Synthesis of natural superlattice structure in the binary ZnO–Fe₂O₃ system by microwave irradiation

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Homologous compounds, Fe₂O₃(ZnO)_m, with the modulated natural superlattice structure were obtained within a short period by solid state reaction of component oxides under 2.45 GHz microwave irradiation. TEM observation revealed that two types of superlattice structures were observed in different Fe concentration; one is longitudinal superlattice structure in a rod shaped precipitation at high Fe concentration, and the other is modulated structure showing zigzag shape at low Fe concentration. It is concluded that the non-equilibrium nature of microwave selective heating, as well as rapid heating and quenching effects, plays a key role to form the superstructure. The obtained products exhibit ferromagnetic behavior with the Curie temperature above 300 K.

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1. Introduction

Oxide superlattices have great potential as new materials because some oxides show various intensive and interesting properties such as dielectricity and superconductivity.^{1,2)} In the experimental studies, most of the superlattice structures are created through artificial processes like molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) techniques, however, “natural superlattice structure” are also formed in some ZnO-based homologous compounds.^{3,4)}

Li et al. studied a series of compounds, InMO₃(ZnO)_m (M = In, Fe, Ga, and Al), and suggested that the superlattice structures in this series are built up from a succession of InO[−] (In–O layer) and MZn_mO_{m+1}¹⁺ (M/Zn–O layer) perpendicular to the *c*-axis of the wurtzite-type structure as depicted in Fig. 1.⁵⁾ In the binary ZnO–Fe₂O₃ system, Kimizuka et al. identified homologous compounds, Fe₂O₃(ZnO)_m, with the distorted InFeO₃(ZnO)_m-type structure.⁶⁾ They pointed out that the formation of Fe₂O₃(ZnO)_m phases are limited to high *m* values (*m* = 8, 9, ...) only in the vicinity of the wurtzite-type ZnO. Formation of a polytype with lower *m* value requires a quenching operation from high reaction temperature above 1550°C. This makes it difficult to synthesize a series of homologous superlattice compounds by conventional solid state reaction.

Microwave processing of inorganic materials is one of the attractive fields in recent materials science. Microwave heating is a self-heating process that occurs via direct absorption of electromagnetic energy. It has many advanced features like reduction of reaction time and temperature, development of fine microstructures, and so on.^{7–9)} Such features possibly come from enhancement of solid state diffusion under microwave electro-

Fig. 1. Schematic crystal structure of InFeO₃(ZnO)₃.

magnetic field. In this study, we successfully synthesized Fe₂O₃(ZnO)_m superlattice structures by simple solid state reaction under 2.45 GHz microwave irradiation.

2. Experimental

Powders of ZnO, α-Fe₂O₃, and γ-Fe₂O₃ were used as starting materials. These powders were weighed in appropriate proportions, Zn_{1-x}Fe_xO_y, with *x* = 0.05 (ZnO: 97.5 mol% and γ-Fe₂O₃: 2.5 mol%) and *x* = 0.67 (ZnO: 50 mol%, α-Fe₂O₃: 45 mol%, and γ-Fe₂O₃: 5 mol%), and mixed using a pestle and mortar. The addition of γ-Fe₂O₃ was required to facilitate rapid heating because γ-Fe₂O₃ strongly couples with microwave energy. The

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Fig. 2. Temperature-time profiles of the powder mixtures under irradiation of 2.45 GHz microwaves at 1.5 kW power output.

Fig. 3. XRD patterns of products after microwave irradiation.

mixed powder was placed in a quartz glass tube and then irradiated with 2.45 GHz microwaves at 1.5 kW power output. Microwave heating equipment (SMW-099, Shikoku Instrumentation Co., Ltd., Japan), which allows the electromagnetic field to be focused by tuning three stub tuners or E-H tuner, was used in this study. The detailed set-up of this equipment is described in our previous paper.¹⁰⁾

Figure 2 shows the temperature-time profile of the powder mixture under microwave irradiation. The mixture clearly shows strong coupling with microwaves and can be heated rapidly to 1000°C within a minute. The irradiation was turned off when the temperature reached to 1000°C. This gave a quenching effect because microwave heating is essentially self-heating processing. The irradiation was repeated five times between 200–1000°C to obtain well homogenized specimens.

After microwave irradiation, the specimens were characterized by field-emission transmission electron microscopy (FETEM) (HF-2000EDX, Hitachi Co., Ltd., Japan), selected area electron diffraction (SAED), and X-ray powder diffraction analysis (XRD) (RINT-2000/PC, Rigaku Co., Ltd., Japan). Chemical composition was analyzed by energy dispersive X-ray spectroscopy (EDX) attached in the FETEM system. Vibrating sample magnetometer (VSM) (VSM-5, Toei Industry Co., Ltd., Japan) was used for magnetization measurements.

3. Results and discussion

Figure 3 shows the XRD patterns of the products after

Fig. 4. TEM observation of the $x = 0.67$ specimen: (a) Low-magnification image, (b) High-magnification image of the single crystal rod, (c) Electron diffraction pattern of the single crystal rod, (d) EDX spectrum of the single crystal rod.

microwave irradiation. Single phase wurtzite-type structure was obtained at $x = 0.05$, while the $x = 0.67$ specimen consisted of spinel-type and small portion of wurtzite-type phases. The lattice parameter of the spinel-type phase was determined to be $a = 0.8437$ nm, nearly equal to that of ZnFe_2O_4 ($a = 0.8441$ nm, JCPDS: No. 22-1012). The XRD pattern revealed that $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ phases completely disappeared and no other iron species such as Fe_3O_4 , FeO , and $\alpha\text{-Fe}$ appeared.

Figure 4(a) shows the TEM image of the $x = 0.67$ specimen, clearly showing the formation of single crystal rod in spinel-type matrix. It was confirmed from the XRD, SAED, and EDX that the matrix is composed of spinel-type ZnFe_2O_4 . The single crystal rod has a superlattice structure and each block has nearly equal thickness and aligns perpendicular to the growth direction (Fig. 4(b)). The electron diffraction pattern of the single crystal rod (Fig. 4(c)) revealed that the rod has basically wurtzite-type structure and the existence of satellite spots implies the formation of the modulated structure. Figure 4(d) shows the EDX spectrum of the rod. Fe peaks are observed as well as Zn and O peaks. The estimated $\text{Fe}/(\text{Fe} + \text{Zn})$ ratio is 0.40, corresponding to the chemical composition of $\text{Fe}_2\text{O}_3(\text{ZnO})_3$.

On the other hand, the TEM image of the $x = 0.05$ specimen shows the similar modulated structure but with the appearance of zigzag shape in each layer, where Fe is in higher concentration (Fig. 5). The observed image is quite similar to that of $\text{Fe}_2\text{O}_3(\text{ZnO})_{1.5}$ reported by Li et al.⁵⁾ Each bright line corresponds to one Fe–O layer, and a few pieces of Fe doped Zn–O layers (Fe/Zn–O layers) are interposed in two adjacent Fe–O layers, consequently, the super structure consists of Fe–O layer and Fe/Zn–O layers stacked alternately along the c -axis. The appearance of the zigzag shape is considered to be due to ordering of Fe atoms within Fe/Zn–O layers as proposed in the modulated structure model of $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m > 6$).¹¹⁾

It is notable that the modulated superlattice structures of $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ could be easily obtained at low temperature (1000°C) within a short reaction time by a simple solid state reaction under microwave irradiation. Especially, the formation

Fig. 5. TEM image of the $x = 0.05$ specimen. Fig. 6. Results of the magnetization measurements for the $x = 0.67$ specimen. The inset shows magnetic field dependence of magnetization for specimen (a) $x = 0.67$ and (b) $x = 0.05$.

of superstructure with low m value ($m = 3$) is surprising because the formation of homologous compounds, $\text{Fe}_2\text{O}_3(\text{ZnO})_m$, were believed to be limited in the vicinity of the wurtzite-type ZnO phase ($m \geq 8$) in previous study.⁶⁾ It is not yet cleared that why $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ compound with low m value could be formed easily by microwave processing. However it is not doubtful that the non-equilibrium nature of microwave selective heating, as well as rapid heating and quenching effects, plays a key role to form the superstructure. Under microwave irradiation, Fe species selectively couples with microwave energy and can be heated to higher temperature. This selective heating produces anisothermal condition to cause a different diffusion mechanism as compared to conventional heating.¹²⁾

Figure 6 shows the results of magnetization measurements. The magnetization curves for the $x = 0.67$ specimen exhibits mixed ferromagnetic and paramagnetic behavior. Based on the XRD and TEM results, paramagnetic component is believed to be spinel-type ZnFe_2O_4 . The $x = 0.05$ specimen also exhibits weak ferromagnetic behavior at room temperature. These results suggest that the series of $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ compounds are ferromagnetic materials with the Curie temperature above room temperature.

4. Conclusion

In summary, homologous compounds, $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 3$), with the modulated superlattice structures can be successfully synthesized at low temperature within a short period by a simple solid state reaction under microwave irradiation. The results indicate that microwave processing is effective in synthesizing such a modulated superstructure phase like $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ which generally requires high reaction temperature, long period heating, and quenching operation because a drastic enhancement of reaction kinetics could be achieved under thermally non-equilibrium condition induced by strong coupling of materials with microwave energy.

It is very interesting that the specimens exhibit ferromagnetic portion. Recently ZnO-based diluted magnetic semiconductors (DMSs) have attracted interests as new material systems in spintronics application.¹³⁾ Although most of DMSs are fabricated by artificial non-equilibrium techniques like MBE and PLD, microwave processing will open a new field in surveying natural superlattice compounds.

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