Magnetic Properties of Phase Separated Glasses and Glass Ceramics in Co$_3$O$_4$-TiO$_2$-SiO$_2$ System

H Nakamura$^1$, T Kishi$^{1,2}$, T Ohgaki$^3$, Y Muro$^{2,4}$ and A Yasumori$^{1,2}$

$^1$ Department of Materials Science and Technology, $^2$ Polyscale Technology Research Centre, $^3$ National Institute for Materials Science, $^4$ Department of Physics Science and Engineering, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

E-mail: yasumori@rs.noda.tus.ac.jp

Abstract. The phase separated glass ceramics in Co$_3$O$_4$-TiO$_2$-SiO$_2$ ternary system were prepared by a melt-quenching method and their magnetic properties were investigated. The samples in the $x$CoO-(48.5-0.5$x$)TiO$_2$-(48.5-0.5$x$)SiO$_2$-3.0Al$_2$O$_3$ ($x$ = 3, 5, 10) consisted of TiO$_2$-rich particles and a SiO$_2$-rich matrix and this phase-separated structure was formed by a nucleation-growth process. This phase-separated glass ceramics showed the magnetic hysteresis loop due to a mixture of ferromagnetic and paramagnetic phases. From the X-ray diffraction measurements, it was confirmed that the samples had the TiO$_2$ rutile phase and amorphous phase without the other crystalline phases. The magnetic susceptibility increased and the coercive force decreased with increasing the amount of Co addition. These results indicated that the prepared samples had the ferromagnetic Co-doped TiO$_2$ rutile phase and the paramagnetic amorphous phase which contains Co divalent ions.

1. Introduction

The development of a magnetic sensor such as a magnetic head used for high density magnetic recording requires higher performance magnetic materials. Recently, Co-doped TiO$_2$ has received considerable attention because of their ferromagnetic properties and extensively studied as one of the promising materials applied to a highly sensitive magnetic sensor [1-9]. Room temperature ferromagnetism in Co-doped TiO$_2$ was reported by various groups in films grown by molecular-beam epitaxy technique [1-3], pulsed laser deposition [4], liquid-delivery metal organic chemical vapor deposition [5], sol-gel process [6], and bulk samples prepared by a solid-state reaction method [7].

On the other hand, phase separation is one of the most famous phenomena in oxide glasses. Phase-separated glasses and glass-ceramics having unique structure are utilized for various applications of functional glasses such as chemical/thermal durable glasses and porous glasses. There are two mechanisms by which phase separation can occur. The first mechanism is nucleation-growth process resulting in microstructure consisting of fine particles and a continuous matrix. The second mechanism is called as spinodal decomposition, which results in three-dimensionally interconnected microstructure. These microstructures of phase separation in glass have been studied for the preparation of the phosphor [10, 11], photocatalytic [12, 13] and magnetic materials [14, 15].
The stable immiscibility region above liquidus temperature exists in both TiO$_2$-SiO$_2$ and CoO-SiO$_2$ binary systems [16, 17]. For example, a phase-separated glass ceramics in the TiO$_2$-SiO$_2$ binary system has a binodal type texture that consists of TiO$_2$-rich particles with a diameter of several tens to hundreds nanometers dispersed in a SiO$_2$-rich glass matrix [12, 13]. In this study, in order to obtain a new functional magnetic material which consists of a CoO-TiO$_2$-rich phase showing ferromagnetism and a SiO$_2$-rich one accompanied with both thermal and chemical stability, the phase-separated glasses and glass ceramics in Co$_3$O$_4$-TiO$_2$-SiO$_2$ system were prepared by a melt-quenching method. The crystalline phases, microstructures and magnetic properties of the samples were examined.

2. Experiments

Phase-separated glasses and glass ceramics with the composition of $x$CoO-(48.5-0.5$x$)TiO$_2$-(48.5-0.5$x$)SiO$_2$-3.0Al$_2$O$_3$ mol% ($x = 3, 5, 10$) were prepared by a conventional melt-quenching method. Reagent grade raw materials of Co$_3$O$_4$, SiO$_2$ ($\alpha$-quartz), TiO$_2$ (anatase), Al$_2$O$_3$ (corundum) were weighed and mixed with ethanol in a ball-mill for 24 hours, and the resulting slurry was dried. The dried powder was molded into a rod shape using a cold isostatic press (150 MPa). The rod samples were sintered at 1300 °C for 24 h in the air using a conventional electric furnace. The sintered rods were melted for 3 min in the air by use of an infrared imaging furnace (PRC MR-H500, ULBAC), and the melts were immediately quenched by turning off the halogen light of the furnace. The samples were cut, polished and etched with NaOH aqueous solution, and their morphology was observed by field emission scanning electron microscopy (FE-SEM, S4200, Hitachi). The melt-quenched samples were crushed into powder by alumina mortar. Crystalline phases of the samples were measured by powder X-ray diffraction (XRD, XRD-6100 Lab X, Shimadzu). Magnetization studies were carried out on the powder samples by using a vibrating sample magnetometer (VSM, BHV-55, Riken Denshi).

3. Results and discussion

Figure 1(a)-(c) shows the FE-SEM images of the etched surfaces of the melt-quenched samples. In this ternary system, the glassy phase is expected to separate into a SiO$_2$-rich phase and TiO$_2$-rich one. Thus, the dark area selectively etched by NaOH aqueous solution is attributed to a SiO$_2$-rich phase, and bright area is TiO$_2$-rich phase. As shown in these figures, all the samples contained a lot of fine particles of TiO$_2$-rich phase, of which size was smaller than a few hundreds of nanometers. This indicates that the samples were phase-separated by a nucleation-growth process.

![Image](image-url)

**Figure 1.** FE-SEM images of etched surfaces of samples: (a) $x = 3$, (b) $x = 5$ and (c) $x = 10$.

The XRD patterns of the samples are shown in Figure 2. The sharp diffraction peaks were all identified as the TiO$_2$ rutile phase, and there are no obvious peaks of the other crystalline phases such as SiO$_2$, CoTiO$_3$ and CoTi$_2$O$_5$ which are stable crystalline phases in this system. The samples also showed amorphous halo at $2\theta = 20^\circ$ in Figure 2. Therefore, the XRD measurement showed that all the samples mainly consisted of the TiO$_2$ rutile phase and the amorphous phase.

Figure 3 shows the magnetization versus magnetic field strength ($M-H$) curves of the samples measured at room temperature. There was hysteresis in the $M-H$ curves of all the samples. The magnetization increased with increase in the field value, and there was no tendency of saturation even...
up to the highest $H$ of 15 (kOe). Thus, the observed $M$-$H$ curves revealed that the samples contained a mixture of ferromagnetic and paramagnetic phases. Since the element in the material that contributes to magnetic properties is only Co, the possible ferromagnetic and paramagnetic phases in the samples are considered to be the Co-doped TiO$_2$ rutile phase and Co divalent ions in the amorphous phase, respectively.

Figure 2. XRD patterns of the samples.

Figure 3. $M$-$H$ curves of the samples at room temperature.

The residual magnetization $M_r$, coercive force $H_c$ and magnetic susceptibility $\chi$, which are estimated from $M$-$H$ curves in Figure 3, are summarized in Table 1. As the Co content increases, the $\chi$ increases, indicating the increase of amount of Co divalent ions that contribute to paramagnetism. The $M_r$ value is independent of the amount of Co addition. On the contrary, the $H_c$ decreases with increase of the Co content. At this moment, it is not sure whether this change of the coercive force was due to the change of magnetic domain structure, that is, the change from the single magnetic domain particles to the multi-domain bulk-like particles. However, the obvious changes of the magnetic properties by Co addition imply that the precipitated crystalline phase in TiO$_2$-rich phase and the fine structure owing to the phase separation in the materials, which were synthesized by quenching the immiscible melts in this ternary system, strongly affected them.

Table 1. The residual magnetization $M_r$, coercive force $H_c$ and magnetic susceptibility $\chi$ of prepared samples with the composition of $x$CoO-(48.5-0.5$x$)TiO$_2$-(48.5-0.5$x$)SiO$_2$-3.0Al$_2$O$_3$ mol%.

| Co content $x$ (mol %) | $M_r$ (emu/g) | $H_c$ (Oe) | $\chi$ (emu/mol) |
|------------------------|--------------|------------|------------------|
| 3                      | $1.1\times10^{-4}$ | 453        | $2.2\times10^{-3}$ |
| 5                      | $1.3\times10^{-4}$ | 332        | $3.3\times10^{-3}$ |
| 10                     | $1.1\times10^{-4}$ | 250        | $9.0\times10^{-3}$ |

4. Summary
The room temperature ferromagnetism was observed in the phase-separated glass ceramics in the Co$_3$O$_4$-TiO$_2$-SiO$_2$ ternary system prepared by the melt-quenching method. All the prepared samples consisted of the TiO$_2$ rutile phase and the amorphous phase, and they exhibited the ferromagnetism along with the paramagnetic behavior. The ferromagnetic and the paramagnetic behaviors could be attributed to the presence of Co-doped TiO$_2$ rutile phase and Co divalent ions in the amorphous phase, respectively. The magnetic susceptibility increased with increasing the Co content, indicating the increase of the amount of Co divalent ions that contribute to its paramagnetism. With increase in the
amount of Co addition, the coercive force decreased, however, the residual magnetization was independent of the Co content. The reason for the change of these magnetic properties was not clear, because the fraction of Co-doped TiO$_2$ phase and their magnetic microstructure that contribute to ferromagnetism were not known. Further examination of the magnetic properties, especially the measurement of $M$-$H$ curves at low temperature, is necessary in order to know the origin of the magnetic property of the phase-separated glass ceramics in the Co$_3$O$_4$-TiO$_2$-SiO$_2$ system.

Acknowledgements
This work was supported by "Academic Frontier" project for private universities: matching fund subsidy from MEXT (Ministry of Education, Culture, Sports, Science and Technology), 2006-2010.

References
[1] Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S and Koinuma H 2001 Science 291 854
[2] Chambers S A, Wang C M, Thevuthasan S, Droubay T, McCready D E, Lea A S, Shuttthanandan V and Windisch Jr. C F 2002 Thin Solid Films 418 197
[3] Murakami M, Matsumoto Y, Hasegawa T, Ahmet, P, Nakajima K, Chikyow T, Ofuchi H, Nkai I and Koinuma H 2004 J. Appl. Phys. 95 5330
[4] Shinde S R, Ogale S B, Sarma S D, Simpson J R, Drew H D, Lofland S E, Lanci C, Buban J P, Browning N D, Kulkarni V N, Higgins J, Sharma R P, Greene R L and Venkatesan T 2003 Phys. Rev. B 67 115211
[5] Seong N -J, Yoon S -G and Cho C -R 2002 Appl. Phys. Lett. 81 4209
[6] Cho J H, Kim B Y, Kim H D, Woo S I, Moon S H, Kim J P, Cho Chae Ryong, Joh Y G, Kim E C and Kim D H 2004 Phys. Stat. Sol. 241 1537
[7] Kong L G, Kang J F, Wang Y, Sun L, Liu L F, Liu X Y, Zhang X and Han R Q 2006 Electrochem. Sol. State Lett. 9 G1
[8] Osada M, Ebina Y, Fukuda K, Ono K, Takeda K, Yamamura K, Takayama-Muromachi E and Sasaki T 2006 Phys. Rev. 73 153301
[9] Suryanarayanan R, Naik V M, Kharel P, Talagala P and Naik R 2005 Sol. Stat. Commun. 133 439
[10] Ohgaki T, Higashida A, Soga K and Yasumori A 2007 J. Electrochem. Soc. 154 1163
[11] Ohgaki T, Nagumo Y, Soga K and Yasumori A 2007 J. Ceram. Soc. Jpn. 115 201
[12] Sone Y, Nishio K and Yasumori A 2004 Mater. Res. Soc. Symp. Proc. 849 KK3.13.
[13] Sone Y, Ohgaki T, Nishio K, Yamasita T and Yasumori A 2006 J. Photopolyym. Sci. Tech. 19 111
[14] Yasumori A, Koike A, Kameshima Y, Okada K and Nishio H 2002 J. Non-Cryst. Solids 297 239
[15] Yasumori A, Koike A, Kameshima Y, Okada K and Inoue S 2000 J. Ceram. Soc. Jpn. 108 813
[16] DeVries R C and Osborn E F 1954 Trans. J. Brit. Ceram. Soc. 53 525
[17] Masse D P and Muan A 1965 Trans. Metall. Soc. AIME 233 1448