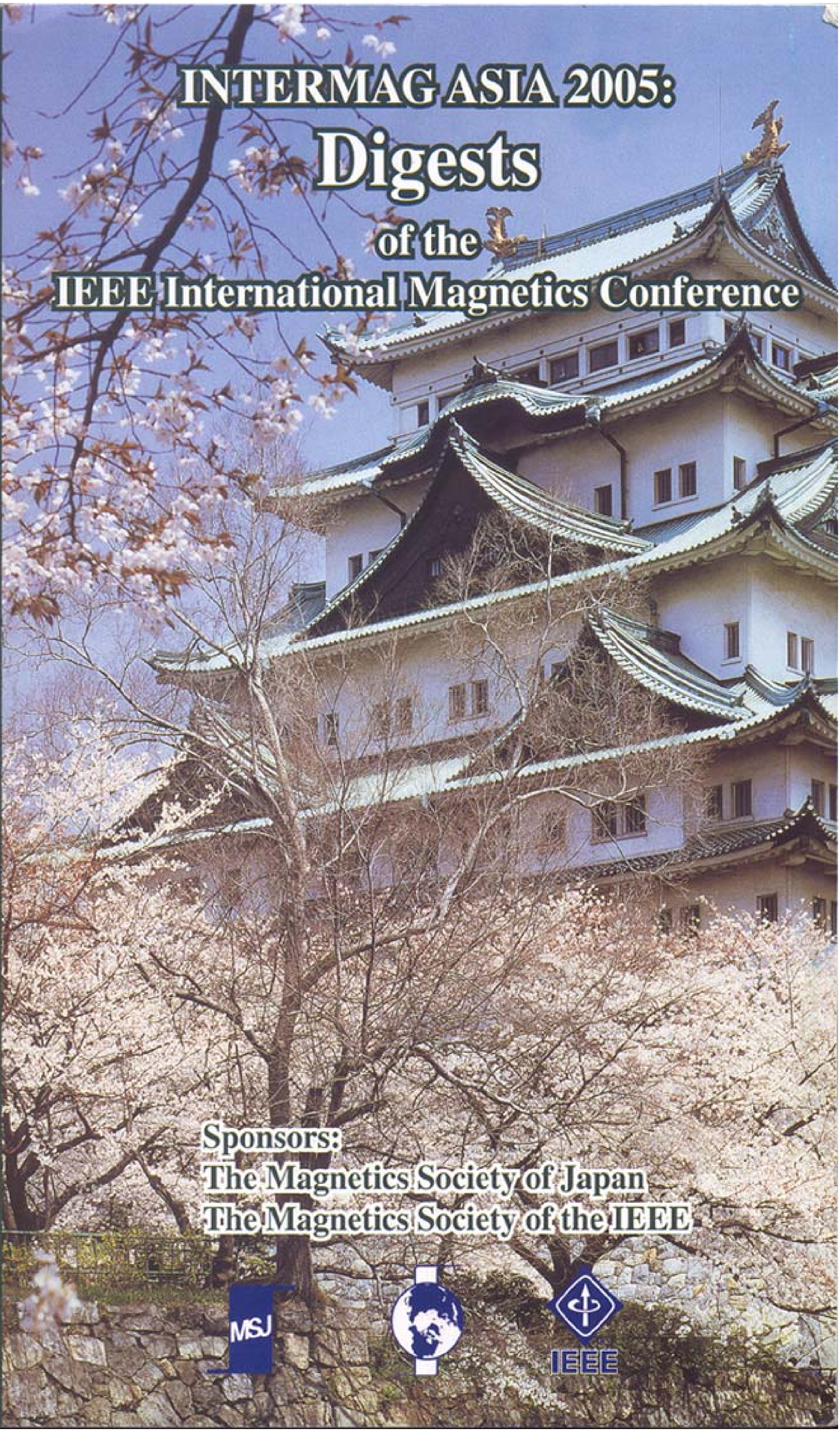

INTERMAG ASIA 2005: Digests of the IEEE International Magnetics Conference

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The 2005 IEEE International Magnetics Conference
April 4 – 8, 2005 • Nagoya Congress Center • Nagoya, Japan

SYNTHESIS AND MÖSSBAEUR STUDIES OF $TbFe_{1-x}Mn_xO_3$ NANOPARTICLES

Bok Yeon Kum, Sung Yong An, Chul Sung Kim
Department of Physics, Kookmin University, Seoul 136-702, Korea

Introduction

The rare earth orthoferrites have attracted interest because of their potential magnetic and electrical applications. It has been widely studied and used as magneto-optical devices, catalysts, cathodes in solid oxide fuel cells, and sensors. The distorted perovskites $TbFe_{1-x}Mn_xO_3$ with a variable Mn concentration are interesting substance for studying the influence of the Jahn-Teller ions Mn^{3+} on the magnetic properties and spin-reorientation transitions[1-4]. In this study, a sol-gel procedure was used for the preparation of $TbFe_{1-x}Mn_xO_3$ (x=0.0, 0.25, 0.50, and 0.75) nanoparticles and their structural and magnetic properties were characterized by using x-ray diffraction (XRD), Mössbauer spectroscopy, vibrating sample magnetometer (VSM), and scanning electron microscopy (SEM).

Experiments

$TbFe_{1-x}Mn_xO_3$ nanoparticles were fabricated by a sol-gel method. Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), manganese acetate ($Mn(CH_3CO_2) \cdot 4H_2O$), and terbium nitrate ($Tb(NO_3)_3 \cdot 6H_2O$) were used as starting materials. These were dissolved in mixed a solvent system (ethanol: distilled water = 6: 1). A small amount of acetic acid was added to the solution for acting as catalyst and to reduce pH. The solution was refluxed at 60 ℃ for 12 hours. Afterwards, it was dried at 120 ℃ for several days and finely powdered. Then, $TbFe_{1-x}Mn_xO_3$ powders were obtained by heating at 800 °C for 3 hours in air.

Results and discussion

Figure 1 shows XRD patterns of the $TbFe_{1-x}Mn_xO_3$ nanoparticles prepared by a sol-gel process. The crystal structure was found to be orthorhombic structure (*pbnm*). No impurity phases have been detected with Cu*Kα* radiation such as garnet $Tb_3Fe_5O_{12}$ and spinel Fe_3O_4 ferrite. The result of XRD measurements shows that the lattice parameters *a* and *c* decrease, with increasing x, from *a*=5.333 and *c*=7.641 Å for x=0.0, to *a*=5.287 and *c*=7.511 Å for x=0.75, respectively. However, the lattice parameter *b* increases from 5.594 to 5.731 Å, with increasing x from x=0.0 to 0.75. Mössbauer spectra of $TbFe_{1-x}Mn_xO_3$ at room temperature are shown in Fig. 2. The Mössbauer spectra for x=0.0 consists of one Zeeman sextets of the Fe^{3+} ions at octahedral sites. The Mössbauer spectra of Zeeman sextet ($x<0.50$) are rapidly changed into a paramagnetic doublet ($x \geq 0.5$), with increases of Mn concentration. The Mössbauer parameters for the sample $TbFeO_3$ gives the values, hyperfine field H_{hf}=500 kOe, isomer shift δ=0.24 mm/s, and quadrupole splitting E_Q=0.0 mm/s, respectively. These values are typical Fe^{3+} ions in the high-spin state. For the $TbFe_{0.75}Mn_{0.25}O_3$ Mössbauer spectrum, we have fitted the spectra to a model based on a random distribution of Fe and Mn ions on the octahedral sites. The probability of an octahedral site having *n* nearest-neighbor Mn atoms was calculated using the binomial formula[5]:

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$$P(n,x)=\frac{6!}{n!(6-n)!}(x)^{n}(1-x)^{6-n}, \qquad (1)$$

where x is the Mn concentration 0.25. The obtained results show that the average of hyperfine

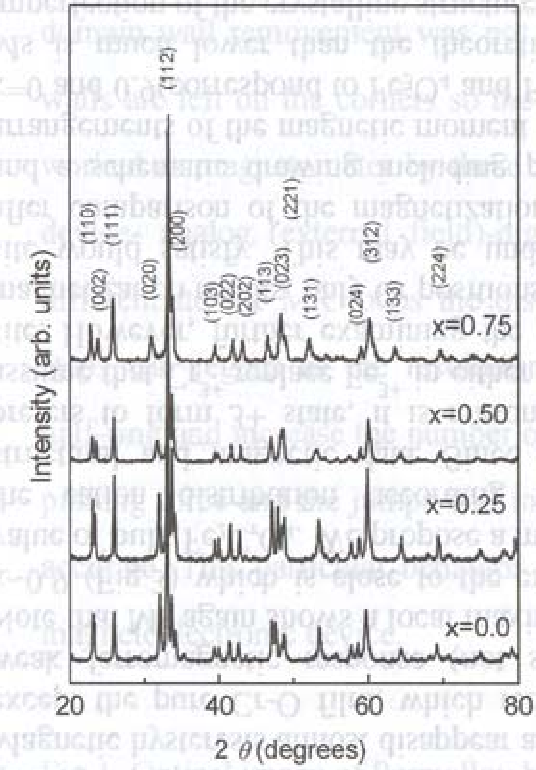

Fig. 1 X-ray diffraction patterns of $TbFe_{1-x}Mn_xO_3$.

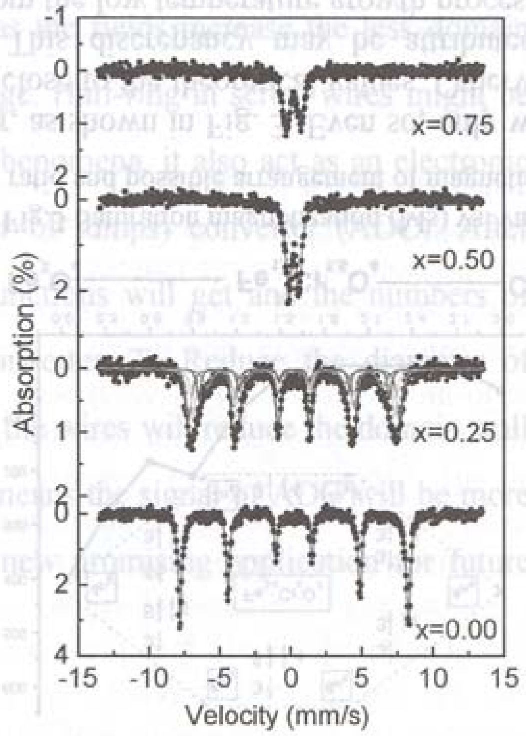

Fig. 2 Mössbauer spectra of $TbFe_{1-x}Mn_xO_3$ at room temperature.

field is H_{hf}=426 kOe, isomer shift δ=0.26 mm/s, and quadrupole splitting E_Q=0.0 mm/s, respectively. While, the only quadrupole doublet spectra is shown for $x \geq 0.5$, due to the effect of Jahn-Teller distortion of Mn^{3+}. The Néel temperature is determined from Mössbauer spectroscopy and VSM measurements. The Néel temperature decreases with increasing the amount of the Mn-substition that of $TbFeO_3$ and $TbMnO_3$ are 650 K and 76 K, respectively. The mean size of the particles was estimated by Scherrer[5] analysis of the broadening of the (202) reflection plane and SEM analysis. The powders present average particle size of 22 nm for $TbFe_{0.25}Mn_{0.75}O_3$ samples as-obtained and annealed at 800 °C. By substituting Mn^{3+} for Fe^{3+}, it is concluded that Mn^{3+} strongly affects the decrease of both the Néel temperature and the magnetization.

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