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X-ray absorption spectroscopy study on yttrium iron garnet ($Y_3Fe_5O_{12}$) nanocrystalline powders synthesized using egg white-based sol–gel route

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ABSTRACT

Nanocrystalline powders of yttrium iron garnet ($Y_3Fe_5O_{12}$) were synthesized using egg white-based sol–gel method. Garnet samples were obtained after calcination in air at 700, 800, 900, and 1000 °C for 3 h. Polycrystalline phases occurring in samples are investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Magnetic properties of the samples were measured using the vibrating sample magnetometer (VSM). X-ray absorption spectroscopy (XAS) including X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (EXAFS) was employed in order to reveal the oxidation state and local structure around Fe atoms in the prepared samples. From XANES study we found that Fe ions in all samples show the oxidation states of 3+ in the tetrahedral and octahedral sites in the structure. In addition, the Fe–O distances (1st shell) in all garnet samples keep the same value, 1.80 ± 0.02 Å. In contrast, the Fe–Fe and Fe–Y distances are significantly different when the samples were calcined at different temperatures.

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1. Introduction

Yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) has attracted much attention as microwave device and memory materials [1–4]. The fundamental magnetic properties of YIG originate from the magnetic ions and their relationship to the surrounding oxygen ions. Yttrium iron garnet can be synthesized by several methods such as solid state reaction [5], sol–gel [4,6], pulse laser ablation [7], citrate gel process [3] etc. Among these synthesized methods, sol–gel route is a widely used method involving atomic scale mixing with higher reaction rate [8]. However, most of these techniques are time and energy consuming, and are not environmental-friendly, due to multi-step syntheses or ageing process. In addition, when extremely small particle sizes are required, the complexity and the cost for manufacture will increase greatly. Therefore, simple and cost effective routes to synthesize $Y_3Fe_5O_{12}$ nanocrystalline powders by utilization of cheap, nontoxic and environmentally benign precursors are still needed.

In this study, we propose a simple synthesis of $Y_3Fe_5O_{12}$ nanocrystalline powders using egg white-based sol–gel method. Egg white proteins are well known for their gelling, foaming and emulsifying characteristics, in addition to their high nutrition quality [9–11]. Due to its solubility in water and its ability to associate with metal ions in solution, egg white has been used as a matrix for entrapment of aluminum ions, up on heat treatment of the gelled precursor at as low as 330 °C. The treatment gave rise to γ-alumina particles with crystalline sizes of 15–80 nm [12]. Most recently, our group has reported the use of egg white solution for the synthesis of a plate-like clusters of CeO_2 nanocrystalline particles with particle size of 6–30 nm [13] and nickel ferrite ($NiFe_2O_4$) nanoparticles with particle size of 60–600 nm [14]. The method is simple, cost effective and environmentally benign, which is a promising synthesis route for preparation of fine oxide particles.

To address the influence of the calcined temperature to their magnetic properties, a phase and structural studies of $Y_3Fe_5O_{12}$ were carried out using X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and X-ray absorption spectroscopy (XAS). The magnetic properties of the samples were also measured using the vibrating sample magnetometer (VSM).

2. Experimental

$Y_3Fe_5O_{12}$ samples were synthesized using egg white-based sol–gel method. The precursor gel was prepared by dissolving the egg white (60 mL) in 40 mL of distilled water and the mixture was

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stirred for 1 h at room temperature. In a following step, the precursor gel for Y and Fe composition prepared using stoichiometric amounts of $YC_6H_9O_6{\cdot}xH_2O$ (6 mmol) and $FeCl_3{\cdot}6H_2O$ (10 mmol) was added in the previous mixture and the resulting mixture was stirred for 1 h at room temperature. Then, this mixture was continuously stirred at 100 °C until obtaining the dried gel sample. Finally, the dried gel powder was ground in an agate mortar and calcined in air for 3 h at 700, 800, 900, and 1000 °C, respectively.

X-ray powder diffraction using Cu$K\alpha$ radiation with $\lambda = 0.15418$ nm (Bruker D2 phaser) was performed to investigate the phase forming of the prepared samples. The transmission electron microscopy (Zeiss EM10A/B) was used to examine the morphology and phase structures inside the prepared YIG samples. The magnetic properties were measured using a vibrating sample magnetometer (Lake Shore VSM 7403). To obtain the oxidation states of Fe atoms and the local environment around these Fe ions at different temperatures X-ray absorption spectroscopy including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) was employed in this study. XANES and EXAFS spectra were acquired at Beamline 5 (SUT-NANOTEC-SLRI beamline) with electron energy of 1.2 GeV; bending magnet; beam current 80–150 mA; $1.1–1.7 \times 10^{11}$ photon s^{-1} at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. The Fe K-edge spectra were measured in the transmission mode. A Ge (220) double crystal monochromator with an energy resolution ($\Delta E/E$) of 3×10^{-4} was used to scan the synchrotron X-ray in the range of 7082–7182 eV with an energy step of 0.2 eV for XANES spectra, and in the range of 6912–7665 eV with an energy step of 10, 0.3 and 0.05 k eV for EXAFS spectra. The photon energy was calibrated against the K-edge of Fe foil at 7112 ± 0.3 eV.

3. Results and discussion

The XRD patterns of $Y_3Fe_5O_{12}$ nanocrystalline powders calcined in air for 3 h at 700, 800, 900, and 1000 °C, respectively, were shown in Fig. 1. For the samples calcined at 700, 800, and 900 °C, most peaks correspond to those of JCPDS file 83–1027 representing $Y_3Fe_5O_{12}$ cubic structure and the rest peaks show the mixture phases of Fe_2O_3, $YFeO_3$ and Y_2O_3. On the other hand, for the sample calcined at 1000 °C, $Y_3Fe_5O_{12}$ cubic phase disappeared whilst the $YFeO_3$ and Y_2O_3 are majority. These observed impurity phases such as $YFeO_3$, Fe_2O_3 and Y_2O_3 were generally reported in the other literatures [15,16]. Again, we can see clearly the higher intensity with the narrower width of the XRD patterns when the calcined temperature increases indicating the better crystallinity of samples. Table 1 shows the crystal size of samples calculated using X-ray line broadening method. It is found that the crystal size of samples is larger when the calcined temperatures increase where the lattice parameters are in the range of 1.2332(3)–1.2368(1) nm.

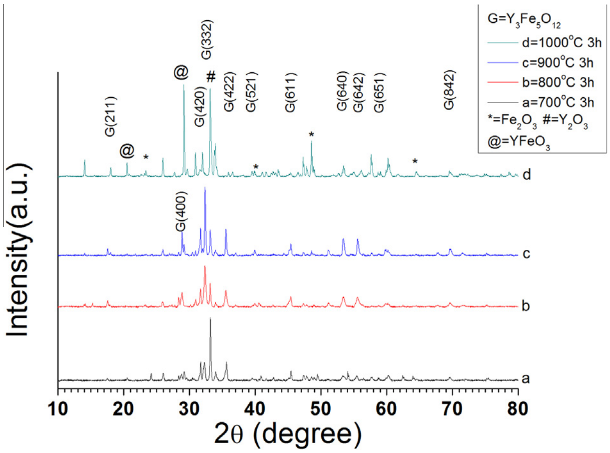

Fig. 1. The XRD patterns of $Y_3Fe_5O_{12}$ nanocrystalline powders calcined in air for 3 h at 700, 800, 900, and 1000 °C, respectively.

Fig. 2 shows the TEM results of prepared $Y_3Fe_5O_{12}$ nanocrystalline powders calcined in air for 3 h at 700, 800, 900, and 1000 °C. The TEM images of the samples exhibited the spherical nanoparticles with sizes of ~100, 150, and 160 nm for the samples caclined at 700, 800, and 900 °C, respectively. Interestingly, the sample caclined at 1000 °C consisted of both nanoparticles with sizes of ~80 nm, and nanorods with sizes of ~200–1000 nm in length. These are consistent with the XRD results. The corresponding selected electron diffraction (SAED) patterns show spotty rings indicating the polycrystalline of all samples with contribution from $Y_3Fe_5O_{12}$, Fe_2O_3, $YFeO_3$, and Y_2O_3, which are in agreement with the XRD results. Note that the samples caclined at 1000 °C consisted of both polycrystalline particles and single crystalline of nanorods. However, because the limitation of our TEM with the size of the SAED analyzed region of about 500 nm, the SAED pattern covers large area including those contributions from a major portion of nanoparticles and a minor portion of nanorods. As a result, the observed SAED pattern shows mainly spotty rings of polycrystalline contributed from the nanoparticles.

Fig. 3 shows the magnetic hysteresis loops of $Y_3Fe_5O_{12}$ nanocrystalline powders calcined in air for 3 h at 700, 800, 900, and 1000 °C, respectively. Specific saturation magnetization (M_s) values of 2.59, 4.17, 7.04, and 0.42 emu/g at 10 kOe for the $Y_3Fe_5O_{12}$ samples calcined at 700, 800, 900, and 1000 °C, respectively. The measured magnetic properties of the samples are also summarized in Table 2. It can be seen that there is a smooth increase in saturation magnetization values of $Y_3Fe_5O_{12}$ samples for the calcination between 700 °C and 900 °C whereas their coercivity values slightly decrease. This can be possibly explained by an increase in particle sizes and a higher amount of pure $Y_3Fe_5O_{12}$ nanocrystalline phase. On the other hand, a significant decrease in saturation magnetization and an increase in coercivity values for the sample calcined at 1000 °C were observed. The difference found in this sample is possibly caused by size, sample shape and the dominant impurity phases.

X-ray absorption spectroscopy (XAS) is a powerful technique which can verify the local structure and environment of any element in a crystal. Fig. 4 shows the normalized Fe K-edge XANES spectra of the $Y_3Fe_5O_{12}$ nanocrystalline powders calcined in air for 3 h at 700, 800, 900, and 1000 °C, respectively, and the standard compounds. XANES is sensitive to the local environment around the probing atoms and thus it can be used to distinguish the chemical species and oxidation states of iron. As seen in Figs. 3 and 4, all powder samples, the edge energies were found at 7128.19 eV (less than 1 eV error) which is consistent with the edge energy of Fe_2O_3 standard sample. This suggests that Fe atoms in all the prepared $Y_3Fe_5O_{12}$ samples have the oxidation states of 3+ in the tetrahedral and octahedral sites in the structure causing the magnetic properties in these samples. Again, we can see clearly the slightly different features in the pre-edge and post-edge ranges of samples when the calcined temperature increases. This implies that the

Table 1
The crystal size of $Y_3Fe_5O_{12}$ nanocrystalline powders calcined in air for 3 h at 700, 800, 900, and 1000 °C calculated using X-ray line broadening method.

Calcination temperature	Crystal size (nm)	Lattice parameter [a] (nm)
700 °C	29.8 ± 6.3	1.2332 ± 0.0003
800 °C	22.6 ± 6.9	1.2369 ± 0.0002
900 °C	47.4 ± 18.8	1.2368 ± 0.0001
1000 °C	70.4 ± 30.5	–

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