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Sol-gel synthesis, crystal structure and magnetic properties of nanocrystalline praseodymium orthoferrite

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Abstract
In this work, nano-sized crystalline praseodymium orthoferrite was successfully synthesized via sol-gel method using water – methanol co-solvent. Single-phase PrFeO₃ nanoparticles were formed after annealing the precursors at 650, 750, 850, and 950 °C during 60 min. The crystal size, lattice volume and coercivity ($H_c$) of nanocrystalline PrFeO₃ increase with the annealing temperature. The obtained praseodymium orthoferrite exhibited paramagnetic properties with $H_c = 28 – 34$ Oe.

Keywords: Sol-gel synthesis, Methanol, Praseodymium orthoferrite, Magnetic property

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1. Introduction

Amongst nano-sized metal oxide semiconductors, rare earth orthoferrites AFeO$_3$ (A = La, Y, Pr, Sm, Ho) have been studied for application in many fields such as inorganic dyes, optical catalysts, gas sensors, magnetic materials or electrodes for Li-ion battery [1–8]. The properties of this type of materials depend not only on the particle size and morphology, but also on the dopant concentration and preparation methods [5–9].

Recently, the sol-gel method has been used for preparation of AFeO$_3$ orthoferrite nanomaterials owing to many advantages of this method: low annealing temperature, narrow particle size distribution, high purity, facile synthesis of highly doped AFeO$_3$ materials, [1–3, 10–12]. However, the challenge of this method lies in the selection of appropriate organic polymer for gel formation and the experimental time is usually prolonged. In previous works [13–14], orthoferrite AFeO$_3$ (A = Nd and Ho) nanomaterials of particle size < 100 nm were synthesized by co-precipitation method using hot ethanol via the hydrolysis of A(III) and Fe(III) cations in hot water (T > 95 °C) and NH$_3$ 5 % solution as the precipitant. Methanol and ethanol have similar dipole moments ($\mu$(C$_2$H$_5$OH) = 1.66 D, $\mu$(CH$_3$OH) = 1.69 D) [15], which are lower than that of water ($\mu$(H$_2$O) = 1.85 D) [16]. Meanwhile, the viscosity of CH$_3$OH (5.9·10$^{-4}$ Pa·s) is lower than that of C$_2$H$_5$OH (1.2·10$^{-3}$ Pa·s), and is also very low compared to organic polymers [15]. As a result, the interaction between A(III) and Fe(III) cations with CH$_3$OH is smaller than with C$_2$H$_5$OH, which leads to the decrease of the size of orthoferrite AFeO$_3$ particles synthesized by sol-gel method using methanol.

In this work, the formation, as well as the structural and magnetic properties of nano-sized orthoferrite praseodymium (o-PrFeO$_3$) prepared by sol-gel method using methanol have been studied and characterized.

2. Experimental and methods

All solvents and chemicals for the synthesis of used nanocrystalline praseodymium orthoferrite were purchased and used as-received: Pr(NO$_3$)$_3$·6H$_2$O (99.8 % purity, Merck), Fe(NO$_3$)$_3$·9H$_2$O (99.6 % purity, Sigma-Aldrich), methanol absolute (99.7 % purity, d = 0.792 g/mL), ammonia solution (Xilong purity, 85 %, d = 0.901 g/mL).

A mixture of Pr(NO$_3$)$_3$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O (1:1 mol to mol ratio) was dissolved in 50 mL solvent of H$_2$O – CH$_3$OH (1:1, V/V). The mixture solution was then added dropwise to a round-bottom flask containing 150 mL boiling H$_2$O – CH$_3$OH co-solvent (T ~ 85 °C). The slow addition of Pr (III) and Fe (III) mixture to the co-solvent at 85 °C would increase the hydrolysis process, thus hinder and control the particle size of orthoferrite PrFeO$_3$. Details of optimized conditions can be found in previous reports on the synthesis of LnFeO$_3$ (Ln = Y, La, Nd) orthoferrites [17–19]. The system continued to be refluxed for an additional 30 minutes before cooling down to ~ 30 °C, resulted in a brownish-yellow mixture. By refluxing, the solvent volume was maintained and the diffusion of toxic CH$_3$OH vapor to the environment could be minimized. Next, NH$_3$ 5 % solution was added dropwise to the system until pH ~ 9÷10 (tested by pH paper). The system was stirred for 30 minutes, then vacuum filtered. After removing all the filtrate, the residue was dry at 50 °C during 3 hours and grounded to obtain brownish-yellow powder (precursor for the synthesis of o-PrFeO$_3$).

Thermogravimetry and differential scanning calorimetry (TG-DSC) curves were recorded under dried air at the heating rate of 10 K·min$^{-1}$, maximum temperature 950 °C, platinum crucibles, using Labsys Evo – TG-DSC 1600 °C (France).

X-ray diffraction (XRD) patterns of PrFeO$_3$ samples were recorded using X-ray powder diffractometer (XRD, D8-ADVANCE, Germany) with CuK$_\alpha$ radiation ($\lambda$ = 1.5406 Å), range 2$\theta$ = 10–75°, step size 0.019 °/s. Crystal size ($D_{XRD}$, nm) of PrFeO$_3$ samples was determined according to Debye–Scherrer equation, lattice parameters ($a$, $b$, $c$, $V$) were calculate according to previous works [12, 19–20]. Phase composition was determined by Rietveld refinement, Fullprof 2009.

The content and surface distribution of the elements (Pr, Fe, O) were studied by energy-dispersive X-ray spectroscopy (EDX and EDX-mapping), FE-SEM S-4800 (Japan). The quantitative elemental composition were taken as the average of 5 different positions of each sample.
Crystal size and morphology of PrFeO₃ samples were characterized by transmission electron spectroscopy (TEM), Joel JEM-1400 (Japan). The crystal size distribution of were determined by IMAGE J.

Hysteresis loop and magnetic properties including coercive force ($H_c$, Oe), remanent magnetization ($M_r$, emu/g) and saturation magnetization ($M_s$, emu/g) were recorded on vibrating sample magnetometer (VSM, MICROSENE EV11) under the magnetic field in the range of -21 000 Oe to +21 000 Oe.

3. Results and discussion

Fig. 1 shows the TG-DSC curves of precursors for the synthesis of α-PrFeO₃ nanomaterial. The total mass loss from room temperature to 950 °C was 23.67 %. This result proves the formation of bonds between Pr(III) and Fe(III) cation with CH₃- group in the precipitate [21]. Indeed, if this precipitate had only included Pr(OH)₃↓ and Fe(OH)₃↓, mass loss deduced from equation (1) would have been 18.07 %.

$$\text{Fe(OH)}_3 + \text{Pr(OH)}_3 \rightarrow \text{PrFeO}_3 + 3\text{H}_2\text{O} \quad (1)$$

The mass loss by decomposition of $\text{M}^{3+}$–CH₃ (M = Pr, Fe) bonds corresponds to the exothermic peak at 270.56 °C on the DSC curve (Fig. 1). The endothermic peaks at 113.37 and 358.52 °C are the dehydrate and decomposition of praseodymium (III) and iron (III) hydroxides. Similar results were also observed in previous works [13, 19] for HoFeO₃ and NdFeO₃ orthoferrite. The exothermic peak at 617.31 °C correspond to the phase formation of PrFeO₃ orthoferrite from Pr₂O₃ and Fe₂O₃, according to equation (2). This inference is in good agreement with the mass change on the TG curve (there were no observable changes in the sample’s mass from ~650 °C). From the TG-DSC results, the sample was annealed at 650, 750, 850, and 950 °C for 60 min to characterize the structural properties of PrFeO₃ crystals by XRD.

$$\text{Fe}_2\text{O}_3 + \text{Pr}_2\text{O}_3 \rightarrow 2\text{PrFeO}_3 \quad (2)$$

XRD patterns of praseodymium orthoferrite precursor after annealing at different temperatures for 60 min were shown in Fig. 2. The results give single phase orthorhombic PrFeO₃. All obtained peaks match well with the standard peaks of PrFeO₃ (JCPDS: 74-1472), without any observable oxide peaks such as Pr₂O₃, Pr₆O₁₁, or Fe₂O₃. The degree of crystallinity and crystal phase content of PrFeO₃ samples increased with the annealing temperature, however, this increment was not linear (Table 1). The crystallinity of the sample annealed at 750 °C (592.04 cts) and that annealed at 950 °C (614.66 cts) were approximate, but the PrFeO₃ crystal phase content of the sample...
annealed at 750 °C was much higher than the others. The full-width at half maximum (FWHM, °) of the sample annealed at 750 °C was the widest, leading to the smallest Debye-Scherrer crystal size \( D_{\text{XRD}} = 48.6 \text{ nm} \) and lattice volume \( V = 235.17 \text{ Å}^3 \) (Table 1). Thus, it can be assumed that 750 °C for 60 min is the appropriate conditions for the formation of single phase praseodymium orthoferrite (o-PrFeO\(_3\)) by sol-gel method using water-methanol co-solvent.

From the EDX and EDX-mapping analysis of PrFeO\(_3\) sample annealed at 750 °C, only

**Table 1. Characteristics of PrFeO\(_3\) samples annealed at different temperatures for 60 min**

| T    | 650 °C | 750 °C | 850 °C | 950 °C |
|------|--------|--------|--------|--------|
| \( \theta \), ° | 32.6092 | 32.5659 | 32.6185 | 32.5584 |
| Height, cts | 288.26 | 592.04 | 490.86 | 614.66 |
| Crystal phase, % | 68.8 | 93.4 | 80.5 | 89.7 |
| Amorphous phase, % | 31.2 | 6.6 | 19.5 | 10.3 |
| FWHM, ° | 0.1309 | 0.1683 | 0.1122 | 0.1122 |
| d-spacing, Å | 2.74604 | 2.74960 | 2.74529 | 2.75022 |
| \( D \), nm | 62.5 | 48.6 | 73.0 | 73.0 |
| \( a \), Å | 5.4556 | 5.4521 | 5.4509 | 5.4501 |
| \( b \), Å | 5.5753 | 5.5840 | 5.6206 | 5.6218 |
| \( c \), Å | 7.8113 | 7.7245 | 7.8169 | 7.8145 |
| \( V \), Å\(^3\) | 237.59 | 235.17 | 239.49 | 239.45 |
| \( H_c \), Oe | 28.0 | 30.8 | 35.7 | – |
| \( M_r \) , emu/g | 0.22 | 0.13 | 0.76 | – |
| \( M_s \) , emu/g | 0.24 | 1.10 | 0.75 | – |
Praseodymium, iron and oxygen peaks were observable without any other signals of impurity elements (Fig. 3). The averages of weight percentage and atomic percentage of the elements Pr, Fe, O from five different positions are shown in Table 2. The obtained results are consistent with expected chemical composition (Table 2).

Particle size and morphology of PrFeO$_3$ powder annealed at 750 °C are shown in the TEM image (Fig. 4a). The obtained particles have slightly angular spherical shape with the size mostly in the range of 20–60 nm (Fig. 4b). Average size calculated by IMAGE J was 46.28 nm. This result is rather close to the crystal size by Debye-Scherrer equation ($D_{XRD} = 48.6$ nm) (Table 1).

Field dependence of the magnetization of PrFeO$_3$ nanomaterials at 300K are shown in Fig. 5. The coercive force ($H_c = 20.8 \div 30.7$ Oe) and saturation magnetization ($M_r = 0.13 \div 0.76$ emu/g) (Table 1) of all three PrFeO$_3$ samples in this work are much lower than those of PrFeO$_3$ prepared by co-precipitation method reported by Sudandararaj T. S. A. et. al. [22] ($H_c = 505.45$ Oe, $M_r = 27.63$ emu/g). The low value of $H_c$ and

Table 2. EDX analysis of PrFeO$_3$ nano-sized powders annealed at 750 °C

|       | Pr  | Fe  | O   |
|-------|-----|-----|-----|
| Wt%   | 56.39 | 22.35 | 60.70 |
| At%   | 21.02 | 18.28 | 60.70 |

Fig 3. EDX and EDX-mapping images of PrFeO$_3$ sample annealed at 750 °C

Fig. 4. (a) TEM image of PrFeO$_3$ sample annealed at 750 °C and (b) Particle size distribution
$M_r$ could be originated from the homogeneity in shape and size of the PrFeO$_3$ nanoparticles with clear particle boundaries (see Fig. 4) while in the TEM image of the corresponding PrFeO$_3$ in [22], the particle boundaries are not observable with severe aggregation that joined the entire area of the material despite the particle size of 36.0 nm (by Image J).

Most interestingly, the magnetic parameters of PrFeO$_3$ nanomaterials changed irregularly with the annealing temperature (Table 1). The PrFeO$_3$ sample annealed at 750 °C has the lowest $M_r$ (0.13 emu/g) while its $M_s$ (1.10 emu/g) has the highest value. This can be ascribed by the highest crystallinity and crystal phase content of the PrFeO$_3$ sample annealed at 750 °C (see Table 1) which decreased the magnetocrystalline anisotropy of the material, leading to the rise in $M_s$ and the decreased in $M_r$ [23–24].

Thus, with low $H_c$, $M_r$ and high $M_s$, obtained PrFeO$_3$ nanomaterials are soft magnetic materials that can be applied as material working under the external field as transformer cores, electromagnet cores, and conductive cores [24].

4. Conclusions

In this study, nanocrystalline praseodymium orthoferrite (o-PrFeO$_3$) was successfully synthesized by sol-gel method using water-methanol co-solvent. The PrFeO$_3$ nanocrystal formed after annealing the precursor at different temperatures (650, 750, 850, and 950 °C) for 1 hour. The crystal size of PrFeO$_3$ samples are in the range of 45–70 nm (XRD, TEM). The PrFeO$_3$ sample annealed at 750 °C had the highest crystallinity (592.04 cts) and crystal phase content (93.4 %) (XRD) with smallest particle size (46.28 nm, TEM). The obtained PrFeO$_3$ nanomaterials are soft magnetic materials with low coercive force and remanent magnetization, high saturation magnetization.

**Conflict of interests**

The authors maintain that they have no conflict of interest to be described in this communication.

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Fig. 5. Field dependence of the magnetization of PrFeO$_3$ nanoparticles annealed at 650, 750, and 850 °C for 1 h.
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