



Pechini synthesis and characteristics of Gd₂CoMnO₆ nanostructures and its structural, optical and photocatalytic properties



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ABSTRACT

GCMO NSs were synthesized by the reaction of metal nitrate salts in the presence of stabilizing agent and PG, by a Pechini method. Citric acid, maleic acid, succinic acid and 1,3,5-benzenetricarboxylic acid were used as stabilizing agents. The structure, morphology, optical, magnetic and photocatalytic properties of the GCMO NSs were investigated using various characterization techniques. Effects of type of stabilizing agent, the molar ratio of stabilizing agent:PG and also calcination temperature on particle size and morphology of the products were investigated. Also the influence of kind of pollutant on photocatalytic behavior of GCMO NSs was evaluated.

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1. Introductions

Much attention has been focused on rare-earth double perovskites (A₂BB'O₆) because of their remarkable physical, field sensitive magnetic, multiferroic and strong magnetic-electrical coupling properties [1] and also application potentials in numerous fields such as magnetocaloric materials and commercial applications [2–4]. Two effects in these compounds including large magnetocapacitance and electrocaloric effects are also interesting phenomena [5, 6]. In Gd₂CoMnO₆ (GCMO), Co³⁺ and Mn³⁺ randomly occupy B-sites. Katari showed that atmosphere and annealing process influence on distribution of CoO₆ and MnO₆ octahedrals [7, 8]. The orthorhombic structure is formed under quenched annealing process while the monoclinic structure will appear via slowed-cooled method [9, 10].

Most studies on M₂CoMnO₆ compounds have been focused on La₂CoMnO₆, but the studies on M₂CoMnO₆ (M = Pr, Nd, Sm, Eu and Gd) are less. Thus exploitation of the new physical properties of these compounds is of great interest. At 2001, Wang et al. synthesized Gd₂CoMnO₆ perovskite manganite by solid state reaction [11]. They investigated magnetic properties of these ceramics and observed a spin glass transition with a very sharp transition width

of 1 K at 112 K, after the paramagnetic to ferromagnetic transition. Also, they observed an antiferromagnetic transition at 43 K. Two years later, Bull et al. refined low- and high-temperature structures of La₂CoMnO₆ and La₂NiMnO₆ using powder neutron diffraction [12]. They investigated the structural and physical properties of the La₂CoMnO₆ and La₂NiMnO₆ and derived structure–property relationships. One year later, Bull and McMillan prepared Ln₂CoMnO₆ and Ln₂NiMnO₆ (Ln = La, Pr, Nd, Sm, Gd) [13]. They investigated optical and magnetic properties of these perovskites and found that band gap and Curie temperature vary systematically as a function of the rare earth cation size. Murthy investigated magnetocaloric effect in double perovskite Gd₂NiMnO₆ and Gd₂CoMnO₆ by magnetic and heat capacity measurements. He observed ferromagnetic ordering at about 130 and 112 K in Gd₂NiMnO₆ and Gd₂CoMnO₆, respectively. Also he observed an antiferromagnetic behavior in Gd₂CoMnO₆, below 50 K, due to 3d–4f exchange interaction. In 2014, Yang compared magnetic and dielectric properties of Nd₂CoMnO₆ and Sm₂CoMnO₆ double perovskite ceramics with those of La₂CoMnO₆ and Ln₂NiMnO₆ ceramics [14]. In same year, Kumar investigated Raman scattering on La₂CoMnO₆ (Ln = La, Pr, Nd) [15]. Li et al. synthesized Re₂CoMnO₆ (Re = Sm, Dy) ceramics by a solid-state reaction method, at 2017 [17]. They investigated magnetic property of the ceramics and observed magnetic field-induced metamagnetic behavior in the samples below the ferromagnetic Curie temperature, which were 123 K and 88 K in Sm₂CoMnO₆ and Dy₂CoMnO₆, respectively. In same year, Murthy investigated

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magnetic property of the Gd_2CoMnO_6 and found that it exhibits a field-induced metamagnetic phase transition from ferrimagnetic to long range ferromagnetic ordering below a critical temperature (~ 112 K) [31]. One year later, Gan et al. synthesized La_2NiMnO ceramics by an ultra-high pressure sintering at 4 GPa pressure and 800 °C temperature over a short duration [16].

Compared with other works, the grain size of the ceramics obtained in this work is remarkably decreased. The ceramics prepared in this work are pure. To the best of our knowledge, this is first attempt on the synthesis of GCMO nanostructures (GCMO NSs) in the presence of the citric acid, maleic acid, succinic acid and 1,3,5-benzenetricarboxylic acid as stabilizing agents. In this work, for the first time pechini method is used for the synthesis of the GCMO NSs and also for the first time effect of acid:propylene glycol (PG) ratio is investigated. This article aims to investigate the photocatalytic, magnetic and optical properties of GCMO NSs. These perovskites have been synthesized via different methods [17]. The pechini is a very simple powder synthesis method. This chemical solution method named after Maggio Pechini, its inventor, in 1967 [18]. It is a modified sol gel process for metals that due to their unfavorable hydrolysis equilibria are not suitable for traditional sol gel type reaction. It includes a combined process of metal complex formation and in situ polymerization of organics. Benefit of this method is based on the elimination of the prerequisite that the metals involved form suitable hydroxo complexes [18].

2. Experimental

2.1. Materials and Experiments

Gadolinium nitrate ($GdNO_3$, purity $\geq 99\%$), manganese nitrate hexahydrate ($Mn(NO_3)_2 \cdot 6H_2O$, purity $\geq 98\%$), cobalt nitrate ($Co(NO_3)_2$, purity $\geq 99\%$), citric acid (purity $\geq 99.5\%$), maleic acid (purity $\geq 99\%$), succinic acid (purity $\geq 99\%$) and 1,3,5-benzenetricarboxylic acid (purity $\geq 95\%$), PG (purity $\geq 99\%$) (all from Merck) were used without additional purification. Microscopic morphology of products was visualized by a TESCAN Mira3 FE-SEM microscope. A Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV was used to obtain TEM images. A diffractometer of Philips company with X'PertPro monochromatized Cu K α radiation was used to collect XRD pattern ($\lambda = 1.54$ Å). The EDS analysis was studied by XL30, Philips microscope. Fourier transform infrared spectrum (FT-IR) of the GCMO NSs was recorded by a Nicolet Magna- 550 spectrophotometer in KBr pellets. The magnetic properties of the samples were detected at room temperature using a vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran). A V-670 UV-Vis-NIR spectrophotometer (Jasco) was used to take diffuse reflectance spectrum (DRS) of the GCMO NSs. Voltammetric study was carried out by Sama 500 potentiostat (Isfahan in Iran). GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses.

2.2. Preparation of Gd_2CoMnO_6 Nanostructures

In a typical experiment, citric acid and $GdNO_3$ were dissolved in distilled water. Then a certain amount of $Co(NO_3)_2$ was added under stirring followed by adding $Mn(NO_3)_2 \cdot 6H_2O$ solution, with stoichiometric ratio 2:1:1 of Gd:Co:Mn. After heating the solution to around 60 °C, PG was added. The molar ratio of citric acid:PG was selected to be 1:1, 1:2 and 1:4. By heating the solution at 120 °C, a highly viscous gel was formed. The gel was dried at 70 °C in an oven for 24 h. The residue formed was collected and then calcined at 800 °C. Some control experiments, in which citric acid and temperature 800 °C were replaced by other stabilizing agents (maleic acid, succinic acid, 1,3,5-benzenetricarboxylic acid) and calcination temperatures (900, 1000 °C), and other operational processes were unchanged, were performed. The results have been listed in Table 1. Scheme 1 shows a diagram illustrating the formation of GCMO NSs.

2.3. Photocatalytic Tests

For investigation of the photocatalytic efficiency of the GCMO NSs under UV illumination, the photocatalytic decomposition of three dyes, including methyl violet, erythrosine and eriochrome black T were performed. 50 mL of 5 ppm solution of the dye and 0.05 g of the GCMO NSs in a glass reactor were utilized. For attaining the adsorption-desorption equilibrium, the obtained suspension after aerating in darkness (for 30 min) was subjected to the UV illumination (with a 125 W mercury lamp). The degradation efficiency of dyes is determined as follow:

$$\%D = \{(A_0 - A_t) / A_0\} \times 100 \quad (1)$$

where A_t and A_0 are the absorbance of dyes after and before irradiation, respectively [19].

3. Results and Discussion

Many fundamental properties of the materials are expressed as a function of the shape and size, thus control of growth and nucleation is becoming critical [20–26]. Using different stabilizing agents leads to the formation of the products with different shapes and sizes, thus different characteristics. The morphology and size distribution of the products were studied by SEM. SEM images of the products obtained in the presence of different stabilizing agents are shown in Figs. 1 and 2. The SEM images in Fig. 1a and b show the formation of agglomerated nanoparticles with diameters ranging from 25 to about 100 nm in the presence of citric acid at 800 °C. By using maleic acid at 800 °C, the products do not separate well and are agglomerated, as shown in Fig. 1c and d. With an exchange of the stabilizing agent from citric acid to succinic acid at 800 °C, the nanoparticles form dense agglomerate and particle sizes are increased (Fig. 2a and b). Fig. 2c and d shows that particles coalesce and turn into

Table 1
The reaction conditions of GCMO NSs synthesized in this work.

Effect	Stabilizing agent	Stabilizing agent: PG ratio	Calcination temperature (°C)	Time (h)	Morphology
Stabilizing agents	Citric acid	1:1	800	5	
	Maleic acid	1:1.2	800	5	
	Succinic acid	1:1.2	800	5	
	1,3,5-Benzenetricarboxylic acid	1:1.2	800	5	
Citric acid:PG ratio	Citric acid	1:2	800	5	
	Citric acid	1:4	800	5	
	Citric acid	1:1	900	5	
Temperature	Citric acid	1:1	900	5	
	Citric acid	1:1	1000	5	

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