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Magnetic properties of sputtered $BaCoTiFe_{10}O_{19}$ films

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Abstract. Amorphous $BaCoTiFe_{10}O_{19}$ films have been prepared by the RF sputtering technique. The magnetic and magneto-optical properties, the structure and the effect of annealing have been investigated. The 4.2 K magnetization increases with increasing magnetic field and is not saturated at a high magnetic field of 65 kOe. Above 100 K the susceptibility obeys a Curie–Weiss law with a low Curie constant of 0.81 and a large negative Weiss constant of −350. The effective paramagnetic moment ($2.54\mu_B$) for ion ions is much smaller than the theoretical moment. Amorphous $BaCoTiFe_{10}O_{19}$ films have a lower magnetization (1.5 emu g^{-1} at 1.5 K) and higher Curie temperature (850 K) and coercivity (700 Oe at room temperature) than crystalline bulk samples do. After annealing above 750 °C, amorphous samples crystallize into single M-type hexaferrite with a magnetization of 320 emu cm^{-3}, a coercivity of 100 Oe and a magneto-optical Faraday rotation of 1° μm^{-1} at room temperature.

1. Introduction

Amorphous magnetic materials are of interest because of the unusual types of magnetic order that they may exhibit. A large number of investigations have been published on amorphous rare-earth–transition-metal intermetallics and on amorphous transition-metal–metalloid compounds. Amorphous oxide materials with a high concentration of magnetic elements have been studied comparatively less extensively.

Magnetic oxide films are expected to be a magneto-optical medium of the second generation because of their large magneto-optical effect and unsurpassed chemical stability. M-type $BaFe_{12}O_{19}$ hexaferrites have a large uniaxial magnetic anisotropy and a large Faraday rotation. Thus they can be used as magneto-optical and perpendicular magnetic recording media [1]. It has been found that in $BaFe_{12}O_{19}$ hexaferrites the substitution of Co for Fe can enhance the Faraday rotation and reduce the coercivity and Curie temperature to values suitable for magnetic recordings [2–4]. Recently we prepared amorphous $BaCoTiFe_{10}O_{19}$ films by RF magnetron sputtering. The structure and the magnetic and magneto-optical properties were investigated. In this paper the structure, magnetic properties and magneto-optical Faraday effect of the sputtered $BaCoTiFe_{10}O_{19}$ films are reported.

2. Experimental details

The films were deposited by RF magnetron sputtering in an Ar atmosphere onto quartz substrates. A sintered polycrystalline target with the composition $BaCoTiFe_{10}O_{19}$ was prepared by standard ceramic techniques from the high-purity oxides $BaCo_3$, CoO, TiO_2

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and Fe_2O_3. The target and substrate were cooled with water. The base pressure of the chamber before introducing argon gas was better than 1×10^{-6} Torr. The pressure of the sputtering gas (argon) was 2×10^{-2} Torr. The deposition rate was about 1 μm h^{-1}. The film thickness was about 1.1 μm. The films exhibit a deep-red colour and transparency. The surface of the as-sputtered films is shiny and homogeneous.

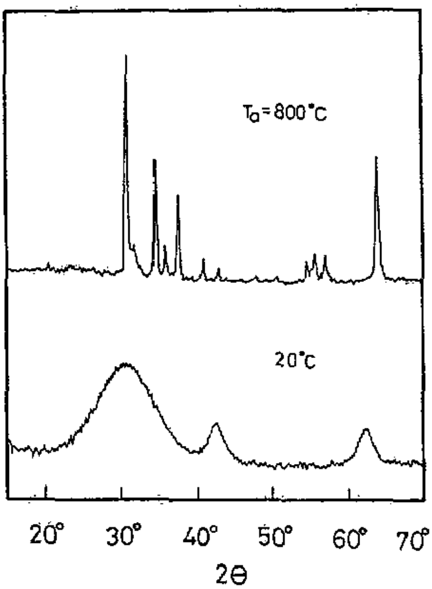

Figure 1. *X-ray diffraction patterns of the as-sputtered film and the films annealed at 800 °C for 60 min.*

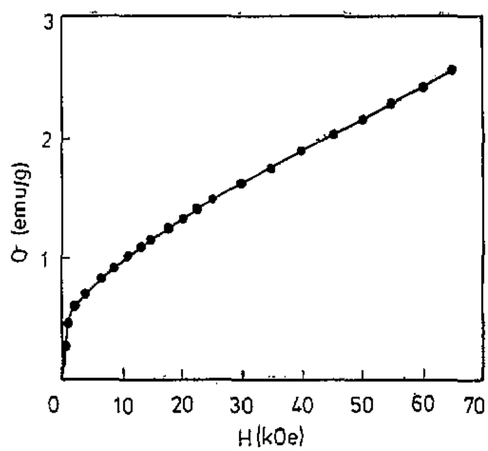

Figure 2. *Magnetization curve of as-sputtered films.*

X-ray diffraction was carried out with Cu Kα radiation to determine the structure and phase composition of the sample, as shown in figure 1. The hysteresis loops were measured on a vibrating-sample magnetometer at room temperature with a maximum field of 20 kOe. The temperature dependence of the magnetization was measured with an extracting-sample magnetometer with a magnetic field of 25 kOe.

3. Results and discussion

3.1. Structure

Figure 1 shows the x-ray diffraction patterns of as-sputtered films and films annealed at 800 °C for 60 min in an oxygen atmosphere. The x-ray diffraction patterns of as-sputtered films exhibit a diffuse broad maximum at around $2\theta = 31°$ and also weak broad peaks at around $2\theta = 43°$ and 64° for Cu K α. No contribution from the crystalline phase is observed, suggesting an amorphous nature. It is noted that the comparison of the x-ray diffraction patterns of amorphous oxides with amorphous alloys reveals a great difference. The patterns of amorphous alloys show only a diffuse broad maximum, while the patterns of amorphous oxides exhibit more diffuse broad maxima. This shows that amorphous oxides have a different structure from amorphous alloys. The structure of amorphous alloys can be explained by the random dense packing model [5]. In amorphous alloys the locally recognizable structure is related to a crystalline structure with the same or similar chemical composition [6]. The amorphous alloys may have a singular structure, while amorphous oxides have a random coordination structure [5]. Because the crystalline hexaferrites have a large molecule, the unit cell is composed of 64 atoms. So a local structure such as the structure of the crystalline $BaCoTiFe_{10}O_{19}$ hexaferrite cannot be formed. Amorphous $BaCoTiFe_{10}O_{19}$ compounds may be composed of several types of amorphous structure. The more diffuse broad maxima of amorphous oxides may originate from the oxygen–oxygen, metal–oxygen and metal–metal structural correlations. When films are annealed at 800 °C for 60 min in an oxygen atmosphere, the x-ray diffraction pattern shows only the expected crystalline M-type $BaCoTiFe_{10}O_{19}$ hexagonal ferrite. A preferred orientation with the (110) plane of $BaCoTiFe_{10}O_{19}$ ferrites parallel to the film surface is observed.

3.2. Magnetic properties

The magnetization curve of as-sputtered samples was measured at 4.2 K. The data are shown in figure 2. When the magnetic field is lower than 2 kOe, the magnetization rises rapidly with increasing magnetic field. When the magnetic field $H > 2$ kOe, the magnetization increases linearly with increasing magnetic field. The susceptibility is essentially field independent. It is noted that the magnetization is not saturated even at a high magnetic field of 65 kOe.

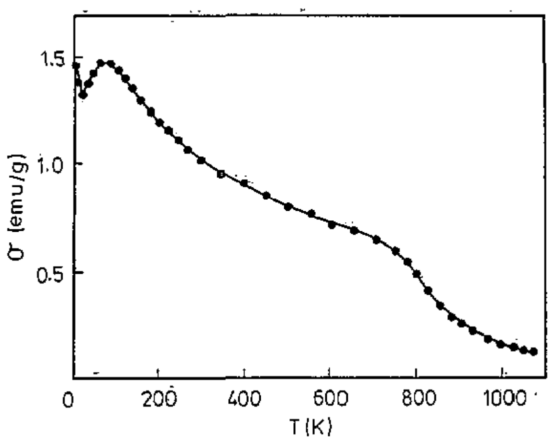

Figure 3. Temperature dependence of the magnetization of as-sputtered films.

Figure 3 shows the temperature dependence of the magnetization. It is noted that

(1) as-sputtered samples have a very small magnetization of 1.5 emu g^{-1} at 1.5 K and 1 emu g^{-1} at room temperature,

(2) the as-sputtered film has a high Curie temperature of about 850 K, which is much higher than 556 K for crystalline $BaCoTiFe_{10}O_{19}$ hexaferrite [7] and

(3) in the temperature range 0 K< T < 75 K a minimum magnetization is observed at about 25 K.

The susceptibility χ and $1/\chi$ are plotted as functions of temperature in figure 4. A maximum susceptibility is observed. The temperature of this maximum of the susceptibility is approximately 65 K. This demonstrates that the amorphous $BaCoTiFe_{10}O_{19}$ compounds are antiferromagnetic. The Néel temperature is about 65 K. It is noted that the crystalline antiferromagnetic oxides have a sharp phase transition at the Néel temperature, while

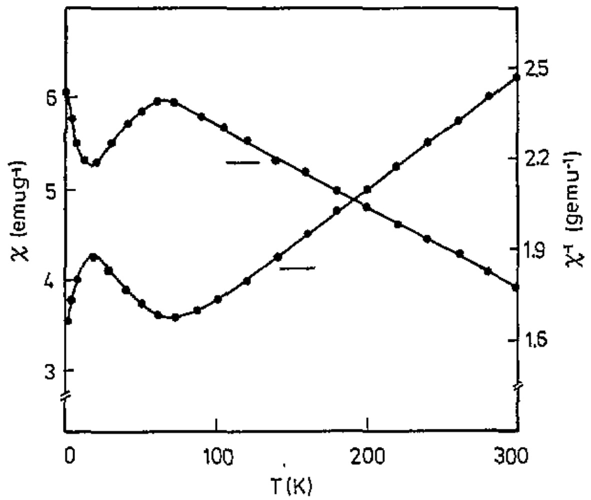

Figure 4. Susceptibility χ and $1/\chi$ of as-sputtered films as functions of temperature.

amorphous oxides exhibit a very broad maximum in the susceptibility near the Néel point. In the temperature range $100\ K < T < 300\ K$ the susceptibility can be described by the Curie–Weiss law

$$1/\chi = (T - 350)/0.81. \tag{1}$$

An extrapolated Weiss constant θ of −350 suggests very strong antiferromagnetic interaction in the as-sputtered films. The Curie constant C = 0.81 is much smaller than the theoretical value (C = 4.37). The surprisingly low Curie constant may be attributed to the effective cancellation of an important fraction of the Fe atomic moments. The effective paramagnetic moment per Fe^{3+} ion of $2.54\mu_B$ is calculated from the slope of the $1/\chi$ versus T curve. This value is much smaller than the theoretical moment of $5.9\mu_B$ for free Fe^{3+} ions. The decrease in the effective moment of Fe^{3+} ions may originate from the broad distribution of antiferromagnetic exchange interactions.

It is of interest to note that the amorphous $BaCoTiFe_{10}O_{19}$ compound exhibits a higher coercivity (700 Oe) and a lower magnetization (1 emu g^{-1}) than the bulk $BaCoTiFe_{10}O_{19}$ compounds at room temperature. When the samples are annealed at a temperature below 750 °C, only a little change is detected in the coercivity and magnetization. On annealing at about 750 °C the coercivity decreases rapidly to 100 Oe and the magnetization increases quickly to 61 emu g^{-1}. These values are in agreement with the bulk values [7]. The rapid changes in the coercivity and magnetization at an annealing temperature of about 750 °C is caused by crystallization of amorphous samples. This result is in good agreement with that obtained from x-ray diffraction. X-ray diffraction analysis shows that the amorphous state is observed up to 700 °C. When the amorphous samples were annealed above 750 °C, they crystallized into the M-type hexaferrite with a magnetoplumbite structure. This demonstrates that the crystallization temperature of amorphous $BaCoTiFe_{10}O_{19}$ is around 750 °C. On annealing above 800 °C the coercivity and saturation magnetization showed no change. The annealing temperature dependences of coercivity and magnetization are shown in figure 5.

Comparison of crystalline magnetic oxide $BaCoTiFe_{10}O_{19}$ with the amorphous compounds reveals large differences.

(1) The results of x-ray diffraction analysis and measurement of the magnetic properties for samples annealed at different temperatures shows that the as-sputtered $BaCoTiFe_{10}O_{19}$ films have a crystallization temperature.

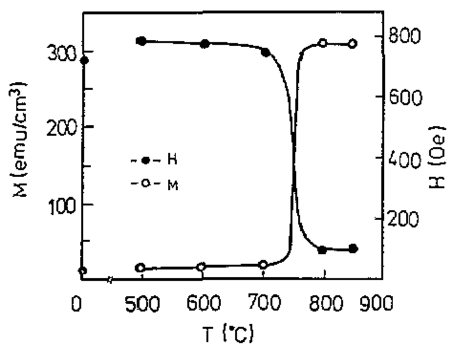

Figure 5. Annealing temperature dependences of coercivity and magnetization.

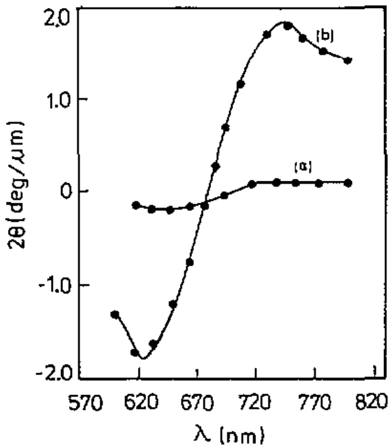

Figure 6. Magneto-optical Faraday rotation spectra of the as-sputtered film (curve a) and the film annealed at 800 °C (curve b).

(2) As-sputtered films have a very much lower magnetization and a higher coercivity than crystalline $BaCoTiFe_{10}O_{19}$ compounds.

(3) As-sputtered films are antiferromagnetic at low temperatures, while crystalline $BaCoTiFe_{10}O_{19}$ is ferrimagnetic.

The different magnetic properties may originate from the different locally recognizable structures in the amorphous and crystalline oxides. The presence of antiferromagnetism at low temperatures in amorphous $BaCoTiFe_{10}O_{19}$ indicates that the amorphous films do not have the same structure as crystalline $BaCoTiFe_{10}O_{19}$ hexaferrites. This implies that our amorphous $BaCoTiFe_{10}O_{19}$ films do not resemble their corresponding crystalline counterparts on a local scale and are thus not microcrystalline.

3.3. Magneto-optical Faraday rotation spectra

The magneto-optical Faraday rotation spectra were measured in the visible region at room temperature. Figure 6 shows the Faraday rotation spectra of the as-sputtered film and of the films annealed at 800 °C in an oxygen atmosphere. It can be seen that the amorphous $BaCoTiFe_{10}O_{19}$ films exhibit no magneto-optical Faraday rotation. This may be because they do not have the same structure as crystalline M-type hexaferrite. When amorphous oxide is annealed above the crystallization temperature, the Faraday rotation increases rapidly. The sample annealed at 800 °C exhibits a large Faraday effect. The Faraday rotation varies strongly with the wavelength. Two peaks of about $-0.1°\ \mu m^{-1}$ and $1°\ \mu m^{-1}$ are observed at wavelengths of 620 nm and 750 nm, respectively. The rapid increase in Faraday rotation with increasing annealing temperature results from crystallization of amorphous samples. X-ray diffraction analysis shows that the amorphous samples crystallize into single M-type hexaferrites at an annealing temperature above 750 °C.

3.4. Conclusion

As-sputtered films are amorphous. The maximum susceptibility is observed at 65 K. Above 100 K the susceptibility obeys a Curie–Weiss law with a low Curie constant and a large negative Weiss constant. These particular properties suggest that the magnetic structure is likely to have an antiferromagnetic interaction order speromagnetically. The amorphous samples exhibit a high coercivity, a low magnetization and a very small magneto-optical effect at room temperature. After annealing above 750 °C amorphous samples crystallize into M-type hexagonal ferrite with the preferred orientation with the (110) plane parallel to the film surface. Crystallized samples have a larger magnetization and a larger magneto-optical Faraday rotation.

Acknowledgments

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