Crystal structure, optical and magnetic properties of PrFeO$_3$ nanoparticles prepared by modified co-precipitation method

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Abstract

In this work, PrFeO$_3$ nanoparticles were synthesized by modified co-precipitation method and annealed at different temperatures up to 850 °C. The annealed PrFeO$_3$ nanoparticles have single phase orthorhombic structure and the average particle size of 25–30 nm. Due to the very small particle size the prepared PrFeO$_3$ nanoparticles are capable of being used as photocatalyst materials thanks to their strong adsorption bands at 230–400 nm and 400–800 nm observed from the UV-Vis spectra. Additionally, the PrFeO$_3$ nanoparticles are paramagnetic materials with $H_c \sim 10$ Oe and $M_r \sim 0$. These findings demonstrate their potential use not only as photocatalysts, but also as magnetic materials.

Keywords: PrFeO$_3$, nanoparticles, improved co-precipitation method, optical and magnetic properties

I. Introduction

Complex oxides with ReMO$_3$ perovskite structure, where Re and M are rare-earth and transition metals, respectively, represent an important class of functional materials [1–3]. Especially, the materials based on orthoferrite rare-earth elements (Re = La, Pr, Nd, Ho, etc.) possess good electrical and magnetic properties which are decreased from microscale to nanoscale [4–9]. Among the rare-earth orthoferrites, PrFeO$_3$ has found applications in magnetic field materials [10–13], photocatalysis [14–16], dyes and inorganic pigments [17,18].

Properties of the orthoferrite ReFeO$_3$ perovskite nanomaterials, such as optical and magnetic properties, depend on the chemical composition, distribution of cations, particle size and synthesis method. Typically, the PrFeO$_3$ nanoparticles with size of 80 nm show a band gap value of 2.4 eV [15], which decreases to 2.08 eV when the particle size is 50 nm [14]. The decrease of the band gap leads to the increase of photocatalytic yield in visible light and offers new areas of application.

Magnetic behaviour of PrFeO$_3$ has also attracted significant attention. Thus, the magnetic characteristics (antiferromagnetic Néel temperature $T_N$, curves of magnetic susceptibility reciprocal $1/\chi$ against temperature and the temperature dependence of magnetization ZFC and FC) of orthoferrite PrFeO$_3$ materials with a parti-
Particle size of 20–30 μm have been investigated under the applied magnetic field of 1000 Oe [10]. In addition, the temperature dependence of magnetization (ZFC and FC) with a magnetic field of 500 Oe has been investigated for the orthoferrite PrFeO₃ thin film (having thickness ~200 nm) [11,12] prepared by a ceramic reaction technique.

Orthoferrite PrFeO₃ nanoparticles have been synthesized via various methods including high-temperature ceramic fabrication [9,13,18], hydrothermal methods [10,16], and sol-gel complex methods [14,15,17,19]. However, orthoferrite PrFeO₃ particles with a size of 25–30 nm (prepared by simple co-precipitation method), a small band gap and the features of magnetism under a high magnetic field (~15000 Oe) have not been reported. Thus, the aim of this work was to prepare PrFeO₃ nanoparticles (20–25 nm) and study their structural, optical, and magnetic properties.

II. Experimental procedure

Pr(NO₃)₃·6H₂O (99.8% purity, Merck), Fe(NO₃)₃·9H₂O (99.6% purity, Sigma-Aldrich) and NH₃ solution (Xilong, 85% purity), were employed as the starting materials. The synthetic process was similar to that described in our previous reports [20–22]. A solution including an equal amounts of Pr(NO₃)₃ and Fe(NO₃)₃ salts was gradually introduced to hot water (> 90°C). Then, the mixture was continuously stirred for 5 min and cooled to room temperature (25–30°C). In the next step a 5% NH₃ solution was slowly added and continuously stirred until the solution colour changed into light pink indicated by phenolphthalein. The precipitate was filtered, washed by deionized water until pH = 7 and dried in air at room temperature (25–30°C). Finally, the products were ground and thermally treated at different temperatures.

Furthermore, the pure oxide materials, i.e. Fe₂O₃ and Pr₂O₃, were also prepared by a similar procedure to compare their structure with the structure of the synthesized PrFeO₃ perovskite materials.

TGA-DSC analyser (Labysys Evo, TG-DSC 1600°C, SETERAM Instrumentation, Caluire, France) was used to determine the appropriate temperature for obtaining the single-phase PrFeO₃ perovskite structure. The sample was placed in a platinum cylindrical crucible and heated from 25 to 1000°C at 10°C/min in dried air.

X-ray powder diffraction (PXRD) patterns were obtained on a D8-ADVANCE (Bruker, Bremen, Germany) with CuKα radiation (λ = 1.5418 Å) using step size of 0.02° in the range of 10–80°. The crystalline sizes of the annealed PrFeO₃ powders were determined based on Scherrer’s equation [23]:

\[
D = \frac{0.894}{\beta \cdot \cos \theta}
\]

where λ is X-ray wavelength of CuKα = 1.5418 Å, θ is the diffraction angle of the maximum reflection and β is the full-width at half maximum (FWHM). The lattice parameters (a, b, c) and cell volume (V) were calculated by Eqs. 2 and 3, respectively [23]:

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]

\[
V = a \cdot b \cdot c
\]

where d is the distance between crystalline planes with Miller indices hkl.

Particle size and morphology of the annealed PrFeO₃ crystals were studied by transmission electron microscopy (TEM, Joel JEM-1400, Joel Ltd., Tokyo, Japan) and field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan). The content and surface distribution of Pr, Fe and O elements were determined by energy-dispersive X-ray spectroscopy (EDX and EDX-mapping, Horiba H-7593, Horiba, Northampton, UK).

The UV-Vis absorption spectra of the PrFeO₃ nanocrystals were recorded on a UV-Visible spectrophotometer (UV-Vis, JASCO V-550, Hachioji, Tokyo, Japan). Magnetic properties of the samples (saturation magnetization Ms, coercivity Hc and remanent magnetization Mr) were measured at room temperature with a vibrating sample magnetometer (VSM, MicroSense EV11, Japan).

III. Results and discussion

3.1. Thermal analysis

To find the optimal temperature range in which single-phase PrFeO₃ perovskite structure will be formed, thermal gravimetric analysis (TGA) was conducted and the results are presented in Fig. 1. Accordingly, the initial weight loss (~7.6%) starts at 60°C, yields a maximum value at 107°C and finishes at ~240°C. An endothermic peak arises on the DSC curve at 107°C, which can be attributed to the loss of surface

![Figure 1. TG-DSC curves of PrFeO₃ precipitate sample](image-url)
water. From 240 to \(\sim 550^\circ C\), the weight loss (\(-16.4\%\)) is due to water removal through crystallization, the dehydration of \(\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}\) (where \(x = 1–5\)) [24] and the pyrolysis of \(\text{PrO(OH)} \cdot y\text{H}_2\text{O}\) [25]. In this stage, two endothermic peaks appeared at 356 and 430 \(^\circ C\), respectively. The small weight loss (\(-4.6\%\)) between 550 and 730 \(^\circ C\) may account for the release of adsorbed \(\text{CO}_2\) from the \(\text{Pr}_2\text{O(CO}_3\text{)}_2 \cdot 1.4\text{H}_2\text{O}\) or \(\text{Pr}_2\text{(CO}_3\text{)}_3 \cdot 8\text{H}_2\text{O}\) structures [25,26]. In addition, in the temperature interval from 600 to 650 \(^\circ C\) there is an exothermic peak with maximum at 619 \(^\circ C\) indicating formation of perovskite phase. Hence, the temperatures of 650, 750 and 850 \(^\circ C\) were chosen for investigating the structure and morphology of the synthesized \(\text{PrFeO}_3\) nanoparticles.

### 3.2. Structure and morphology

PXRD patterns of the samples \(\text{PrFeO}_3\), \(\text{Fe}_2\text{O}_3\) and \(\text{Pr}_6\text{O}_{11}\) after annealing for 1 h at 750 \(^\circ C\) are presented in Fig. 2. For the pure Pr-based sample, the stable \(\text{Pr}_6\text{O}_{11}\) phase was generated after annealing the hydroxide praseodymium precipitate instead of the unstable \(\text{Pr}_2\text{O}_3\) phase. This is clearly explained by the following equation [25]:

\[
6\text{Pr(OH)}_3 + \text{O}_2 \rightarrow \text{Pr}_6\text{O}_{11} + 9\text{H}_2\text{O} \quad (4)
\]

Interestingly, the observed reflections of the \(\text{PrFeO}_3\) sample are in good agreement with the standard JCPDS 047-0065 of the orthorhombic \(\text{PrFeO}_3\) phase without any XRD peaks of \(\text{Fe}_2\text{O}_3\) and \(\text{Pr}_6\text{O}_{11}\) phases. This is clear confirmation of the TGA-DSC results and indication that the reaction between precursors is completed after annealing.

Further on, the diffraction pattern of the \(\text{PrFeO}_3\) samples annealed at 650, 750 and 850 \(^\circ C\) for 1 h are shown in Fig. 3. All three samples have single-phase orthorhombic \(\text{PrFeO}_3\) structure. The increase of annealing temperature leads to the increase of the peak intensity and decrease in the full-width at half maximum (FWHM). The crystal size, calculated by the Scherrer’s equation, decreases from 21.3 to 27.4 nm when the annealing temperature increases from 650 to 850 \(^\circ C\) (Table 1).

![Figure 3. PXRD patterns of \(\text{PrFeO}_3\) nanopowders annealed at 650, 750 and 850 \(^\circ C\) for 1 h](image)

The lattice parameters \((a, b, c)\) and cell volume \((V)\), calculated by Eqs. 2 and 3, are shown in Table 1. It is clear that the change of parameter \(a\) and \(b\) is non-linear, however, unit cell volume \((V)\) increases with the annealing temperature. A similar result was also observed in the previous report [18].

SEM and TEM images (Fig. 4) of the orthoferrite \(\text{PrFeO}_3\) powder annealed at 750 \(^\circ C\) confirm that the particles are equiaxial and have an average size of 25–30 nm. EDX spectra and EDX-mapping are given in Fig. 5 indicating the uniform distribution of praseodymium, iron and oxygen as the elementary components. Analysis of the weight and atomic percent of \(\text{PrFeO}_3\) nanoparticles were in agreement with the theoretical values calculated from the chemical formula.

### 3.3. Optical and magnetic properties

The UV-Vis absorption spectra of the \(\text{PrFeO}_3\) nanoparticles annealed at 750 \(^\circ C\) showed strong absorption in the ultraviolet (\(-230–400\) nm) and visible

![Figure 2. PXRD patterns of \(\text{PrFeO}_3\), \(\text{Fe}_2\text{O}_3\) and \(\text{Pr}_6\text{O}_{11}\) powders annealed at 750 \(^\circ C\) for 1 h](image)

![Table 1. XRD peak intensity \((I)\), crystal size \((D)\) and lattice parameters of \(\text{PrFeO}_3\) samples annealed at 650, 750 and 850 \(^\circ C\) for 1 h](table)

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>(I) (count)</th>
<th>FWHM ((^\circ))</th>
<th>(D) (nm)</th>
<th>Lattice constants [(\text{Å})]</th>
<th>Cell volume (V) [(\text{Å}^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>650 (^\circ C)</td>
<td>142</td>
<td>0.384</td>
<td>21.3</td>
<td>5.4564 5.5756 7.8032</td>
<td>237.40</td>
</tr>
<tr>
<td>750 (^\circ C)</td>
<td>165</td>
<td>0.336</td>
<td>24.4</td>
<td>5.4756 5.5821 7.7900</td>
<td>238.11</td>
</tr>
<tr>
<td>850 (^\circ C)</td>
<td>178</td>
<td>0.312</td>
<td>27.4</td>
<td>5.4418 5.6150 7.8111</td>
<td>238.67</td>
</tr>
</tbody>
</table>
light regions (∼400–800 nm). This is interesting because PrFeO$_3$ could be applied as a new visible-light photocatalyst. The direct band gap energy ($E_g$) was determined by fitting the absorption data to the direct transition using the following equation:

$$A \nu = \sqrt{\alpha (\nu - E_g)}$$

(5)

where $A$ is the optical absorption coefficient, $\nu$ is the photon energy, $E_g$ is the direct band gap and $\alpha$ is a constant [27]. The extrapolation of the linear portions of the curves toward absorption equal to zero ($(A \nu)^2 = 0$) gives $E_g$ for direct transitions (Fig. 6b). As a consequence, the band gap value of the PrFeO$_3$ nanoparticles is ∼1.660 eV which is lower than in the previous works. For example, Tijare et al. [14] and Peisong et al. [15] have reported direct band gap values of 2.08 and 2.40 eV for PrFeO$_3$ nanoparticles synthesized by sol-gel method, respectively. The band gap values obtained are 2.03 and 1.88 eV for PrFeO$_3$ synthesized by template and combustion methods, respectively [14]. This is probably because the PrFeO$_3$ nanoparticles synthesized in this study have a smaller particle size than in previous works [14,15]. With $E_g = 1.660$ eV, the obtained PrFeO$_3$ nanoparticles are in the form of semiconductor material, suitable for application in photocatalysis, sensor and electrode materials in solid oxide fuel cells [1,14–16].
Magnetic properties of PrFeO$_3$ materials at 300 K are shown in Fig. 7. The value of coercivity is very low (especially for PrFeO$_3$ annealed at 750 and 850 °C, $H_c \sim 10$ Oe) and gradually decreases with an increase of the annealing temperature (Table 2). Herein, it can be explained that the phase structure of PrFeO$_3$ per-
ovskite becomes complete after increasing the annealing temperature. This can lead to a reduction of crystal anisotropy i.e. reduction of lattice defects [31]. Interestingly, the synthesized PrFeO$_3$ nanomaterials possess a value of the remanent magnetization almost zero ($M_r \approx 0$) and the magnetization ($M_s$) curve rises with an increase of the magnetic field (Fig. 7). Moreover, the value of coercivity is much lower than for the RFeO$_3$ (R = Pr, Ho, La, Nd, Y) materials reported previously [28]. The small value obtained for the coercivity can be explained by the small particle size and less agglomeration of the synthesized nanoparticles PrFeO$_3$ in this study compared with previous work [28].

Therefore, the synthetic PrFeO$_3$ nanoparticles are paramagnetic material and can be applied in biomedical physics, involving rapid responses with external magnetic fields [32].

IV. Conclusions

The PrFeO$_3$ nanoparticles were prepared by modified co-precipitation method and annealed at different temperatures (650, 750 and 850 °C). It was found that after annealing the single-phase orthorhombic PrFeO$_3$ was generated possessing the average particle sizes in the range of 25–30 nm and unit cell volumes in the range of 237–239 Å$^3$. As a result of these structural features, the PrFeO$_3$ nanoparticles adopted the strong adsorption bands in the UV-Vis range. This can lead to potential applications for photocatalytic materials. The PrFeO$_3$ nanoparticles are paramagnetic with low coercivity and remanent magnetization, which makes them the potential candidates for making the devices operating at a high magnetic field.

References

16. S.K. Megarajan, S. Rayalu, M. Nishibori, N. Labhsetwar,


