Structural and magnetic properties of combustion synthesized $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) pyrochlore oxides

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Abstract. Nanostructured pyrochlore oxides $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) have been synthesized through a single step auto-igniting citrate complex combustion process. The structure and phase formation of the prepared combustion product were characterized by X-ray diffraction (XRD) analysis. From the XRD patterns, the average crystallite size and lattice strain were calculated using the Williamson–Hall method. Pyrochlore oxides $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) exhibit a cubic pyrochlore structure with the $fd3m$ space group. The microstructure and average grain size of the samples were examined by scanning electron microscopy. The surface area and pore size of the materials were obtained from Brunauer–Emmett–Teller (BET) analysis. The obtained higher BET surface area of the $Gd_2Ti_2O_7$ material suggests the possibility of excellent photocatalyst activity. The vibrating sample magnetometer studies show that these materials show paramagnetic behaviour at room temperature. These materials have an entropy change that increases when the temperature decreases. So these materials may be used as active magnetic refrigerants at low-temperature.

Keywords. Pyrochlore oxides; X-ray diffraction; surface area; photocatalyst; magnetization.

1. Introduction

Pyrochlore oxides have a general formula $A_2B_2O_7$, where ‘A’ is mostly a trivalent (A^{3+}) rare-earth cation, which includes lanthanides and sometimes Y and Sc, and ‘B’ is mostly a tetravalent (B^{4+}) cation, either a transition metal or a p-block element [1]. A^{3+} larger cations occupying the 16d site are coordinated with eight oxygen ions, while B^{4+} smaller cations occupy the 16c site, located at the centre of the distorted octahedra of oxygen ions and the crystallographic positions of O^{2-} ions are sited at 48f and 8b [2]. The stability of the pyrochlore structure is governed by the radius ratio (r_A/r_B) of A and B cations, which extends from 1.46 to 1.78 [3].

Recently, pyrochlore structured rare earth titanates ($RE_2Ti_2O_7$) have attracted much attention because of the spin-ice behaviour of $Dy_2Ti_2O_7$ compounds, low-temperature magnetic properties and large magnetic moments of paramagnetic materials [4–12]. $Gd_2Ti_2O_7$ and $Er_2Ti_2O_7$ have paramagnetic ordering at room temperature, but they exhibit antiferromagnetic ordering at very low-temperatures, because of predominant antiferromagnetic coupling [13–15]. In the paramagnetic behaviour of pyrochlore oxides, at very low-temperature the value of an entropy change increases when the temperature decreases.

$A_2B_2O_7$ type pyrochlore oxides have been prepared by traditional solid state reactions (1300°C for 40 h) [16], sol-gel [17,18], the polymerized complex method [19,20] and

high-energy ball milling [21] at high temperature and long reaction times. Among these different synthesis methods, solution combustion synthesis is the finest method of producing nanocrystalline ultrafine powders with extremely pure and highly homogeneous as compared to powders prepared with conventional methods. This technique offers an easy and cost effective synthesis with shorter duration (2 h), low-reaction temperature (250°C) and lower calcination temperature (700°C) for synthesizing nanostructured metal oxides. This process involves an exothermic redox reaction between metal nitrates (oxidizing agents) and fuel (a reducing agent). In the combustion process, the product properties such as crystallite size, phase, degree, nature of agglomeration and surface area are generally controlled by adjusting the oxidant–fuel ratio. Here, we report on the preparation details and room temperature magnetic properties of nano-sized $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) pyrochlore oxides by the auto-ignition combustion process.

2. Materials and methods

2.1 Synthesis of $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) nanoparticles

Nanocrystalline pyrochlore oxides $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) have been successfully synthesized by the auto-ignition combustion technique. Analytical reagent grade

Figure 1. XRD pattern of $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) nanoparticles.

metal oxides A_2O_3 ($A = Gd, Dy$ and Y) (99.99% purity, Sigma Aldrich) and titanium dioxide (TiO_2) (99.99% purity, Sigma Aldrich) were used as the starting materials for the preparation. A_2O_3 and TiO_2 were dissolved in nitric acid and then the two solutions are mixed together. An appropriate amount of citric acid was added into the solution containing A^{3+} metal ions and Ti^{4+} metal ions, maintaining the citric acid to cation ratio unity. Ammonium hydroxide was added to the system to adjust the oxidant fuel ratio and the solution was stirred well for uniform mixing using a magnetic stirrer. The solution containing the complex precursor at neutral pH (~ 7) was heated on a hot plate to about $250^\circ C$ in a ventilated fume hood. The solution boiled on heating, which underwent dehydration followed by decomposition leading to a smooth deflation producing a dark form. The form gets auto-ignited on persistent heating yielding a fluffy and voluminous combustion powder in the container.

2.2 Characterization

The prepared combustion powders were calcined at $700^\circ C$. Powder X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) analysis, scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) measurements were used for characterizing the samples. Powder XRD patterns were recorded with an X'pert pro Bruker D-8 diffractometer with $CuK\alpha$ radiation ($1.5406 \text{ \AA}$). Specific surface area measurements were taken with a QuadraSorb (version 6.0) BET surface area analyser (Quantachrome Instruments). The prepared powders have been mixed with polyvinyl alcohol and pressed to form cylindrical compacts at a pressure of about 350 MPa using a hydraulic press, which were then sintered at $1300^\circ C$ for 4 h. The microstructures of the sintered specimens were examined using a high-resolution scanning

Figure 2. The W–H analysis of (a) $Gd_2Ti_2O_7$, (b) $Dy_2Ti_2O_7$ and (c) $Y_2Ti_2O_7$.

electron microscope (HR-SEM) (JOEL, JSM-6390LV). The magnetic studies were performed with a vibrating sample magnetometer (Lakeshore VSM 7410) at room temperature.

Table 1. Strain and average crystallite size calculated from the Scherrer equation and W–H analysis of A₂Ti₂O₇ (A = Gd, Dy and Y) nanoparticles.

Materials	Strain (ε) no unit	Crystallite size from Scherrer equation (nm)	Crystallite size from W–H analysis (nm)
Gd ₂ Ti ₂ O ₇	0.483×10^{-3}	28	27.73
Dy ₂ Ti ₂ O ₇	0.897×10^{-3}	45	43.32
Y ₂ Ti ₂ O ₇	0.812×10^{-3}	31	30.81

Figure 3. (a) BET isotherm of Gd₂Ti₂O₇ and (b) multipoint BET plot of Gd₂Ti₂O₇.

3. Results and discussion

3.1 Powder XRD

The phase formation and phase purity of the calcined powders were studied by the powder XRD method. Figure 1 depicts the XRD pattern of A₂Ti₂O₇ (A = Gd, Dy and Y) nanoparticles, in the 2θ range of 10–70°. All the peaks in the XRD patterns were indexed. XRD analysis revealed the formation of A₂Ti₂O₇ (A = Gd, Dy and Y) nanomaterials with

Figure 4. (a) BET isotherm of Dy₂Ti₂O₇ and (b) multipoint BET plot of Dy₂Ti₂O₇.

a cubic pyrochlore structure in the *fd3m* space group. The lattice constants calculated from the X-ray line broadening of the diffraction peaks are found to be *a* = 10.17, 10.12 and 10.09 Å for Gd₂Ti₂O₇, Dy₂Ti₂O₇ and Y₂Ti₂O₇, respectively. These calculated lattice constants are in well agreement with the standard ICDD data (ICDD card no: 02-4207 for Gd₂Ti₂O₇, 17-0453 for Dy₂Ti₂O₇ and 42-0413 for Y₂Ti₂O₇). No other characteristic peaks related to impurity or any other phases were observed in the XRD pattern, which indicates

the formation of phase pure $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) nanopowders.

The average crystallite size (D) was calculated from the XRD pattern using the Debye–Scherrer formula as follows:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D = average crystallite size, k = constant (0.9), λ = wavelength of the radiation (1.5406 Å), β = full width at half maximum and θ = peak position.

Figure 5. (a) BET isotherm of $Y_2Ti_2O_7$ and (b) multipoint BET plot of $Y_2Ti_2O_7$.

The separation of the particle size and lattice strain broadening analysis depending on different θ positions were carried out using the Williamson–Hall (W–H) method. A graph was plotted with $4 \sin \theta$ along the x -axis and $\beta \cos \theta$ along the y -axis for W–H analysis of $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) nanomaterials. The strain was extracted from the slope and the crystallite size was extracted from the y -intercept of the linear fitted data. Figure 2 shows the W–H analysis of $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) nanoparticles. The average crystallite size obtained from the Scherrer equation matched well with the W–H method. The average crystallite size obtained from the W–H method showed a small variation as compared with the Scherrer equation; this may be due to the fact that the W–H analysis included the strain correction factor which led to the obtainment of a less crystallite size from the Scherrer equation. The values of strain and average crystallite size calculated from the Scherrer equation and W–H analysis are compared in table 1.

3.2 BET surface area analysis

The BET gas adsorption technique is used to determine the surface area and pore size of the nanomaterials. The ratio of the surface area to the total volume of the particle increases with a decrease in the size of the particles. To evaluate the surface area of the nanopowder and to estimate the adsorbed monolayer volume of the nitrogen gas, the corresponding multi-point BET plots are drawn. The following equation can be used to determine the specific surface area (S_{BET}) of the $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) samples,

$$S_{BET} = N_m \times A_m \times N_A \quad (2)$$

where N_m is the value of the gas adsorption by monolayer and A_m is the cross-sectional surface area of a single adsorbed gas molecule and N_A is Avogadro's number. The particle size of the powdered material can be determined using the following equation by assuming that the particles are having identical spherical shape.

$$D = \frac{6 \times 10^3}{\rho S_{BET}} \text{ nm} \quad (3)$$

where D is the particle size, ρ is the density of the sample and S_{BET} is the specific surface area of the nanopowder. The adsorption–desorption isotherms and multipoint BET plot of $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) nanomaterials are shown in figures 3–5.

Table 2. Particle size, pore size and surface area of $A_2Ti_2O_7$ ($A = Gd, Dy$ and Y) nanopowders.

Samples	Particle size (μm)	Pore size (nm)	Surface area (S_A) ($\text{m}^2 \text{g}^{-1}$)
$Gd_2Ti_2O_7$	0.57	3.609	18.063
$Dy_2Ti_2O_7$	0.31	4.442	11.050
$Y_2Ti_2O_7$	0.89	5.020	7.820

Figure 6. HR-SEM image of sintered pellets of $\text{Gd}_2\text{Ti}_2\text{O}_7$.

Figure 8. HR-SEM image of sintered pellets of $\text{Y}_2\text{Ti}_2\text{O}_7$.

Figure 7. HR-SEM image of sintered pellets of $\text{Dy}_2\text{Ti}_2\text{O}_7$.

From the BET isotherm graph, the adsorption and desorption of nitrogen gas were specified by the blue lined graph and red lined graph, respectively. The porosity of the sample was realized between the hysteresis effect of the adsorption–desorption isotherms. Obviously, $\text{Gd}_2\text{Ti}_2\text{O}_7$ exhibited a higher BET specific surface area ($18.063 \text{ m}^2 \text{ g}^{-1}$) as compared with $\text{Dy}_2\text{Ti}_2\text{O}_7$ ($11.05 \text{ m}^2 \text{ g}^{-1}$) and $\text{Y}_2\text{Ti}_2\text{O}_7$ ($7.82 \text{ m}^2 \text{ g}^{-1}$) materials. The properties of a larger BET specific surface are very helpful for a photocatalyst to reach excellent activity and may result in enhanced behaviour in hydrogen storage. The obtained values of the particle size, pore size and surface area of $\text{A}_2\text{Ti}_2\text{O}_7$ ($\text{A} = \text{Gd}, \text{Dy}$ and Y) nanoparticles are listed in table 2.

3.3 SEM analysis

The morphological features of sintered pellets of $\text{A}_2\text{Ti}_2\text{O}_7$ ($\text{A} = \text{Gd}, \text{Dy}$ and Y) were characterized by using a HR-SEM. The HR-SEM images of $\text{A}_2\text{Ti}_2\text{O}_7$ ($\text{A} = \text{Gd}, \text{Dy}$ and

Figure 9. (a) M – H curves of $\text{Gd}_2\text{Ti}_2\text{O}_7$ and (b) Langevin fit of the magnetization for $\text{Gd}_2\text{Ti}_2\text{O}_7$.

Figure 10. (a) M - H curves of $\text{Dy}_2\text{Ti}_2\text{O}_7$ and (b) Langevin fit of the magnetization for $\text{Dy}_2\text{Ti}_2\text{O}_7$.

Y) samples are shown in figures 6–8. The SEM micrograph showed well crystallized submicron grains with sharp grain boundaries and the grains are in different sizes. The average grain size determined from the SEM micrograph was found to be around 500, 700 and 600 nm for $\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Y}_2\text{Ti}_2\text{O}_7$, respectively. Due to high-densification, no cracks were observed on the surface and the porosity was very less. The calculated values of porosity are ~ 3 , ~ 3 and $\sim 2\%$ for $\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Y}_2\text{Ti}_2\text{O}_7$, respectively. High-densification was achieved without significant microstructural coarsening.

3.4 Magnetic properties

The magnetization (M) vs. applied field (H) curves (M - H) of the entire samples exhibit an almost linear line dependence, which corresponds to the common feature of either paramagnetic or antiferromagnetic compounds. Figures 9–11 show the magnetic hysteresis curves and modified-Langevin fit for the initial magnetization of the $\text{A}_2\text{Ti}_2\text{O}_7$ ($\text{A} = \text{Gd}, \text{Dy}$ and Y) samples at room temperature. The magnetization is

Figure 11. (a) M - H curves of $\text{Y}_2\text{Ti}_2\text{O}_7$ and (b) Langevin fit of the magnetization for $\text{Y}_2\text{Ti}_2\text{O}_7$.

unsaturated in the highest applied field in all the cases of the M - H curves. On decreasing the crystallite size or annealing temperature, the magnetization is increased to a maximum. Furthermore, the retentivity (M_r) and coercivity (H_c) were characterized and the hysteresis loops are symmetrical with respect to both the axes [22]. For the magnetization M for an applied field H at absolute temperature T , the value of $M(H, T)$ is given by:

$$M(H, T) = M_0(T) + \chi_{\text{AF}} H(T) \quad (4)$$

where $M_0(T)$ is responsible for the rapid increase in the magnetization due to non-compensation of the surface spins and $\chi_{\text{AF}} H(T)$ is responsible for the non-saturation of the magnetization at high-fields due to the antiferromagnetic contribution. Substituting for $M_0(T)$ that depends on the surface part, which is given by:

$$M(H, T) = M_S [\coth(\mu H / k_B T) - k_B T / \mu H] + \chi_{\text{AF}} H(T) \quad (5)$$

Table 3. Magnetic parameters of $A_2Ti_2O_7$ ($A = \text{Gd, Dy and Y}$) samples at room temperature.

Compounds	M_S (emu g ⁻¹)	μ (10 ³ μ_B^*)	χ_{AF} (10 ⁻⁶ emu g ⁻¹)	H_c (Oe)
Gd ₂ Ti ₂ O ₇	0.02083	0.0224	80.66	10.14
Dy ₂ Ti ₂ O ₇	0.02091	0.0223	167.82	8.54
Y ₂ Ti ₂ O ₇	0.01033	2.7867	4.75	59.97

* μ_B represents Bohr magneton.

where M_S is the saturation magnetization, k_B is Boltzmann's constant, μ is the uncompensated magnetic moment and χ_{AF} is the antiferromagnetic susceptibility. Modified Langevin equation (5) is used for nonlinear least squares fitting of the initial magnetization curves.

Langevin fitting lines pass through the origin of the $M-H$ curves, which indicate the paramagnetic behaviour of $A_2Ti_2O_7$ ($A = \text{Gd, Dy and Y}$) nanomaterials. The magnetic parameters such as saturation magnetization (M_S), uncompensated magnetic moment (μ), antiferromagnetic susceptibility (χ_{AF}) and coercivity (H_c) are obtained from the modified-Langevin equation for nonlinear least squares fitting curves. $A_2Ti_2O_7$ ($A = \text{Gd, Dy and Y}$) pyrochlore oxides show paramagnetic behaviour at room temperature, but the magnetization of paramagnetic materials increases quickly when the temperature decreases in the low-temperature region, because the entropy change increases when the temperatures decrease. This property suggests the possibility of using these materials as active magnetic refrigerants at very low-temperature in the range of 5–100 K [23]. The obtained magnetic parameters of $A_2Ti_2O_7$ ($A = \text{Gd, Dy and Y}$) samples at room temperature are summarized in table 3.

4. Conclusions

Pyrochlore structured $A_2Ti_2O_7$ ($A = \text{Gd, Dy and Y}$) ceramic materials were successfully synthesized by a citric acid based auto-ignition combustion process. XRD analysis confirmed the phase purity and phase formation of the prepared materials. The lattice strain and average crystallite size were evaluated by the $W-H$ method. The surface morphology and average grain size of the samples were determined using SEM. The surface area, pore size and particle size of the samples were obtained from BET analysis and the obtained higher BET surface area may result in an enhanced behaviour in photocatalyst activity and hydrogen storage. Langevin fitting lines passing through the origin of the $M-H$ curves specifies the paramagnetic behaviour of $A_2Ti_2O_7$ ($A = \text{Gd, Dy and Y}$) nanomaterials and these materials can be used as active magnetic refrigerants at low temperatures.

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