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Structural, optical, and magnetic characterization of Pd/Co-co doped lanthanum oxychloride nanopowders synthesized by solvothermal route: Considerable effect of hydrogen post-treatment

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ABSTRACT

The aim of this study was to investigate the influence of doping and hydrogenation on the structural, optical and magnetic properties of dia-magnet Lanthanum oxychloride (LaOCl). LaOCl codoped with palladium and cobalt samples were successfully synthesized by solvothermal route, followed by a subsequent heat treatment process (annealing) at 600, 750 and 900 °C. Furthermore, annealing in hydrogen gas (hydrogenation) was carried out to the samples at 400 °C. The crystallite size (CS) of the samples were found to be influenced by annealing and hydrogenation processes as it ranged from 10.6 to 38 nm, as confirmed by X-ray diffraction (XRD) technique. Results also revealed dramatic changes in magnetic properties of the synthesized samples treated with annealing and hydrogenation. Vibrating sample magnetometer (VSM) analysis showed that Pd/Co-codoped LaOCl nanopowders own room temperature ferromagnetic (RT-FM) properties when post-annealed in air at 750 °C. It is also confirmed that created saturation magnetization is strongly affected by hydrogenation as it raised by ~50 time, (8.6 memu/g before and 410 memu/g after hydrogenation). The physical explanations and discussions were given in the framework of bound magnetic polarons (BMP) theory explaining how magnetic properties can be tailored from diamagnetic (DM) in pure LaOCl compound to FM under doping and hydrogenation.

1. Introduction

Lanthanum oxychlorides (LaOCl) are very interesting compounds that can be formed in pure state or doped with transition-metal (TM) ions or rare-earth ions. They are well known to their intensive use in fluorescence, effective cathode ray, and X-ray luminophores applications [1]. They are also applied as gas sensors, catalyst activity and luminescence materials for medical diagnosis and bioimaging probes, etc. [2–5].

LaOCl crystallizes in tetragonal structure with space group *P*4/nmm (No. 129, Z = 2) of parameters a = 4.1090 Å, b = 4.1090 Å, c = 6.8650 Å, and V_{cell} = 115.908 Å^3 [6]. La^{3+} ion in LaOCl structure is coordinated with four oxygen and five chlorine ions so that the coordination number (CN) of La^{3+} is 9(IX) [7]. There are many various methods to synthesize pure and doped LaOCl nanopowders, such as high-temperature solid state reaction [8], precipitation method [15], hydrothermal–solvothermal method [16], sol–gel method [17,18], and precursor thermal decomposition method [19].

In general, introducing FM properties in DM crystals by doping comprises a control on the electronic medium (EMI) of the doped crystal, through which the spin-spin (S·S) exchange interaction between dopant magnetic ions takes place. One of the possible methods to control and manage the EMI can be realized by a creation of structural oxygen vacancies (V_O) where superexchange interaction takes place. According to basic principles of bound magnetic polarons (BMP) theory [9,10], the O-vacancies bound some electrons (polarons) through which the S·S exchange interaction couples the spins of dopant ions causing long-range FM ordering. LaOCl crystals are found to own low cut-off vibrational phonon energy which enhances the phononic energy transfer to the doped ions introduced in the LaOCl and hence, prompt doping process [8]. Therefore, Cobalt ions can be easily doped into the crystals, altering their magnetic behaviour from DM to RT-FM.

Furthermore, it is possible to create structural O-vacancies by annealing the sample in hydrogen gas (hydrogenation) at certain conditions (temperature and duration), thus stimulate the interaction of H-gas with structural oxygen. Dissociation of H_2 molecules into two H atoms is essential for S·S exchange interaction and this can be achieved by the presence of TM dopant which plays the role of catalyst [11,12]. The elaborated H atoms diffuse in the host crystal lattice through interstitial sites or vacancies and interact with structural oxygen forming oxygen vacancies, which, thus, alter the magnetic properties of the doped host crystal [13]. Such considerable effect of hydrogenation is not known to arise in undoped LaOCl crystals. The combination of

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dopant metallic catalyst of TM ions and hydrogenation is needed to alter magnetic behaviour of the crystals. The TM Palladium (Pd) ion is well known to have a strong influence on hydrogen dissociation and hence, the presence of two dopant ions Pd and Co during hydrogenation is proposed to create considerable FM properties. Moreover, the 9-coordination number ionic radius of La^{3+} (0.1216 nm) is slightly larger than that of the largest ionic radius of Co^{2+} (0.09 nm) and Pd^{2+} (0.086 nm) [14]. LaOCl can be considered as a good host for doping with Co^{2+}/Pd^{2+} ions as the natural crystalline structure is not destroyed by the occupation of Co^{2+}/Pd^{2+} ions within the La^{3+} ion sites.

In the present work, Co-doped LaOCl nanopowders are synthesized by solvothermal route followed by annealing and hydrogenation. The effect of doping, annealing and hydrogenation was investigated on the structural, optical, and magnetic properties of the nanopowders in different conditions of temperature and atmosphere.

2. Experimental procedure

2.1. Synthesis of Pd/Co-co doped LaOCl nanopowders

Lanthanum oxychloride (LaOCl) codoped with palladium and cobalt nanopowder was synthesized by solvothermal route including pure $La(OH)_3$, bis(dimethylglyoximato)palladium(II) $Pd(C_4H_7N_2O_2)_2$ [abb. Pd(Hdmg)2], tris(acetylacetonato)cobalt(III) [abb. $Co(acac)_3$] fine powders of analytical grade (supplied from Sigma-Aldrich products) with pure methanol and HCl acid as starting materials. A mixture of controlled amounts of $Pd(Hdmg)_2$ and $Co(acac)_3$ powders were completely dissolved in ~5 ml methanol forming solution 1. A certain amount (~1.4 g) of $La(OH)_3$ fine powder was slowly added with continuous mild magnetic stirring to ~15 ml dilute (~3%) HCl acid, forming solution 2.

Then, solution1 was slowly added to solution 2 forming one solution of grassy color and continuous mild magnetic stirring was applied in closed glass tube at room temperature for ~24 h. Finally, the suspended precipitate was collected by soft continuous heating at ~80 °C with stirring. The produced precipitated powder was flash calcined in closed oven at 600 °C for 1 h followed by natural cooling to room temperature. It was reported that the calcination temperature should be more than 450 °C in order to obtain LaOCl [20].

The synthesized powder of molar ratio Co/La of 4.2% and Pd/La of 1.8% was used as the starting precursor (SP) powder. The structural characterization of the SP powder reveals that it has LaOCl crystalline structure. Amounts of the synthesized SP were annealed at 750 °C and 900 °C for ~1 h and cooled naturally with the oven to the room temperature. Moreover, some amount from each synthesized powder was post-annealed in hydrogen atmosphere at 400 °C for 30 min (hydrogenation). The following table shows the preparation conditions for each sample investigated in the present work.

Sample	Description of preparation conditions
LaOCl:Pd:Co-600	Pd and Co-codoped starting precursor (SP) powder synthesized in air at 600 °C/1 h
LaOCl:Pd:Co-600-H	Hydrogenated SP powder
LaOCl:Pd:Co-750	SP powder annealed in air at 750 °C/1 h
LaOCl:Pd:Co-750-H	SP powder annealed in air at 750 °C/1 h, followed by hydrogenation
LaOCl:Pd:Co-900	SP powder annealed in air at 900 °C/1 h
LaOCl:Pd:Co-900-H	SP powder annealed in air at 900 °C/1 h, followed by hydrogenation

The elemental compositions of the prepared samples were studied by X-ray fluorescence (XRF) method. The structural measurements and analysis were carried out by using a Rigaku Ultima VI θ-2θ X-ray diffractometer equipped with CuK_α radiation (0.15406 nm). The UV–Vis optical properties of the prepared powders in the range (190–800 nm) were studied by diffuse reflectance spectroscopy (DRS) with a Shimadzu UV-3600 double beam spectrophotometer equipped with an integrating sphere. The magnetic characterizations were measured using a vibrating sample magnetometer (VSM) type Micro-Mag Model 3900 with a step field of 25 Oe and an averaging time of 1 s. Magnetization curves were measured at room temperature in the field range +1 to −1 T.

3. Results and discussion

3.1. Structural characterization

The elemental content of the prepared precursor powder was studied by X-ray fluorescence (XRF) and the result is shown in Fig. 1. The XRF spectrum (in semilog scale for clarity) shows La L-spectrum (at 4.65 keV, 5.04 keV, 5.38 keV, and 5.78 keV for L_α, $L_{\beta1}$, $L_{\beta2}$, and $L_{\gamma1}$signals, respectively), Co K_α-signal (6.93 keV), and almost totally overlapped Cl K_α (2.62 keV) with Pd L_α (2.83 keV) signals. The exciting CuK_α and K_β-signals (8.04 keV and 8.90 keV, respectively) were also detected. No additional XRF signals were detected verifying the excellent purity of the synthesized powder.

Fig. 2 shows the XRD patterns of Pd/Co-codoped LaOCl samples. For comparison, data of undoped LaOCl were obtained too. The structural analysis including CS, strain and lattice parameter were obtained by calculated by Halder-Wagner method and Rietveld refinement, respectively, which are the built-in softwares of the used XRD apparatus (Table 1). The values of statistical fit parameters [R_{wp} (%) weighted profile R-factor; R_p (%) profile R-factor; R_e (%) expected R-factor; $S = R_{wp}/R_e$ and $\chi^2 = S^2$] indicate a good fitting, which can be noticed graphically in Fig. 2b, for example.

From Table 1, it can be noticed that the CS of the Pd/Co-codoped LaOCl is increasing from 25.7 nm to 38 nm with annealing temperature. However, when annealing is combined with hydrogenation, the CS is not proportional to the annealing temperature anymore.

The Crystalline structure of the LaOCl samples was revealed not to be affected by codoping, annealing and hydrogenation as the XRD peaks from Fig. 2 did not show any sign of alteration between different LaOCl samples and were indexed according to the known crystalline structure of LaOCl [6]. Also, no other phases are shown to be contributed to the LaOCl phase, confirming the formation of single phase material with incorporation of Pd^{2+} and Co^{2+} dopant ions in its lattice structure.

To discuss the nature of incorporation of dopant ions in LaOCl structure, the electronegativity (en) is considered as a good indicator. Accordingly, the O(3.5 Pau) and Cl(3.0 Pau) prefer to interact with La^{3+}(1.1 Pau) ions more than with Co^{2+}(1.8 Pau) ions. Therefore, occupying empty La^{3+} sites (as point defects) by Co^{2+} ions is most favourable rather than substitution for La^{3+} ions, i. e. the formation of substitutional solid

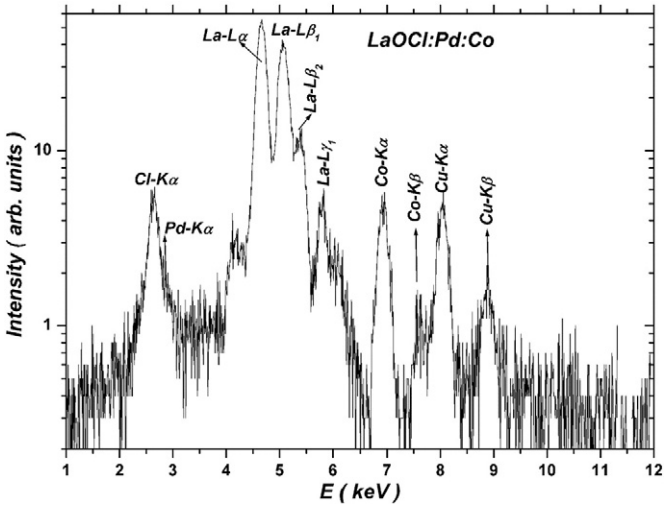

Fig. 1. XRF spectrum of Pd/Co-codoped LaOCl compound.