Hydrothermal synthesis and magnetic properties of multiferroic rare-earth orthoferrites

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ABSTRACT

Rare-earth orthoferrites $RFeO_3$ are gifted with fantastic magnetic properties. They have become a research focus for developing multiferroics in recent years. However, it is difficult to obtain pure-phase $RFeO_3$ from the high-temperature synthesis methods. In this work, we report hydrothermal synthesis of well-crystallized pure-phase orthoferrites $RFeO_3$ (R = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in low temperatures. Structures, morphologies and magnetic properties of the products were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), magnetic property measurement system (MPMS), vibrating sample magnetometer (VSM), etc. The expected products were determined to be orthorhombic crystals of perovskite structure. The influences of alkalinity, reaction temperature and time on the formation and growth of $RFeO_3$ crystals were investigated in details, and a dissolution–precipitation mechanism was proposed for describing the formation and growth. Optimum hydrothermal conditions for synthesizing orthoferrites $RFeO_3$ were concluded. The magnetic properties were systematically characterized and studied, including antiferromagnetic transition of Fe (T_{N1}), spin reorientation (T_{SR}), compensation effect (T_{comp}), ordering of R (T_{N2}), etc. The relation between the magnetic properties of $RFeO_3$ and the ionic radii of R was investigated and discussed. The experimental results in this work may provide fundamental support to the research and development of multiferroic materials.

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1. Introduction

Rare-earth orthoferrites $RFeO_3$ (R = rare earth) attract great attention due to their fantastic magnetic properties. Their existing and promising applications cover catalysis [1–4], gas separating [5], fuel cells [6], sensing [7], magnetooptic devices [8], electromagnetic equipment, environmental monitoring [9], spin valves [10], advanced information storage, etc. Especially with the rise of multiferroic materials in recent years, rare-earth orthoferrites $RFeO_3$ have become a research focus for developing multiferroics [11,12]. Some orthoferrites $RFeO_3$ may exhibit uncommon coexistence of ferroelectricity and weak ferromagnetism [13,14].

Rare-earth orthoferrites $RFeO_3$ (*Pbnm*) are Dzyaloshinsky–Moriya type canted weak ferromagnets, unusually exhibiting large antisymmetric exchange interactions, very small anisotropy of Fe spins in *a–c* plane, and very large anisotropy towards *b* axis [15]. The fantastic magnetic properties such as spin reorientation (T_{SR}), antiferromagnetic transition of Fe (T_{N1}), compensation effect (T_{comp}), ordering of R (T_{N2}) and weak ferromagnetism (canted antiferromagnetism). as well as the ferroelectricity of orthoferrites

$RFeO_3$ mainly originate from the competing Fe–Fe, R–Fe and R–R superexchange interactions and the distorted orthorhombic perovskite structure [16]. The multiferroics of orthoferrites $RFeO_3$ is closely related with the magnetic transition and magnetic ordering. Some work has been reported concerning multiferroic properties of orthoferrites $RFeO_3$ [14,16–23]. Tokunaga et al. reported that $DyFeO_3$ single crystal shows gigantic magnetoelectric phenomena and spontaneous polarization below T_{N2} [21]. Lee et al. reported that the canted antiferromagnetic ordering causes extraordinary polarization in $SmFeO_3$ [24].

The small Fe ion is located at the center of an octahedron of oxygen anions and the large trivalent R ions at the unit cell corners. An interesting aspect of orthoferrites $RFeO_3$ is found that variations in R–O and Fe–O interactions can been observed with varying of the R ionic sizes as well as distortion of the oxygen octahedron, which finally affects the antiferromagnetic Néel temperature (T_{N1}) [25]. The R ionic moments in orthoferrites $RFeO_3$ affect the crystal field of Fe ions and the anisotropy energies of Fe sublattice [26,27], which drives the spin reorientation transition. It can be expected that R may affect the magnetic properties of orthoferrites $RFeO_3$ in aspects.

The fantastic properties of orthoferrites $RFeO_3$ also depend on the quality of the crystals. Therefore, synthesis of high-quality

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crystals is a prerequisite for developing the properties and realizing the various applications of $RFeO_3$. It is accepted that the orthoferrite is a metastable phase in high temperatures compared with the thermodynamically stable garnet phase ($R_3Fe_5O_{12}$) [28]. The phases obtained from high-temperature reactions are generally thermodynamically stable ones, and so low-temperature methods are needed for synthesizing pure metastable orthoferrites $RFeO_3$. Some efforts were done to prepare pure orthoferrites $RFeO_3$ in relatively low temperatures. Siemons' group prepared some orthoferrites $RFeO_3$ via a polyol-mediated route and by annealing the amorphous precursors at 700 °C [29]; Xu et al. prepared some orthoferrites $RFeO_3$ using nanosized heterobimetallic precursors at 500 °C [30]. $LaFeO_3$ and $YFeO_3$ were tentatively prepared by hydrothermal technique at 240 °C [31,32]. But till now, as far as we know, there is no systematic report on the hydrothermal synthesis and corresponding magnetic property investigation of serial rare-earth orthoferrites. Hydrothermal technique shows possible advantages in synthesis of metastable oxides and in control of particle size and morphology.

In this work, we report successful preparation of pure orthoferrites $RFeO_3$ (R = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) crystals via hydrothermal synthesis in one step. The conditions affecting the crystallization and crystal growth were investigated and discussed. A dissolution–precipitation mechanism was proposed for describing the formation and growth of $RFeO_3$. Optimum hydrothermal conditions for synthesizing orthoferrites $RFeO_3$ were concluded. The magnetic properties of the as-prepared samples were characterized and investigated, including antiferromagnetic transition of Fe (T_{N1}), spin reorientation (T_{SR}), compensation effect (T_{comp}), ordering of R (T_{N2}), etc.

2. Experimental

Analytical reagents $Fe(NO_3)_3 \cdot 9H_2O$ ($\geqslant 98.5\%$), $R(NO_3)_3 \cdot 6H_2O$ (99.99%) (R = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) and KOH ($\geqslant 82.0\%$) were used as starting materials. The salts were diluted in aqueous solutions using deionized water to ensure intensive mixing of the starting materials. KOH pellets were employed as a mineralizer. The typical synthesis route of $PrFeO_3$ was as follows: 10 mL $Fe(NO_3)_3$ (0.40 M) and 10 mL $Pr(NO_3)_3$ (0.40 M) were mixed at room temperature, and KOH pellets were added into the mixture and stirred to reach a concentration of 20 M (molar number of KOH/solvent volume). The final mixture was transferred into a 40 mL Teflon-lined stainless steel autoclave to complete crystallization and growth under autogenous pressure at 240 °C for 48 h. After naturally cooled to room temperature, the autoclave was opened, and the solid compound was filtered from the suspension. The powder was then thoroughly washed with deionized water and dried in air at 60 °C to present the final sample.

Powder X-ray diffraction (XRD) was done on a Rigaku D/Max 2500 V/PC X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) at 50 kV and 200 mA at room temperature by step scanning in the angle range $20° \leqslant 2\theta \leqslant 80°$ with increments of 0.02°. Rietveld refinement was performed with Accelrys MS Modeling 4.0. The morphologies were observed with a JEOL JSM-6700F scanning electron microscope (SEM) operated at 5 kV. The temperature dependence of the magnetic moments from 373 K to 773 K was measured using a Lake shore 7407 vibrating sample magnetometer (VSM) under an applied field of 100 Oe. The zero-field-cooled (ZFC) and field-cooled (FC) curves were recorded in an applied field of 1000 Oe at 4–350 K and 2–7 K with different density of sampling point by Quantum Design MPMS-XL (SQUID). Differential scanning calorimetry (DSC) was performed in a temperature range from 580 K to 730 K at a scanning rate of 10 K/min in N_2 protection by TA Instrument's Q100 DSC.

3. Results and discussion

3.1. Structural analysis

Fig. 1a shows the XRD patterns of the $RFeO_3$ samples prepared in alkalinity 20 M at 240 °C for 48 h. The strong intensities and sharp shapes of the diffraction peaks indicate good crystallization. The XRD patterns of these samples were refined by the Rietveld method and the results are given Table 1. Fig. 1b shows the XRD pattern and the results of the Rietveld refinement of $PrFeO_3$ as a
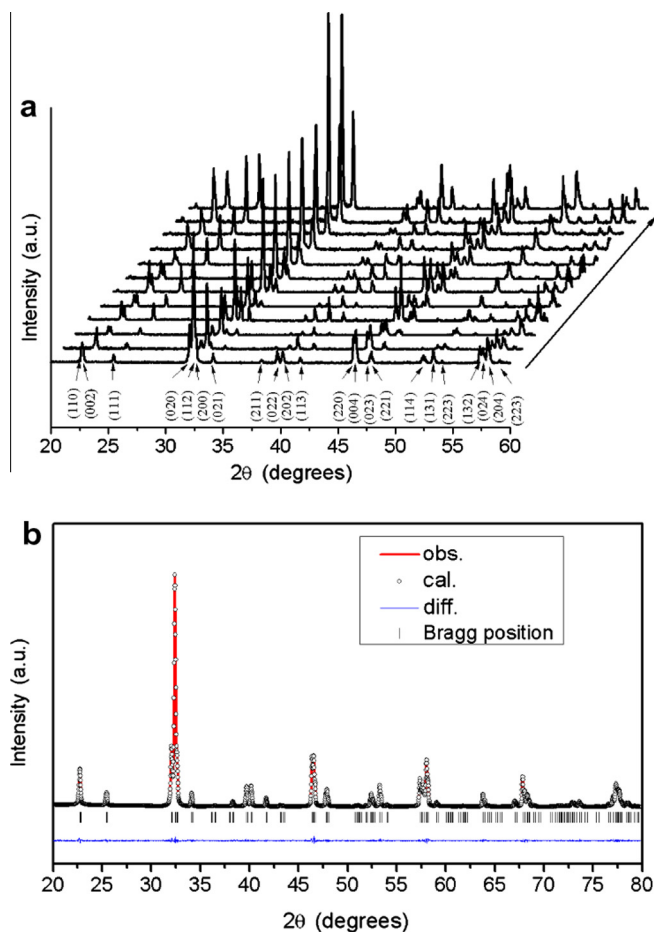

Fig. 1. XRD patterns of the hydrothermally synthesized rare-earth orthoferrites $RFeO_3$ from $PrFeO_3$ to $LuFeO_3$ along the arrow direction (a); Rietveld refinement of $PrFeO_3$ as an example (b).

typical example. The XRD patterns indicate that each sample has a single phase with no detectable impurities. The indexation of the XRD data proves that all the samples are of orthorhombic perovskite structure with space group *Pbnm*. The lattice parameters, cell volumes, atomic occupations, reliability factors, selected bond lengths and bond angles are shown in Table 1. The variation of the lattice parameters and unit cell volumes as a function of the effective ionic radii of R (r_R^{3+}) is shown in Fig. 2 with ionic radii values tabulated in Table 2 (Nine-coordination ionic radii for the rare earth elements are used, since no information of 12 coordinated ionic radii is reported in Shannon table for some trivalent rare earth ions). It can be seen that the value of *b* is almost constant, but *a*, *c* and the unit cell volume *V* decrease with the decrease of r_R^{3+}. The decrease is consistent with the expected "lanthanide contraction" and is associated with an increase of structural distortion in the perovskite structure from Pr to Lu. The geometrical parameters characterizing the crystal structure of $RFeO_3$, for example, the tolerance factor *t*, the orthorhombic deformation *D*, the FeO_6 octahedral tilt angles φ_1 and φ_2 and their average tilt angle $<\varphi>$ were calculated and given in Table 2. The structural distortion basically increases with the decrease of r_R^{3+} and can be evaluated by these geometrical parameters. The orthorhombic deformation *D* increases with the decrease of r_R^{3+} while the tolerance factor *t* decreases accordingly, indicating that the lattices become more distorted with decrease of r_R^{3+}. The tolerance factor *t* being smaller than unity also means that the FeO_6 octahedron has to tilt for self accommodating in the lattice matrix. In the orthorhombic phase, there are two Fe–O–Fe angles θ_1 and θ_2, the Fe–O–Fe angles are