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Synthesis and magnetic properties of $PrFeO_3$ nanopowders by the co-precipitation method using ethanol

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Praseodymium orthoferrite nanoparticles were synthesized by a simple co-precipitation method via the hydrolysis of Pr (III) and Fe (III) cations in boiling ethanol with 5% aqueous ammonia. The single-phase $PrFeO_3$ product formed after annealing the precipitates at 650, 750, and 850°C for 1 h had an average crystal size of 20–30 nm (XRD, SEM, TEM). The synthesized nanopowders were soft ferromagnetic materials with low coercive force and excessive magnetization values.

Keywords: o-$PrFeO_3$, nanoparticles, magnetic properties, co-precipitation, ethanol.

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1. Introduction

Among semiconductors, oxides with a perovskite-like structure of the $ReMeO_3$ type (Re – rare-earth elements; Me – transition metals) have both significance and importance for their application and fundamental research [1–8], since these oxides have a high sensitivity of properties to decrease in particle size to nanometer values. Among the rare-earth orthoferrites, $PrFeO_3$ was obtained and used in some fields, such as magneto-optical devices and electromagnetic equipment [9–13], photocatalysts [14–16], dyes, and inorganic pigments [17, 18].

A wide variety of techniques have been developed for the synthesis of praseodymium orthoferrite nanoparticles (o-$PrFeO_3$), for example, high-temperature ceramic fabrication [9, 11, 18], hydrothermal methods [13, 16], and sol-gel complex methods [14, 15, 17, 19]. Several studies [20–25] describe the formation of $ReFe_{1-x}M_xO_3$ orthoferrites nanoparticles (Re = Nd, Y, La; M = Mn, Co, Ni), by a simple co-precipitation method in boiling water followed by the addition of appropriate precipitants. According to published data, the replacement of water as a solvent with ethanol for the synthesis of o-$PrFeO_3$ nanoparticles was not studied.

The goal of this study the synthesis of praseodymium orthoferrite (o-$PrFeO_3$) nanoparticles with low coercive force and excessive magnetization by co-precipitation via hydrolysis of praseodymium (III) and iron (III) cations in boiling ethanol with the addition of an ammonia solution.

2. Experimental

In this study, we used $Pr(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, absolute ethanol (d=0.79 g/ml), 25 % ammonia solution (d=0.901 g/ml) (all reagents were of CP grade), distilled water. The procedure for $PrFeO_3$ nanoparticles synthesis was similar to that of $ReFeO_3$ (Re = Nd, Y, La) nanomaterials [20, 21], with ethanol as the solvent instead of water.

Complex thermal analysis of the $PrFeO_3$ sample was carried out TG-DSC analyzer (Labsys Evo, TG-DSC 1600°C, SETARAM Instrumentation). The sample was placed in a platinum cylindrical crucible and heated from 30 to 1000°C at 10 K min^{-1} in dried air. X-ray phase analysis was carried out on a D8-ADVANCE diffractometer (CuKα radiation, $\lambda = 0.15418$ Å). The qualitative and quantitative elemental composition was established using a local X-ray spectral microanalysis (EDX, Horiba H-7593. Particle size and morphology were determined using

scanning electron microscopy (FESEM S-4800) and high voltage transmission electron microscopy (HRTEM; JEOL-1400). The average crystal size was determined according to the Debye Scherrer equation; parameters a, b, c and the unit cell volume V were determined using the Rietveld method, implemented in the X'pert High Score Plus 2.2b software package.

The magnetic characteristics of $PrFeO_3$ nanopowders (coercive force H_c, remanent magnetization M_r, and magnetization M_s) were studied using vibrating sample magnetometer at room temperature (VSM, MICROSENE EV11).

3. Results and discussions

The complex thermal analysis of the dried precipitate showed (Fig. 1) that the mass loss during heating of the sample in the range of 60–1000°C was 27.01 %. The most significant mass loss (about 25.85 %) was observed in the range of 50–600°C. The processes occurring during heating of the precipitate were accompanied by three endothermic thermal effects at 93.38, 327.62, and 420.78°C (Fig. 1), characteristic for water evaporation, decomposition of iron (III) hydroxides and praseodymium (III) (20, 26 In the 600–700°C range, an exothermic thermal effect (636.10°C, Fig. 1) was observed corresponding to the formation of perovskite $PrFeO_3$.

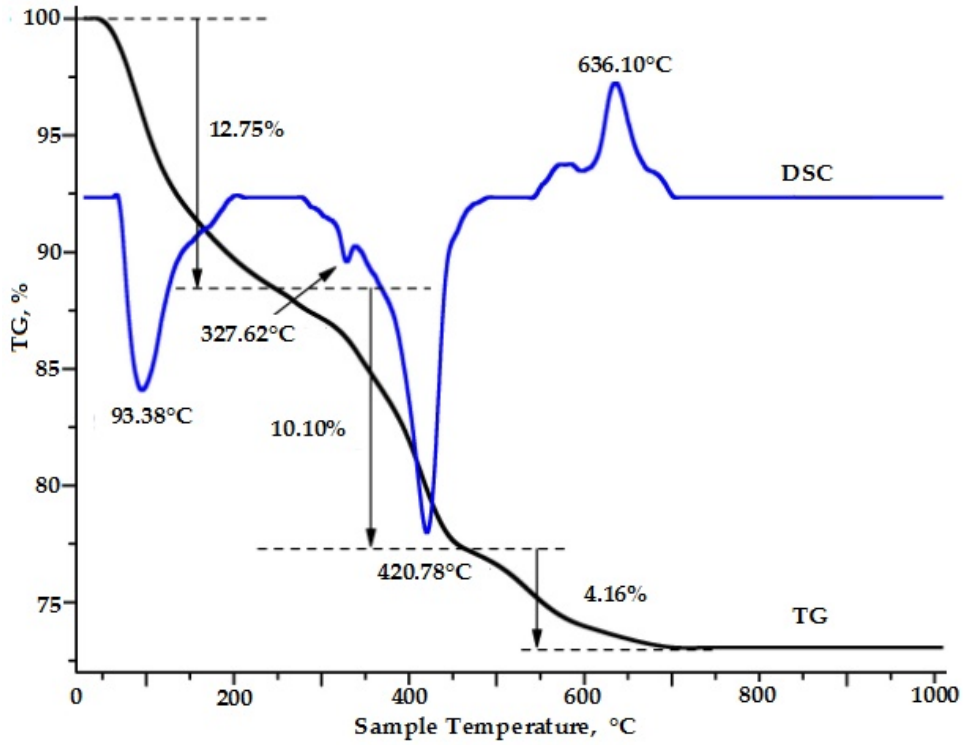

FIG. 1. TG-DSC curves of the powders prepared by a simple co-precipitation method using ethanol

In accordance with the data of complex thermal analysis for the synthesis of praseodymium orthoferrite, the temperatures of 650, 750 and 850°C were chosen to calcine the precipitate for 1 h. XRD patterns of the samples annealed at 650, 750, and 850°C for 1 h showed single-phase orthoferrite $PrFeO_3$ (JCPDC No 00-047-0065) (Fig. 2). The average crystal diameter and cell volume of $PrFeO_3$ samples increase with increasing annealing temperature, (Table 1).

According to the results of local X-ray spectral microanalysis, $PrFeO_3$ sample contained only three elements – Pr, Fe, and O (Fig. 4). Mass percentage and elemental percentage of obtained $PrFeO_3$ nanopowders are rather close to expected chemical composition (Fig. 4). It can be seen from SEM, TEM, and HRTEM images (Fig. 5) that, after annealing at 750°C for 1 h, $PrFeO_3$ nanoparticles were isometric, and the average size of individual particles was about 30 nm. Interestingly, the synthesized $PrFeO_3$ nanoparticles were characterized by a lower degree of agglomeration compared to the orthoferrites of other rare-earth elements, such as $NdFeO_3$ [20], $YFeO_3$ [21], and $LaFeO_3$ [25], obtained by the co-precipitation method via the hydrolysis of cations in boiling water. This was explained by the fact that a lower polarity of ethanol than water (the dipole moments of water and ethanol are 1.85 and 1.66 D, respectively [26, 27]) led to an insignificant interaction between the cations of iron (III) and praseodymium (III) with

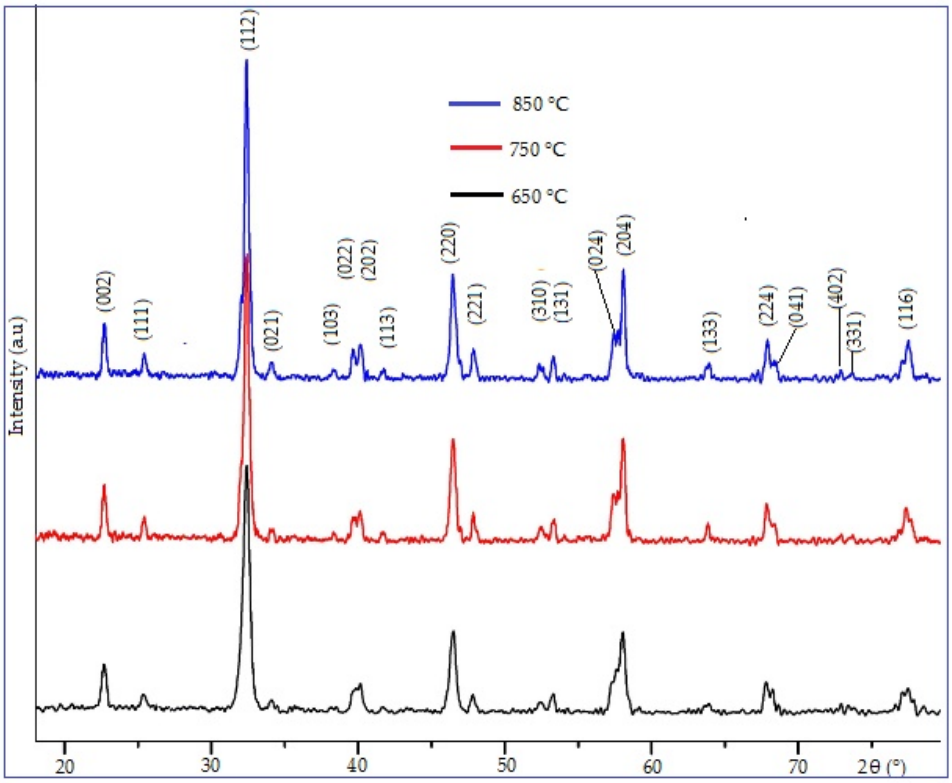

FIG. 2. XRD patterns of $PrFeO_3$ nanopowders annealed at 650, 750, and 850°C for 1 h

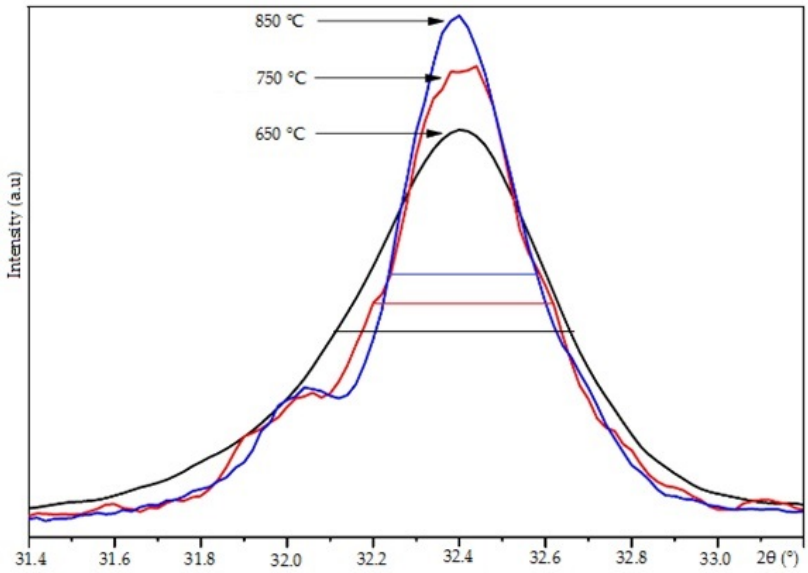

FIG. 3. Slow-scan XRD patterns of peak (121) of $PrFeO_3$ nanopowders annealed at 650, 750, and 850°C for 1 h

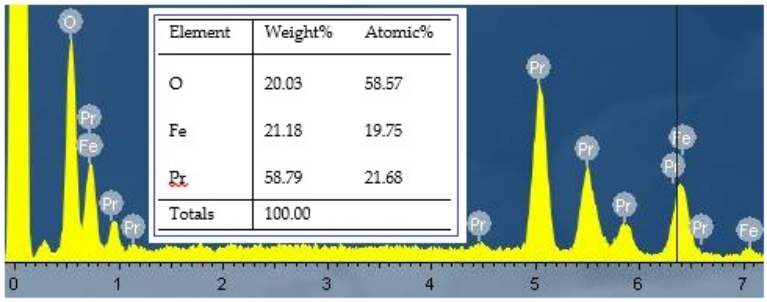

FIG. 4. EDX image of $PrFeO_3$ sample annealed at 750°C for 1 h

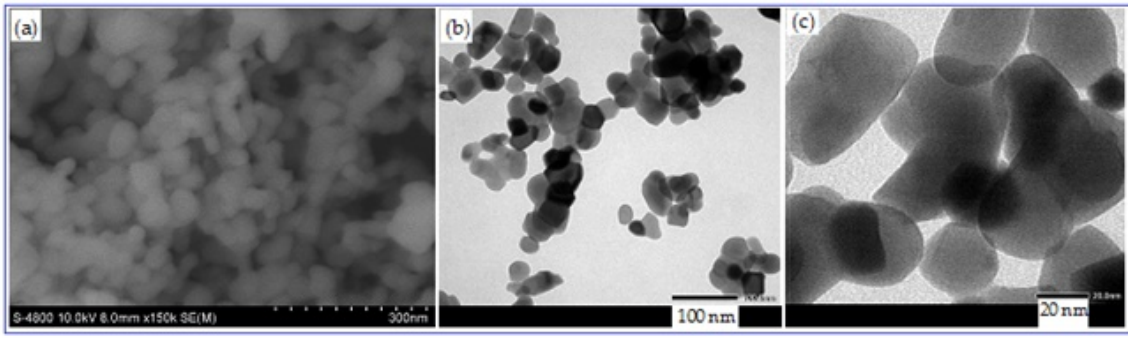

FIG. 5. SEM (a), TEM (b), and HRTEM (c) images of $PrFeO_3$ nanoparticles annealed at 750°C for 1 h

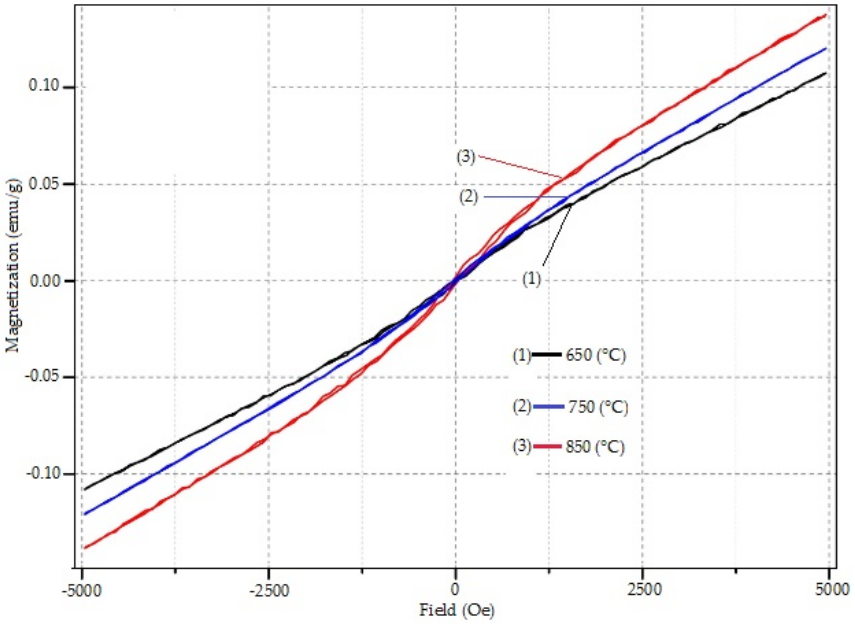

FIG. 6. Field dependence of the magnetization of $PrFeO_3$ nanopowders, annealed at 650, 750, and 850°C for 1 h

TABLE 1. XRD patterns of $PrFeO_3$ nanopowders annealed at 650, 750, and 850°C for 1 h

Indices	$PrFeO_3$		
	650°C	750°C	850°C
a, Å	5.4576	5.4732	5.4513
b, Å	5.5742	5.5831	5.6207
c, Å	7.8110	7.7995	7.8178
Volume, $Å^3$	237.62	238.33	239.54
Average crystal diameter, nm	19.73	22.37	25.48
Coercive force H_c, Oe	17.45	29.45	33.38
Remanent magnetization M_r, emu/g	$0.44 \cdot 10^{-3}$	$1.10 \cdot 10^{-3}$	$1.77 \cdot 10^{-3}$
Magnetization M, emu/g	0.11	0.12	0.14

ethanol molecules. Accordingly, the formed sediment particles were more easily separated from each other and from the solvent.

The study of $PrFeO_3$ samples using the magnetometer MICROSENE EV11 at 300 K in a maximum field of 5000 Oe showed that all certain magnetic characteristics H_c, M_r and M_s (Fig. 6, Table 1). Probably, this was due to the fact that annealing at a higher temperature led to larger $PrFeO_3$ particles (Table 1). Nanoscale particles ($D < 100$ nm) can be considered as single-domain particles. Then, H_c depends on the particle size according to the following formula [28]:

$$H_c = g - \frac{h}{D^{3/2}} \tag{1}$$

where g and h are constants, and D is the particle diameter. Clearly, H_c will increase with the particle size. Indeed, when the crystallite size rises from 19.73 to 25.48 nm, H_c also increases from 17.45 to 33.38 Oe. A similar pattern was observed in [25]. It is more interesting that the synthesized $PrFeO_3$ nanocrystals were characterized by lower H_c and M_r values, but higher M_s at 300 K compared to the orthoferrite particles of other rare-earth elements, such as $HoFeO_3$ (H_c=2659 Oe, M_r=4.08, [29]), $LaFeO_3$ (H_c=1217.6 Oe, M_r=$5.43 \cdot 10^{-4}$ emu/g, M_s=$6.49 \cdot 10^{-3}$ emu/g, [30]), $NdFeO_3$ (H_c ~850 Oe, M_r=1.5 emu/g, [31]) and even o-$PrFeO_3$ (M_s=0.05 emu/g, [13]).

The studied o-$PrFeO_3$ samples with low values of coercive force, excess magnetization, and higher magnetization not reaching magnetic saturation at a maximum field of 5000 Oe were a soft magnetic ferromagnet and can be used for the manufacture of magnetic cores, transformers, electric motors, and generators.

4. Conclusion

In this study, o-$PrFeO_3$ nanoparticles with an average crystal size < 30 nm were formed by co-precipitation method by aqueous ammonia solution via simple process of the hydrolysis of Pr (III) and Fe (III) cations in boiling ethanol, followed by annealing at 650, 750, and 850°C for 1 h. The synthesized o-$PrFeO_3$ nanopowders were characterized by a narrow hysteresis loop, low values of excess magnetization and coercive force, but high magnetization, which makes them promising for use as soft ferromagnetic material in the manufacture of magnetic cores, transformers, electric motors, generators, and radio engineering.

Conflict of interests

The authors maintain that they have no conflict of interest with respect to this communication.

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