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Research Article

Effects of Annealing Temperature on Structure and Magnetic Properties of $Tb_xY_{3-x}Fe_5O_{12}$ ($x = 0.2$ and 0.4) Thin Films

N. B. Ibrahim, Ftema W. Aldbea, and Mustaffa Hj Abdullah

School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia

Correspondence should be addressed to N. B. Ibrahim, baayah@ukm.my

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Terbium-substituted yttrium iron garnet ($Tb_xY_{3-x}Fe_5O_{12}$ ($x = 0.2$ and 0.4)) thin films have been successfully prepared by a sol-gel method followed by spin-coating process. The annealing of the films was performed at different temperatures like 700, 800, and 900°C and found that the films annealed at 900°C turned out to be crystallized into a pure garnet phase. All of the films were bearing grains of nanometer in size. Increasing the annealing temperature gave extra energy to the grains causing to be agglomerates. The lattice contraction occurred as the grain's sizes were decreased due to the decrease of Fe^{2+} formation. The magnetic measurements show that all of the films are soft magnetic materials with low saturation magnetization values. The hysteresis loops of the films which were annealed at 900°C were found angular in shape similar to the single crystal-like YIG film.

1. Introduction

Yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) and its rare-earth-substituted films have been progressively studied due to their wide potential applications, such as in telecommunication and magneto-optical devices [1]. Y site in YIG has been substituted with different materials such Bi, Ca, and Ce [2–4]. Bulk Tb-substituted YIG (Tb-YIG) has the potential in sensor application. However there are few published reports on it [5–7] and none of them report the material in the thin film form. Marins et al. [5] have reported that the magnetic properties of $Tb_{(3-x)}Y_xFe_5O_{12}$ powder calcined at 1000°C depend on the sintering temperature, and also the small coercive field value is related to the increased sintering temperature. Guillot et al. [6] have studied the magnetization of $Tb_xY_{3-x}Fe_5O_{12}$ in polycrystalline and single crystal form at magnetic field of 180 kOe. They found that, in case of the polycrystalline ($x = 2, 1, 0.37$), the compensation points depend on the Tb concentration while for the single crystals ($x = 2, 1, 0.37$) a strong magnetic anisotropy was observed with the change of easy direction of magnetization from [111] to [100] when x was decreased. They also reported occurrence of abrupt field-induced transitions at low temperature when the external field was applied along the [100] direction. Rodić et al. [7] reported that the compensation temperature of $Tb_xY_{3-x}Fe_5O_{12}$ ($x = 1, 1.98, 2.5$, and 3) powder was proportional to the concentration of the terbium ion.

This paper reports the preparation of $Tb_xY_{3-x}Fe_5O_{12}$ ($x = 0.2$ and 0.4) thin films by a cheap, and simple method, that is a sol-gel method followed by spin coating process. In order to obtain crystalline films, annealing process was employed. The effects of annealing temperature on the structures and magnetic properties of the films were studied.

2. Experimental Procedure

Yttrium (III) nitrate hexahydrate $Y(NO_3)_3 \cdot 6H_2O$ with 99.99% purity and iron (III) nitrate nanohydrate $Fe(NO_3)_3 \cdot 9H_2O$ with 98.0% purity were first dissolved in 2-methaoxythanol and refluxed at 80°C for 3 hours. The doping agent in the form of $Tb(COOCH_3)_3 \cdot H_2O$ with 99.9% purity was first dissolved in 1 mL acetic acid and then added to the yttrium and iron solution. The ratio of yttrium and terbium was altered in order to obtain $Tb_{0.2}Y_{2.8}Fe_5O_{12}$ and $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ solution followed by addition of 1 mL distilled water and 3 mL of nitric acid. Diethylamine was added to the solution to obtain a pH 3 solution. The solution was again refluxed at 80°C for 3 hours.

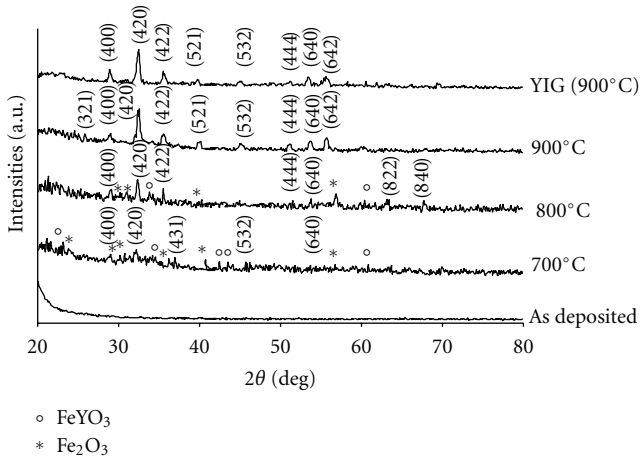


Figure 1: XRD spectrum for series 1 film.

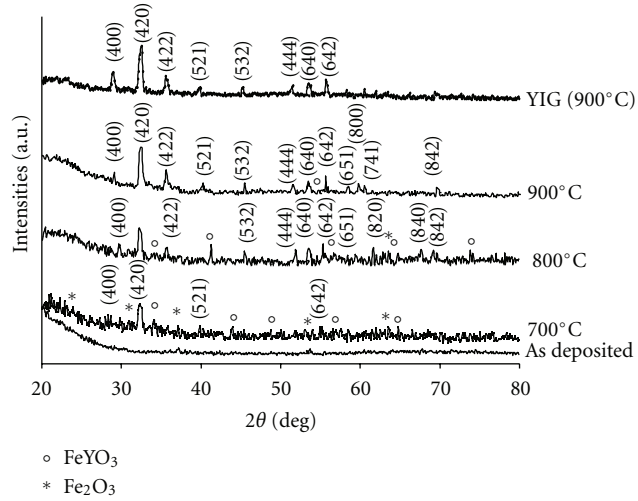


Figure 2: XRD spectrum for series 2 film.

To obtain the films, 25 μL of the gel was dropped onto a clean quartz substrate. Using a spin coater, the substrate was spin first at 500 rpm for 15 seconds, then at 3500 rpm for 30 seconds. The film was heated at 90°C for 2 hours to get rid of residual solvent, and followed by 350°C for 15 min at heating rate of 3°C/min to burn-off the organic compounds. Then both $Tb_{0.2}Y_{2.8}Fe_5O_{12}$ and $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ films were annealed at 700, 800 and 900°C in order to study the effect of the annealing temperature on their physical properties. The films were identified as series 1 for $Tb_{0.2}Y_{2.8}Fe_5O_{12}$ and series 2 for $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ films.

An X-ray diffractometer (XRD) with Cu-Kα radiation was used to study the film's structures and phases. A field emission scanning electron microscopy (FE SEM) was used to measure the grain's size and thicknesses of the films. A vibrating sample magnetometer (VSM) was used to study the in-plane magnetic properties of the films.

3. Results and Discussion

The XRD results in Figures 1 and 2 show that both series were crystallized into pure YIG phase after being annealed at 900°C. The films which were annealed at temperatures less than 900°C were displaying mixed phases of YIG, Fe_2O_3, and $YFeO_3$ because of incomplete crystallization. No peaks belonging to Tb_2O_3 were found in the results, thus indicating the incorporation of Tb atoms in the garnet structure.

The lattice parameters for both series were calculated from the XRD spectra and Bradley and Jay's extrapolation method was employed to minimize the errors [8]. The lattice parameter value for each 2θ was obtained and a graph presenting the lattice parameter versus $\cos^2\theta$ was plotted. The extrapolated value at the y-axis was considered as the desired value. While the films annealed at 700 and 800°C were displaying mixed phases, only the 2θ of Tb-YIG was used to calculate the lattice parameter. Figure 3 shows the results for both series. The lattice parameter of both series was increased with the increase in annealing temperature. Similar results have also been reported for nanoparticle oxide system [9, 10].

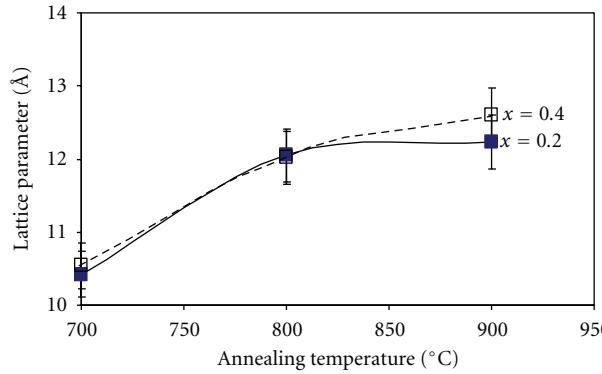


Figure 3: The plot of lattice parameter versus annealing temperature for series 1 and 2.

According to Rajendran et al. [11], oxygen vacancies can occur at the particle's surface during the film preparation and may cause the formation of Fe^{2+}. The oxygen vacancies could occur due to the preparation condition. The annealing processes were carried out in air; thus increasing the annealing temperature could promote the formation of Fe^{2+} ions. As Fe^{2+} ions are larger than Fe^{3+}, the increment of their formation will further expand the unit cell. To confirm this, XPS measurements were performed on the films annealed at 900°C. Figure 4 is clearly exhibiting the results confirming the formation of Fe^{2+} in both films.

The thickness of the films was measured from the film's cross section. The films were cut and the back scattered images from the cross sections were taken using the FESEM. Figure 5 shows the typical FESEM cross-section a micrograph of a Tb-YIG film showing different contrast of the film and substrate. Figure 6 shows that the thickness decreases as the temperature increases for series 1 ($x = 0.2$). The thinning of the films as the temperature increases could be due to the densification process, where the small empty spaces or pores were filled by the grains [12]. However for series 2 ($x = 0.4$), increasing annealing process from 700 to 800°C increases

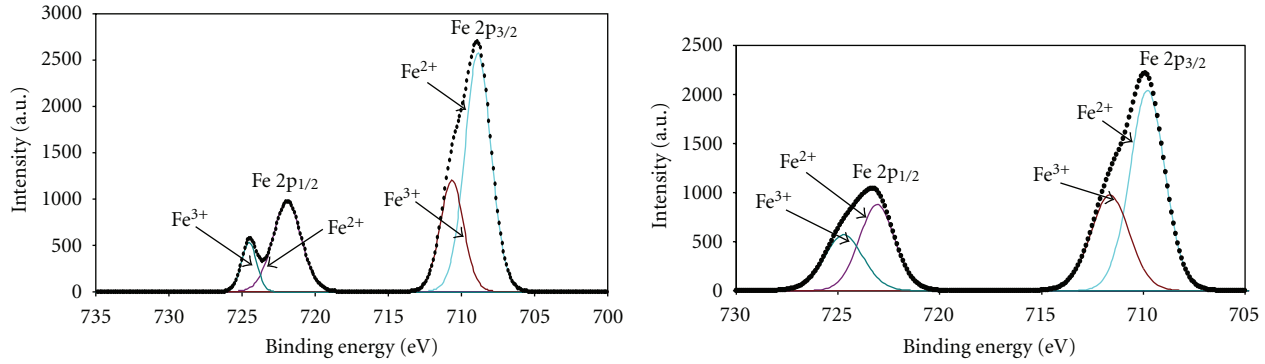


Figure 4: The XPS spectra for films annealed at 900°C.

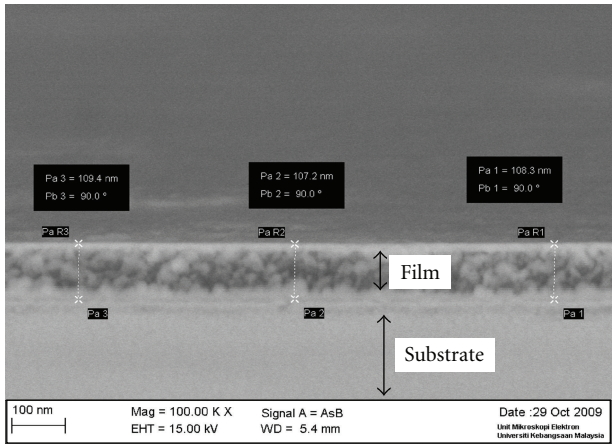


Figure 5: A typical cross-sectional view of a Tb-YIG film ($x = 0.2$) showing the contrast (back scattered electron) between the film and substrate.

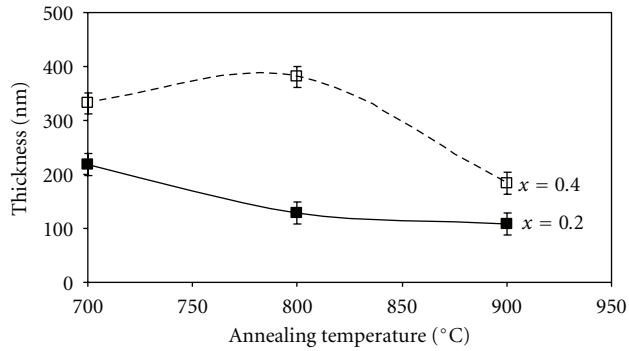
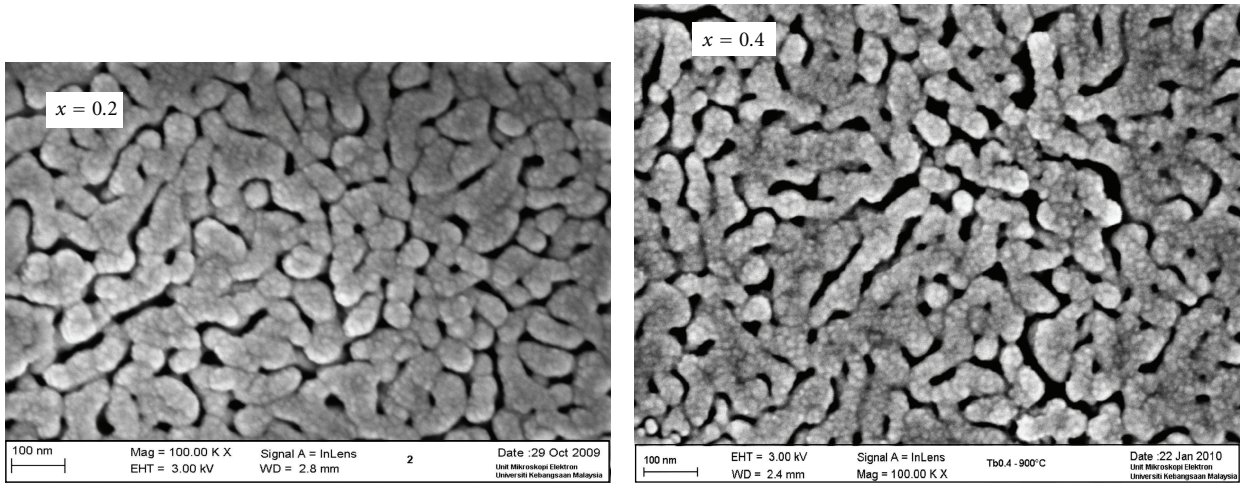


Figure 6: The relation between film thickness and annealing temperature for series 1 and 2.

the film thickness due to the increment of the grains (see Figure 8). Further temperature increment to 900°C decreases the film thickness due to the densification process.

The grains sizes were measured from the surface micrographs obtained from the FESEM. Figure 7 shows the FE SEM micrographs of $Tb_{0.2}Y_{2.8}Fe_5O_{12}$ and $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ films annealed at 900°C. The relation between grain size and annealing temperature is shown in Figure 8. All of the films have grains sizes in nanometer range (9–60 nm). Both series show a similar graph pattern. The grains become larger as the annealing temperature increases. The nanometer size grains possess large overall surface area which means that their total surface energy is also high. However the energy can be minimized when the annealing process was carried out, thus allowing the grains to agglomerate. Further increasing the annealing temperature reduced the surface energy of the grains and thus allowed them to become more agglomerate.

The VSM was used to measure the in-plane magnetic properties of both series at room temperature (25°C). No demagnetization corrections were required as the films were very thin compared to the lateral dimensions; hence the in-plane demagnetization was leaned towards zero. However the linear ramp due to the paramagnetic quartz substrate was subtracted from the data. Figures 9 and 10 show the hysteresis loops of series 1 and 2, respectively. The samples are soft magnetic materials with low saturation magnetization (M_s) values. Also the films annealed at 900°C show angular shape hysteresis loops which are similar to those reported by Ibrahim et al. [4] for their single crystal-like YIG film. Their film's easy axis does not lie in the film plane. The angular hysteresis shows that it is possible to magnetize in-plane up to certain limit (M_{easy}) by growth of easy domains giving the initial steep region. Further magnetization would need rotation away from the easy directions giving the second stage which is the harder process. As shown in Figure 11 the M_s of both series increase with the annealing temperature. $Tb_{0.2}Y_{2.8}Fe_5O_{12}$ and $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ films annealed at 700 and 800°C have similar M_s; the low values of magnetization could be due to the existence of the antiferromagnetic Fe_2O_3 phase in the samples. Increasing the annealing temperature improves the film crystallization and thus increases the M_s; however it is lower than 138.3 emu/cm^3 for YIG film containing micrometer grain size range [13]. Similar reduction has also been reported by Sánchez et al. for their nanograin YIG. Nanograin YIG possesses high surface-to-volume ratio; thus increasing the surface spin effects the films [14].



(a) (b)

Figure 7: FESEM micrographs of $Tb_{0.2}Y_{2.8}Fe_5O_{12}$ and $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ films, annealed at 900°C.

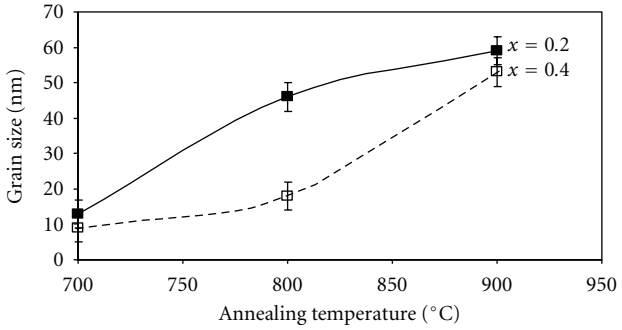


Figure 8: The relation between particle size and annealing temperature for series 1 and 2.

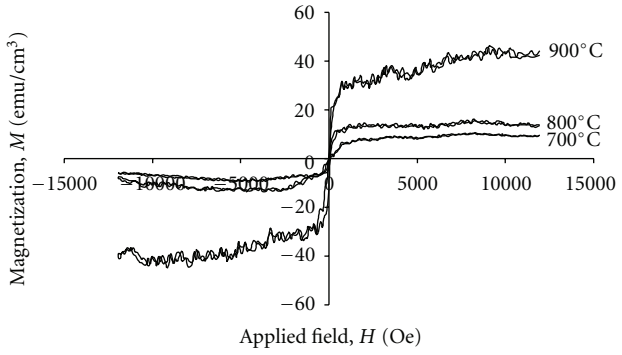


Figure 9: The hysteresis loop of series 1.

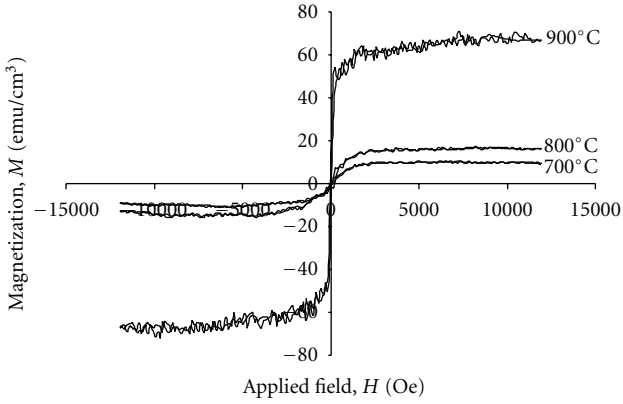


Figure 10: The hysteresis loop of series 2.

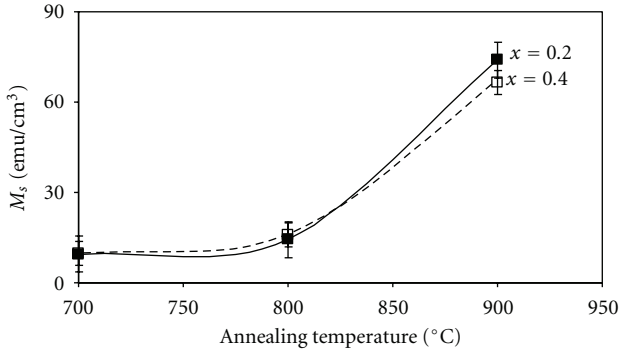


Figure 11: The plot of M_s versus annealing temperature of both series.

Figure 12 shows the plot of coercivity field (H_c) versus annealing temperature of both series. It can be clearly seen that both series show similar trends. The H_c becomes smaller as the annealing temperature increases. As measured from the FE SEM images, the increment in annealing temperature led to bigger grain sizes. Theoretically it has been proved that the coercivity of small particle (H_c) is proportional to $1/L^v$ (L is the particle size and v is a constant that lies between 1/2 and 1) [15]. The increment of grain size with the annealing temperature also reduced the strain in the films resulting in reducing the H_c values.

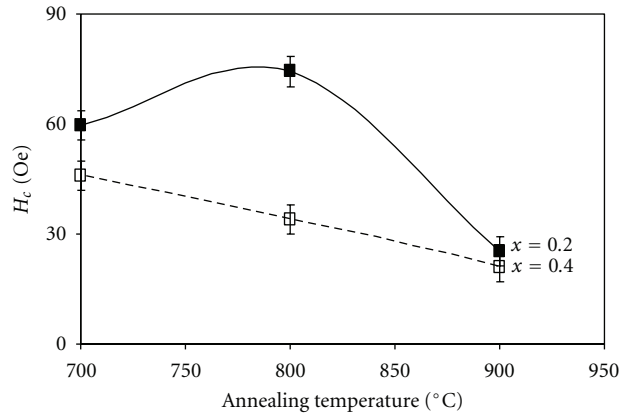


FIGURE 12: The plot of H_c versus annealing temperature of both series.

4. Conclusion

The structure and magnetic properties of $Tb_{0.2}Y_{2.8}Fe_5O_{12}$ and $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ films prepared onto quartz substrates by a sol-gel method followed by spin-coating process have been reported. The films subjected to the annealing temperature of 900°C were found to be crystallized into pure garnet phase. The films have grains sizes in the range of 9–60 nm. Increment in the annealing temperature from 700 to 900°C led to the increased formation of Fe^{2+}. The films annealed at 900°C show hysteresis loops similar to the single crystal-like YIG. Although the substitution of Tb ions into YIG films reduced their M_s values, the films have potential in microwave application due to their low coercivity values and soft magnetic nature.

Acknowledgments

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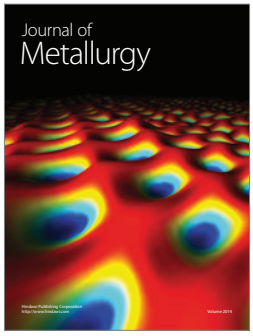

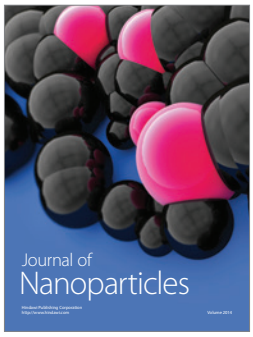

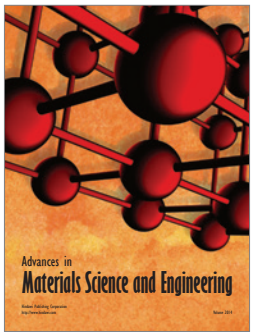

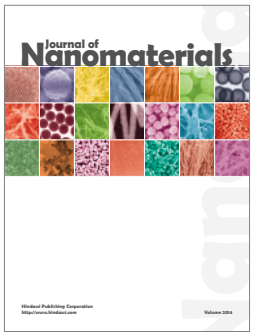

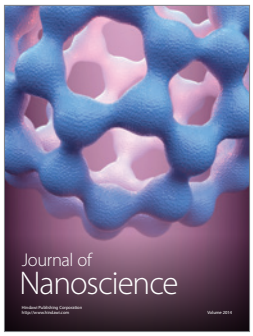

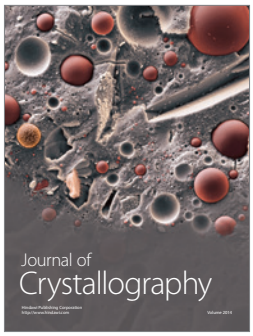

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