of conduction electrons and improves its conductivity. On the other hand, doping could create in CdO exotic properties, such as magnetic, optical, or mechanical, that would diversify more field of its applications. The present work is aimed to study the conditions necessary to tailoring room temperature ferromagnetism (RT-FM) properties to CdO, in order to use it in the field of dilute magnetic semiconductors (DMS). For that purpose, it is necessary first to dope CdO with some transition or rare earth ions, which could create in CdO FM properties under some necessary conditions, which related to the electronic medium of spin-spin (S-S) exchange interaction between localised spins of dopant ions in host CdO.

Doped CdO can be synthesised by several chemical and physical methods. The method of the present work is to prepare doped CdO through preparation and thermal decomposition of Cd Hydroxychloride [Cd(OH)Cl].

Indeed, more experimental and theoretical works are needed to explain the real cause of RT-FM in DMS materials, although some previous papers were reported in the literature dealing with that issue. Many researchers attribute the creation of RT-FM in DMS to the defects, such as oxygen (O) vacancies, however, the role of O-vacancies to create or boost the RT-FM is still unknown.

Terbium ions are used in the present work as source of FM. The present study also investigates how to control the electronic medium for S-S interaction by annealing in hydrogen atmosphere (hydrogenation). Doping CdO with Tb³⁺ ions of slightly smaller size than that of Cd²⁺ (ionic radii of Tb³⁺ and Cd²⁺ are 0.0923 nm and 0.095nm, respectively) could create substitutional solid solution (SSS).

2. Experimental procedure

The starting materials, pure Cd and Tb oxide powders (Sigma-Aldrich products) of analytical grade, were used to synthesize CdO doped with Tb via fabrication of Cd hydroxychloride Cd(OH)Cl. The method of synthesis is simple; A mixture of controlled amounts of the above oxides was dissolved in dilute (~ 3 wt%) HCl acid. The obtained dark brown solution was put on the magnetic stirrer with mild stirring at room temperature for ~24 h, until the solution color turned into fatty-milky. Finally, white precipitate powder formed by heating at 70 °C, which, then, was flash calcined at 500 °C for 1 hr followed by natural cooling to room temperature. The yielded white powder, which is considered as precursor powder, was investigated using X-ray diffraction (XRD) technique; where established that it was Cd(OH)Cl. The precursor powder was, then, calcined at 800 °C for 2h in order to obtain CdO structure. Some amount from the as-synthesised powder was post-annealed in hydrogen atmosphere at 350 °C for 30 min. The used Tb/Cd molar ratio was 2.6%.

As a reference sample, undoped CdO was also prepared by similar procedure. However, it was observed that the formed precursor powder in this case was CdCl₂·H₂O.
The structural analysis was performed with a Rigaku Ultima IV 0-20 X-ray diffractometer equipped with Cu Kα radiation. Elemental analysis and purity was carried out by X-ray fluorescence (XRF) method. Optical properties were studied by diffuse reflectance spectroscopy (DRS). Magnetic characterization was measured with a Micro-Mag Model 3900. Undoped and Tb-doped CdO powders are referred by S0 and S1, respectively, and the hydrogenated samples are referred by S0-H and S1-H.

It should be mentioned that thermal decomposition of Cd(OH)Cl into CdO at temperature T >720 °C was studied in Ref. 7. It was found the formation of an intermediate product (CdCl2) in the temperature range 295-410 °C, which began to volatilize at 485 °C so that the weight loss for volatilization of CdCl2 is 61%.

3. Results and Discussion

3.1 Structural analysis

Fig.1 shows the XRF spectra of the prepared powder S1 and its precursor Cd(OH)Cl. The spectra reveal Cd L-spectrum (3.13 - 3.53 keV), Tb L-signal (6.27 keV), Cl Kα signal (2.6 keV), and Cu Kα1 and Kα2-signals (8.04 keV and 8.90 keV, respectively). No additional XRF signals were detected referring to the purity of the studied powders and to the elemental content in sample S1 and its powder precursor.

The XRD patterns shown in Fig.2 reveal that the precursor powder is Cd(OH)Cl for the Tb-doped CdO, and CdCl2.H2O for the undoped CdO. No diffraction peaks arising from pure, oxide, or any Tb related phases were detected. This means that Tb dopant ions were incorporated and, thus, induced formation of Cd(OH)Cl structure. It is known that the crystalline structure of undoped Cd Hydroxychloride [Cd(OH)Cl] is hexagonal of space group P63mc and lattice parameters, 0.36648 nm, 1.02305 nm, and unit cell volume (Vcell) of 0.118948 nm3.8. However, in the present work, the lattice parameters of Cd(OH)Cl are 0.366196 nm, 1.02393 nm, and Vcell=0.118913 nm3. The slight increase of Vcell comparing to undoped pure Cd(OH)Cl is due to the incorporation of Tb ions in the crystalline structure.

Also, it is known that the crystalline structure of pure Cd chloride hydrate [CdCl2.H2O] is orthorhombic of space group Pnam and lattice parameters, a=0.9261 nm, b=1.1730 nm, and c=0.3794 nm. In the present work, the lattice parameters of formed CdCl2.H2O are a=0.9377 nm, b=1.1430 nm, and c=0.3751 nm.

The XRD patterns of samples S0 and S1 are shown in fig.3. They show that the synthesised powder samples are polycrystalline in nature of cubic CdO structure. No diffraction peaks arising from pure related Tb phases were detected in S1. Table 1 presents the results of the structural analysis; lattice parameter (calculated by Rietveld crystal refinement), crystallite size (CS), and strain (calculated by Halder-Wagner method). The lattice parameter found for the un-doped CdO powder is close to the know value in JCPDS card No. 05-0640 (Fm-3m, a=0.9261 nm) 10. However, the lattice parameter and, thus the unit-cell volume (Vcell) of the Tb-doped CdO were slightly reduced due to the incorporation of Tb3+ ions of slight smaller ionic radius than that of Cd2+.

Let us discuss the possible kind of incorporation of Tb ions in CdO lattice. The ionic radius of Tb3+ (0.0923 nm) is close to that of Cd2+ (0.095 nm [6]), therefore, the incorporation of Tb3+ in the crystalline lattice of host CdO by substitution...
for Cd$^{2+}$ ions is most likely to occur, forming substitutional solid solution (SSS), according to the Hume-Rothery rules. Tb$^{3+}$ ions might also occupy some interstitial positions, but in small fraction in order to undistort strongly the cubic crystalline structure of host CdO, that was not observed experimentally. However, due to the substitutions, the charge balance of host CdO unit cell would be disturbed. Therefore, in order to retain the charge balance of host CdO unit cell, appropriate number of Cd ($V_{Cd}$) and/or O ($V_{O}$) vacancies would be naturally created and/or annihilated depending on the doping levels. All these factors altogether (incorporation and vacancies) would control the variation in $V_{cell}$ of host CdO. Table 1 shows very slight variation in $V_{cell}$ of S1 reflecting small change in the concentration of structural oxygen vacancies ($V_{O}$). Furthermore, it is known fact that high-temperature (800 °C) annealing in air would strongly reduce the oxygen-vacancy concentration.

The XRD pattern of S1-H, shown in fig.3, reveals preserve CdO crystalline structure. However, it is possible to notice two modifications due to the hydrogenation; the first is that the highest intensity reflection changed from (111) in S1 to (200) in S1-H. Secondly, additional very weak peaks attributed to metallic Cd nanograins were formed. Peaks of Cd were identified according to the known hexagonal HCP (P6$_3$/mmc) structure with lattice constants $a=0.29794$ nm and $c=0.56186$ nm. This can be explained as the interaction of hydrogen with structural oxygen ions removes them from CdO crystalline structure, i.e. (CdO + H$_2$ → Cd + H$_2$O). In the results, structural O-vacancies are created and free Cd ions are expelled outside the CdO lattice. This phenomenon did not happen with pure CdO, it might need metallic catalyst.

Table 1 shows that the crystal imperfection (strain %) increased and CS decreased with hydrogenation of S1. This happened due to the interaction and removing structural oxygen of S1. The reduction of oxygen content increases the unit-cell volume ($V_{cell}$), which is clearly observed in data of table 1. Such observation was also mentioned in Refs. 13 and 14. Furthermore, it was known that oxygen vacancies enhance or create FM, therefore it should be expected that sample S1-H would have FM properties.

### 3.2 Optical Properties

Diffuse reflection spectroscopy (DRS) method is used to study the optical properties of the synthesised powders. The spectral diffuse reflectance in the range 250 - 900 nm for the prepared powders is shown in the inset of Fig. 4. These spectra can be used to estimate the values of the bandgap by using Kubelka-Munk (K-M) equation $^{15}$: $K(S)=\frac{F(R)}{(1-R)^2/2R}$, where $S$ is the scattering coefficient, $K$ is the K-M absorption coefficient or $K=2a$, $a$ is the absorption coefficient, $F(R)$ is the K-M function, and $R=\frac{R_{sample}}{R_{BaSO4}}$, i.e. the diffuse reflectance of thick sample is measured relative to the standard reflectance ($R_{BaSO4}$) from a powder BaSO$_4$ supplied by Schemadzu. By considering $S$ as constant with respect to the wavelength, it is possible to use the well-known Tauc plot to estimate the direct $E_g$, i.e. the extrapolation of the linear portion of $F(R)\times E^2$ vs. $E$ plot, as shown in Fig. 4, gives the direct bandgap (table 1). The obtained bandgap for undoped CdO is less than that given in the range (2.2 eV - 2.6 eV), which is known for undoped CdO thin films prepared by different techniques. The bandgap of host CdO was increased by $\sim$10% due to 2.5% Tb doping. Moreover, the hydrogenation further increased the bandgap (table 1). The increasing of bandgap ($E_g$) with hydrogenation could be explained by Moss-Burstein effect $^{16}$; i.e. $E_g$ increases with increasing of concentration of free carriers ($N_e$). The increasing of $N_e$ in transition metal TM-doped CdO by hydrogenation was observed before in many cases $^{17,18}$. Therefore, annealing of semiconducting oxides under H$_2$ gas at relatively low temperature (350°C) and for a short time (30 min) is very beneficial for the creation of more free carriers that enhances the electronic-magnetic medium for spin-spin interaction.

### 3.3 Magnetic Properties

It is well known that pure, un-doped CdO shows diamagnetic (DM) behaviour at room temperature $^{19}$. However, some Authors observed that structural defects (vacancies) in CdO could create weak ferromagnetism (FM) component overlapped with its major DM characteristics $^{20}$. In the present work, the sample S1(CdO:Tb) shows paramagnetic behavior (PM) defeating the DM behavior of the host Cd, as shown in fig. 5. The effective magnetic moment of the dopant ions can be estimated by using the measured PM susceptibility per unit mass $\chi_{\text{max}}$ in Curie equation for volume susceptibility $\chi_{\text{vol}}$ in cgs units: $\chi_{\text{vol}}(T)=\frac{n_{\text{ion}} \mu_m^2}{3k_B T}$, where $n_{\text{ion}}$ is the volume concentration of dopant ions, $\mu_m$ is the magnetic moment of dopant ion, $k_B$ is the Boltzmann constant, and $T$ is the working temperature. From M-H graph of S1 sample, $\chi_{\text{max}}=8.105\times10^4$ cgs and, thus $\mu_m=9.68 \mu_B$. However the calculated value of $\mu$ for Tb$^{3+}$ (4f$^5$s$^2$p$^6$F$^6$) is the defect-induced ferromagnetic properties of Tb-doped CdO synthesized via Cd Hydroxychloride: Effect of hydrogen post treatment.
ions is 9.72 μ₀ [11]. Thus, the obtained value is compatible with the calculated one, referring to the participation of almost all doped Tb³⁺ ions in the paramagnetic interaction with the external field.

After hydrogenation, the PM susceptibility increased to 1.3×10⁻⁵ cgs. Furthermore, a RT-FM component in M-H behaviour was formed overlapped with the major PM behaviour, as shown in the inset of fig.5. The hysteresis parameters: coercive force (Hc), remanence (Mr), and saturation magnetisation (Ms) are 96.1 Oe, 0.3 memu/g, and 4.1 memu/g, respectively. This means that the hydrogenation induced some structural and electronic variations responsible for enhancing the electronic-magnetic medium in the host CdO crystal and, thus, generated RT-FM. The interaction between hydrogen and structural oxygen in Cd oxide lattice creates oxygen vacancies and liberate Cd ions of different amounts depending on annealing in H₂ conditions (time and temperature). The O-vacancies supply/enhance magnetic medium for S-S interaction and, thus, generate FM. It is possible to quantify the quality of the FM created with energy product EP=HM, parameter ²¹, which is equal to 28.8 merg.

Generally, the realisation of S-S exchange interaction depends on the interionic distances and the electronic-magnetic medium in which they present. It was found ²²,²³ that the S-S exchange interaction requires that the interionic distance (R) is not more than ~ (1.5 a), where a is the lattice parameter of host medium. To estimate R, one can consider a sphere of radius R around each Tb³⁺ ion. For a uniform distribution of Tb³⁺ dopants within the host CdO, the value of R can be estimated by N_{V=1}³, where N_{V=1} is the dopant Tb³⁺ concentration and V = (4/3)πR³. Thus, the calculated value of R is ~ 0.63 nm, which is less that (1.5 a). Thus the S-S interaction in the present work is possible if there is a suitable electronic-magnetic medium, which was generated only by hydrogenation.

4. Conclusions

Terbium ions were successfully doped into CdO lattice by thermal decomposition of Tb-doped Cd(OH)Cl method. The structural study showed that annealing in hydrogen gas atmosphere of CdO:Tb powders liberate free Cd ions and create O-vacancies in CdO structure. The optical study showed blue shift of band gap due to Tb doping as well as hydrogenation. The results show that doping with Tb³⁺ ions are necessary but not sufficient for creation of RT-FM in host CdO; it needs to create and enhance the electronic magnetic medium essential for spin-spin interaction. The hydrogenation creates O-vacancies and enhances the electron concentration; these two factors can support the electronic-magnetic medium for spin-spin interaction and, thus, create RT-FM behaviour. Therefore, it was proved, for the first time, the possibility of preparing Tb-doped CdO powders with tailored magnetic properties hence becoming a potential candidate for future DMS applications.

References


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