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# Effects of $(Ho_xIn_{1-x})_{1.9}Sn_{0.1}O_3$ matrix on magnetization of dispersed Fe<sub>3</sub>O<sub>4</sub> nanocrystals

### Minemaru Tanabe<sup>1</sup>, Takuro Manabe<sup>1</sup>, Shigemi Kohiki<sup>\*,1</sup>, Masanori Mitome<sup>2</sup>, and Kunio Yubuta<sup>3</sup>

<sup>1</sup> Department of Materials Science, Kyushu Institute of Technology, Kitakyushu, Japan

<sup>2</sup> National Institute for Materials Science, Tsukuba, Japan

<sup>3</sup> Institute for Materials Research, Tohoku University, Sendai, Japan

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\* Corresponding author: e-mail kohiki@che.kyutech.ac.jp, Phone: +81 93 884 3310, Fax: +81 93 884 3300

Solid solutions  $(Ho_xIn_{1-x})_{1.9}Sn_{0.1}O_3$  with x = 0 - 0.3 were synthesized to employ as dispersion matrix for oleic acid coated Fe<sub>3</sub>O<sub>4</sub> nanocrystals. The x = 0.05 matrix exhibited a resistance minimum at a non-zero temperature in each temperature dependent resistivity with magnetic fields of 0 T and 1 T, and a negative magnetoresistance. The sample of oleic acid coated Fe<sub>3</sub>O<sub>4</sub> nanocrystals dispersed in the x = 0.05 matrix showed enhanced spontaneous magnetization as the factor of  $\approx 1.3$  relative to as-synthesized oleic acid coated Fe<sub>3</sub>O<sub>4</sub> nanocrystals.

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**1 Introduction** Transparent conducting oxides doped with 3*d* transition metal elements exhibiting room temperature ferromagnetism (RT-FM) have been studied intensively for realizing spintronics devices [1-20]. Tin doped indium sesquioxide (ITO) exhibiting RT-FM is promising for practical device applications because ITO has been the most widely used transparent conducting oxide in electronic and semiconductor industry.

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is well known as a half-metal material accompanied with fully spin-polarized carriers due to the minority-spin of octahedrally coordinated Fe<sup>2+</sup>. Spontaneous magnetization (Ms) of Fe<sub>3</sub>O<sub>4</sub> below 585 °C, resulted from uncompensated majority-spin of octahedrally coordinated Fe<sup>2+</sup>, is antiparallel to the spin of polarized carriers. Okada et al. [21] reported that pulsed-laser-deposited Fe<sub>3</sub>O<sub>4</sub> nanocrystals (NCs) dispersed in a single-crystalline ITO film exhibited RT-FM and a negative magnetoresistance (MR) due to collinear arrangement of Ms of the Fe<sub>3</sub>O<sub>4</sub> NCs. Okada et al. [22] modified the matrix from ITO to  $(Ho_xIn_{1-x})_2O_3$ , and observed enlarged Ms. If the spin of polarized carriers itinerating around the conduction band of  $(Ho_x In_{1-x})_2 O_3$  is antiparallel to the magnetic moments of localized Ho<sup>3+</sup> (10.6  $\mu_B$ ), localized Ho<sup>3+</sup> moments align parallel with Ms of dispersed Fe<sub>3</sub>O<sub>4</sub> NCs, and enlarge observed Ms.

It is known as the Kondo effect for diluted magnetic conductors that antiparallel arrangement between the spin of carriers and the localized magnetic moments accompanies a resistance minimum at a non-zero temperature in temperature dependent resistivity ( $\rho$ -T). Therefore, it is of great interest to examine effects of matrix with and without a resistance minimum at a non-zero temperature on magnetization (M-H) of dispersed Fe<sub>3</sub>O<sub>4</sub> NCs. We employed  $(Ho_x In_{1-x})_{1.9} Sn_{0.1}O_3$  with x = 0 - 0.3 as dispersion matrix. Hereafter, we denote  $(Ho_xIn_{1-x})_{1.9}Sn_{0.1}O_3$  as  $Ho_xITO$  for convenience. The Ho<sub>x</sub>ITO matrix with x = 0.05 demonstrated a resistance minimum and a negative MR. We dispersed oleic acid coated (OA-)  $Fe_3O_4$  NCs in  $Ho_xITO$  (x = 0 - 0.3) matrix, and examined changes in M-H with x. Carboxyl groups of OA were reported to combine with Fe atoms at surface of Fe<sub>3</sub>O<sub>4</sub> NCs, and OA layer with thickness  $\approx$ 3 nm was formed on the surface [23]. It is expected that spin-polarized carriers of Fe<sub>3</sub>O<sub>4</sub> NCs tunnel into Ho<sub>x</sub>ITO matrix through insulating OA layer, and the carriers in the matrix facilitate parallelization of localized Ho<sup>3+</sup> moments and Ms of dispersed OA-Fe<sub>3</sub>O<sub>4</sub> NCs if the matrix exhibits both a resistance minimum and a negative MR.

## **2 Experiment 2.1 Sample preparation** $Ho_xITO$ with x = 0 - 0.3 were synthesized from powders of $Ho_2O_3$ and $In_2O_3$ mixed

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flowing Ar gas. OA-Fe<sub>3</sub>O<sub>4</sub> NCs were synthesized from Fe(acac)<sub>3</sub> in a solution of dibenzylether mixed with OA [24]. Fe(acac)<sub>3</sub>, dibenzylether, and OA, weighed with the molar ratio of [1] : [26] : [2], were mixed with vigorous stirring for 1 h at RT. The mixture was kept at 300 °C for half an hour. After cooling to RT, OA-Fe<sub>3</sub>O<sub>4</sub> NCs were precipitated from the crude solution by adding toluene/hexane (1:1) followed by centrifugation. The precipitation was washed with anhydrous chloroform.

As-synthesized OA-Fe<sub>3</sub>O<sub>4</sub> NCs were dispersed into Ho<sub>x</sub>ITO powders with the molar ratio of  $[Fe_3O_4]$  :  $[Ho_{x-}ITO] = [0.05]$  : [1]. The mixtures were heated at 900 °C for 1 h in flowing Ar gas.

**2.2 Characterization** X-ray diffraction (XRD) was measured with a Rigaku CN2013 diffractometer with Cu  $K\alpha$  radiation at RT. For electrical measurement by four probes method, Ho<sub>x</sub>ITO powders were pressed into a cointype pellet before heating at 1200 °C for 2 h in flowing Ar gas. Then, the pellet was cut into a bar-shaped sample. Pt electrodes were bonded by gold wires to a Quantum Design MPMS 5S system. Current-voltage (*I-V*) characteristics at various temperatures under H = 0 and 1 T were measured for all the samples and some selected samples, respectively. *M-H* curve at 300 K was recorded by using a Quantum Design MPMS 5S SQUID magnetometer.

### **3 Results and discussion**

**3.1 Ho**<sub>*x*</sub>**ITO matrix** As shown in the lower panel of Fig. 1, Ho<sub>*x*</sub>ITO matrix showed diffraction peaks can be indexed only to the *C*-rare earth type cubic lattice. Both Ho<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> are known to crystallize into the *C*-rare earth type cubic lattice, and the lattice constant *a* of Ho<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> are 1.0606 nm (JCPDS 43-1018) and 1.0118 nm (JCPDS 06-0416), respectively. As shown in the upper panel of FIG. 1, the *a* value of Ho<sub>x</sub>ITO matrix varied linearly with *x* from 0 to 0.3, obeying the Vegard's law.

Temperature dependent resistivity at H = 0 T ( $\rho^0$ -T) 44 45 for all the Ho<sub>x</sub>ITO matrices are shown in Fig. 2. The  $x \leq$ 0.1 matrices were conductive ( $\rho^0 < 0.1 \ \Omega cm$ ), but the x >46 0.2 matrices were rather resistive ( $\rho^0 > 1 \Omega$ cm). The x =47 0.05 matrix showed larger  $\rho^0$  than the x = 0.025 and 0.1 48 49 matrices.  $\rho^0$  of the x = 0.025 and 0.1 matrices were so close 50 each other, and larger than the x = 0 matrix. In each  $\rho^0$ -T, the x = 0.025 and 0.05 matrices exhibited the resistance 51 52 minimum respectively at  $\approx 150$  K and  $\approx 125$  K, while the x 53 = 0 and 0.1 matrices indicated no resistance minimum. As 54 known as the Kondo effect, the resistance minimum for di-55 luted magnetic conductors accompanied with antiparallel 56 configuration between spin of carriers and localized mag-57



**Figure 1** Lower panel: XRD pattern of the Ho<sub>x</sub>ITO matrix with x = 0 (a), 0.025 (b), 0.05 (c), 0.1 (d), 0.2 (e), and 0.3 (f). Upper panel: lattice constant *a* of the matrix with *x*. Straight line is a guide for eye.



**Figure 2**  $\rho^0$  - *T* measured with H = 0 T for the Ho<sub>x</sub>ITO matrix with x = 0 (a), 0.025 (b), 0.05 (c), 0.1 (d), 0.2 (e), and 0.3 (f), shown by open circle.  $\rho^H$  - *T* measured with H = 1 T for the matrix with x = 0.025 (b) and 0.05 (c), shown by closed circle.

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netic moments. Such antiparallel arrangement is expected to bring about MR =  $(\rho^{H} - \rho^{0})/\rho^{0}$  with a negative sign, here  $\rho^{H}$  represents  $\rho$  measured at  $H \neq 0$ . Figures 2b and 2c show also temperature dependent resistivity at H = 1 T ( $\rho^{H}$ -T) for the x = 0.025 and 0.05 matrices, respectively. For the x =0.025 matrix, the resistance minimum disappeared in  $\rho^{H}$ -T, and  $\rho^{H}$  was larger than  $\rho^{0}$ . The x = 0.05 matrix demonstrated  $\rho^{H}$ -T with the resistance minimum at  $\approx 175$  K, and  $\rho^{H}$ smaller than  $\rho^{0}$ . Such a negative MR supports antiparallel arrangement between the spin of carriers and the localized magnetic moments of Ho<sup>3+</sup> in the x = 0.05 matrix.

**3.2 OA-Fe<sub>3</sub>O<sub>4</sub> NCs** XRD pattern and *M*-*H* curve of as-synthesized OA-Fe<sub>3</sub>O<sub>4</sub> NCs are shown in Fig. 3. All the XRD peaks were attributable to the inverse spinel type Fe<sub>3</sub>O<sub>4</sub> cubic lattice (JCPDS 19-0629). Crystallite size of  $\approx$ 65 nm for the NCs was estimated from the (511) reflection by Scherrer's equation.

At 300 K, as-synthesized OA-Fe<sub>3</sub>O<sub>4</sub> NCs demonstrated sigmoidal *M*-*H* curve almost saturated at H = 0.3 T. The small coercive field (*H*c  $\approx$ 27 Oe) indicates that OA prevented agglomeration of Fe<sub>3</sub>O<sub>4</sub> NCs leading to larger second particle formation. Present *M*-*H* curve looks similar to those of reported OA-Fe<sub>3</sub>O<sub>4</sub> NCs [23,25-27]. The magnetization at 1 T (*M*<sub>1T</sub>) of  $\approx$ 1 µ<sub>B</sub>/Fe atom for present NCs is rather large than those reported ( $\approx$ 0.85 µ<sub>B</sub>/Fe atom [23] and  $\approx$ 0.82 µ<sub>B</sub>/Fe atom [25]), and almost the same to that ( $\approx$ 0.95 µ<sub>B</sub>/Fe atom) reported in ref. 26.

3.3 OA-Fe<sub>3</sub>O<sub>4</sub> NCs/Ho<sub>x</sub>ITO matrix All the samples of OA-Fe<sub>3</sub>O<sub>4</sub> NCs dispersed in the Ho<sub>x</sub>ITO matrix showed hysteresis loop at 300 K, as seen in Fig. 4. The M-*H* curve of the  $x \le 0.05$  samples almost saturated at H = 0.5T, although the  $x \ge 0.1$  samples showed no saturation below H = 1 T. Ms of the samples, derived from an intercept of a tangent line for each M-H curve, were larger than that of the as-synthesized NCs. As shown in Fig. 5, Ms of the samples normalized to that of the as-synthesized NCs, increased slightly with x from 0 to 0.025, peaked at x = 0.05, decreased at x = 0.1, and then slightly decreased with further increases in x to 0.3. The x = 0.05 sample showed enhancement of Ms as the factor of  $\approx 1.3$ . Both  $M_{0.5T}$  and  $M_{1T}$ behaved almost parallel to Ms for the  $x \leq 0.05$  samples, while those for the  $x \ge 0.1$  samples deviated from Ms. Increments in  $M_{0.5T}$  and  $M_{1T}$  for the  $x \ge 0.1$  samples reflect increases of thermally excitable Ho<sup>3+</sup> paramagnetic moment at 300 K with x of the matrix.

Figure 6 shows  $\rho^0$ -*T* and  $\rho^H$ -*T* for the sample of OA-Fe<sub>3</sub>O<sub>4</sub> NCs dispersed in the Ho<sub>x</sub>ITO matrix with x = 0.05. The resistance minimum in both  $\rho^0$ -*T* and  $\rho^H$ -*T* disappeared for the x = 0.05 sample. A positive MR ( $\rho^H > \rho^0$ ) can arise from parallel configuration of localized Ho<sup>3+</sup> moments with *M*s of dispersed OA-Fe<sub>3</sub>O<sub>4</sub> NCs.

As shown in Fig.7, Hc of the samples also varied with x, and peaked at x = 0.05. The x dependence of Hclooks similar to that of Ms for the samples. Enlarged Hcand enlarged Ms for the x = 0.05 sample suggest carriers facilitated parallelization of localized  $Ho^{3+}$  moments and *Ms* of dispersed OA-Fe<sub>3</sub>O<sub>4</sub> NCs.



**Figure 3** Lower panel: XRD pattern of as-synthesized OA-Fe<sub>3</sub>O<sub>4</sub> NCs. Upper panel: M-H ( $H \ge 1$  T) curve of as-synthesized OA-Fe<sub>3</sub>O<sub>4</sub> NCs.



**Figure 4** *M*-*H* curve for the samples of OA-Fe<sub>3</sub>O<sub>4</sub> NCs dispersed in the Ho<sub>x</sub>ITO matrix with x = 0 (a), 0.025 (b), 0.05 (c), 0.1 (d), 0.2 (e), and 0.3 (f).



**Figure 5**  $M_{\rm S}$ ,  $M_{0.5T}$  and  $M_{1T}$  for the samples with *x*. Values were normalized to those of as-synthesized OA-Fe<sub>3</sub>O<sub>4</sub> NCs.



**Figure 6**  $\rho^0$  - *T* with H = 0 T and  $\rho^H$  - *T* with H = 1 T for the sample of OA-Fe<sub>3</sub>O<sub>4</sub> NCs dispersed in the Ho<sub>x</sub>ITO matrix with *x* = 0.05.



**Figure 7** *H*c for the samples with *x*. Values were normalized to that of as-synthesized OA-Fe<sub>3</sub>O<sub>4</sub> NCs.

**4 Summary** The Ho<sub>x</sub>ITO matrix with x = 0.05 exhibited both a resistance minimum at a non-zero temperature and a negative MR. The sample of OA-Fe<sub>3</sub>O<sub>4</sub> NCs dispersed in the Ho<sub>x</sub>ITO matrix with x = 0.05 demonstrated enlarged *M*s as the factor of  $\approx 1.3$  relative to the assynthesized NCs. In the sample of OA-Fe<sub>3</sub>O<sub>4</sub> NCs dispersed in the Ho<sub>x</sub>ITO matrix with x = 0.05, the resistance minimum in both  $\rho^0$ -*T* and  $\rho^H$ -*T* disappeared, and the sign of MR turned from negative to positive. Similar behavior in *M*s and *H*c with *x* also supports that the enlarged *M*s for the x = 0.05 sample arose from parallel configuration of localized Ho<sup>3+</sup> moments in the Ho<sub>x</sub>ITO matrix to *M*s of dispersed OA-Fe<sub>3</sub>O<sub>4</sub> NCs.

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