# Field-Cooling Effect in the Amorphous Magnetic Oxide

# Field-Cooling Effect in the Amorphous Magnetic Oxide*

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Synopsis

Amorphous magnetic oxides of $BaO-Mn_2O_3-B_2O_3$ system are prepared by a rapid quenching technique. Magnetic measurements down to 4.2 K reveal weak ferromagnetic components with $T_c \sim 50$ K. The origin of the ferromagnetism is suggested to be due to manganese-rich clusters arising from concentration fluctuations in the glass. The field-cooling effect in this system is compared with that in the amorphous $BaO-Fe_2O_3-B_2O_3$ system.

## I. Introduction

Although considerable interest has been paid to the study of amorphous magnetic oxides,[1-5] lack of appropriate materials seems to have prevented from understanding its structure and the magnetic order in it. In the previous papers,[6-8] we reported the formation of homogeneous glasses of $BaO-Fe_2O_3-B_2O_3$ system (Fe-series) and studied the structural and magnetic properties, mostly by Mössbauer spectroscopy. It has been shown that homogeneous glasses containing a large amount of transition metal ions are possible to be prepared and that the concept of antiferromagnetic ordering in short range (so-called speromagnetism)[5] is applicable to this system.

In the present study, we tried to prepare glassy specimens of the $BaO-M_2O_3-B_2O_3$ system where M = Mn, Cr, Co or Ni by the same rapid quenching technique used in the preparation of the amorphous $BaO-Fe_2O_3-B_2O_3$ system.[6-8] Only the Mn-series glass was successfully prepared besides the Fe-series glass. The present paper reports the results of the magnetic measurement of both the Fe- and Mn-series glasses, with special emphasis on the field cooling experiments.

## II. Sample preparation

Laser-impact quenching technique[6,9] was applied for the preparation of amorphous specimens of $BaO-Mn_2O_3-B_2O_3$ system (Mn-series).

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Starting materials for $BaO-Mn_2O_3-B_2O_3$ glasses were prepared by mixing $BaCO_3$, $Mn_2O_3$ and $H_3BO_3$ in a desired proportion and firing at 1100 °C for several hours in air. A small amount of sintered starting material was placed on a water-cooled copper plate, melted with a focused $CO_2$ laser instantaneously, and quenched by striking with another copper block. Chemical composition was determined by Chemical Analysis Laboratory of RIISOM. The amount of $B_2O_3$ in the prepared specimens was reduced to about 50 % of the nominal value due to evaporation.

The specimens prepared were examined by X-ray diffraction analysis. The halo patterns characteristic of amorphous material were clearly observed. No indication of the crystalline phase was observed.

## III. Magnetic measurements

Magnetization was measured from 4.2 K to room temperature by a pendulum-type magnetometer. Calibration of magnetization was made by measuring magnetic susceptibility of $Gd_2O_3$.

Accuracy of magnetization measurements for the measuring fields less than 2 kOe is not sufficient to obtain reliable values. Hence, remanent magnetization is determined by extrapolating magnetization data at higher measuring fields.

### (i) Fe-series glasses

As previously reported, magnetic susceptibility of the amorphous $BaO-Fe_2O_3-B_2O_3$ system shows a broad maximum around the magnetic

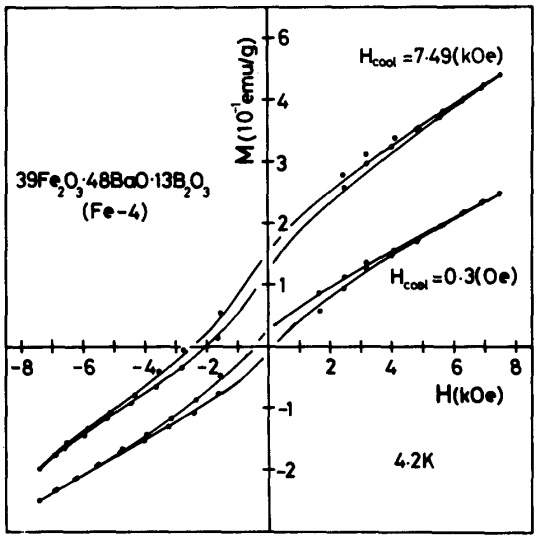



Fig. 1. Hysteresis curves at 4.2 K of the amorphous specimen, Fe-4, with cooling fields of 7.49 kOe and 0.3 Oe.

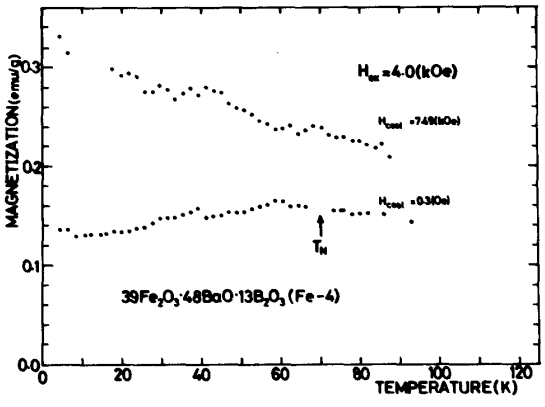



Fig. 2. Temperature variation of magnetization of the amorphous specimen, Fe-4, with cooling fields of 7.49 kOe and 0.3 Oe. Measuring field is 4.0 kOe.

ordering temperature, $T_N$, determined from Mössbauer measurements.[8] The magnetic ordering temperature was found to decrease considerably with the decrease in iron concentration. The magnetic susceptibility obeys the Curie-Weiss law at high temperatures, giving effective Bohr magneton number, $P_{eff}$, of 5.4∿6.2 $\mu_B$ and paramagnetic Curie temperature, $\theta_p$, of -300 K.

The amorphous specimen acquires small remanence when cooled in a magnetic field across $T_N$. Fig. 1 shows the hysteresis curves at 4.2 K for $39Fe_2O_3 \cdot 48BaO \cdot 13B_2O_3$ (Fe-4) glass with cooling field of 7.49 kOe and 0.3 Oe. When the specimen was cooled in a magnetic field, positive shift of magnetization curve is observed. The acquired remanence decreases monotonically with increasing temperature and almost vanishes around $T_N$ as shown in Fig. 2, where the temperature variation of the magnetization in measuring field of 4.0 kOe is plotted.

(ii) Mn-series glasses

Table I summarizes the chemical composition and magnetic parameters of the Mn-series glasses presently obtained.

Remarkable ferromagnetic components are observed in the case of the amorphous $BaO-Mn_2O_3-B_2O_3$ system. Fig. 3 shows the temperature variation of magnetization of $65Mn_2O_3 \cdot 29BaO \cdot 6B_2O_3$ glass (Mn-6) measured in a magnetic field of 4.0 kOe. The magnetization of the specimen cooled in terrestrial magnetic field (0.3 Oe) at 4.2 K is about

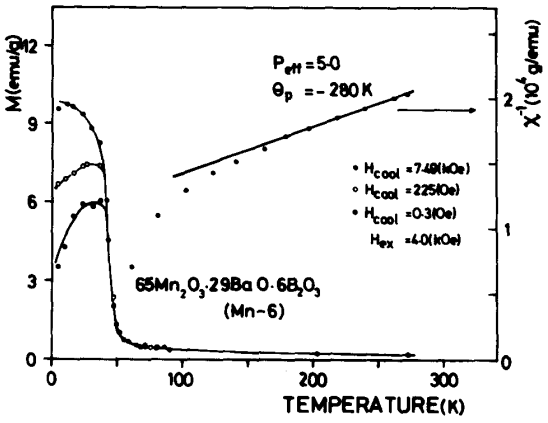



Fig. 3. Temperature dependences of magnetization measured in a field of 4.0 kOe and the inverse of magnetic susceptibility of the amorphous specimen, Mn-6. Magnetization at low temperatures increases with increasing cooling field.

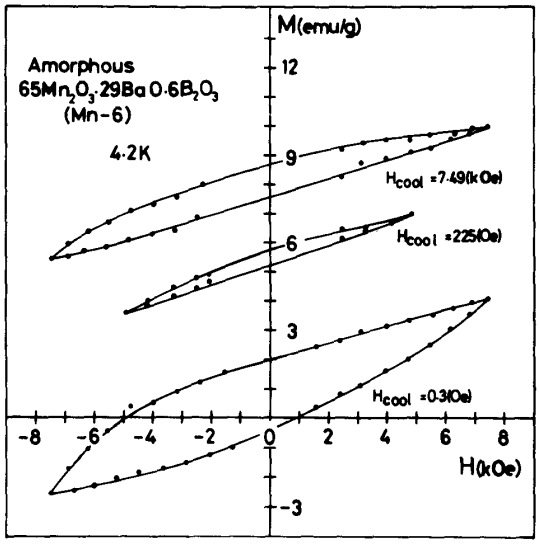



Fig. 4. Hysteresis curves at 4.2 K of the amorphous specimen, Mn-6, with cooling fields of 7.49 kOe, 225 Oe and 0.3 Oe.

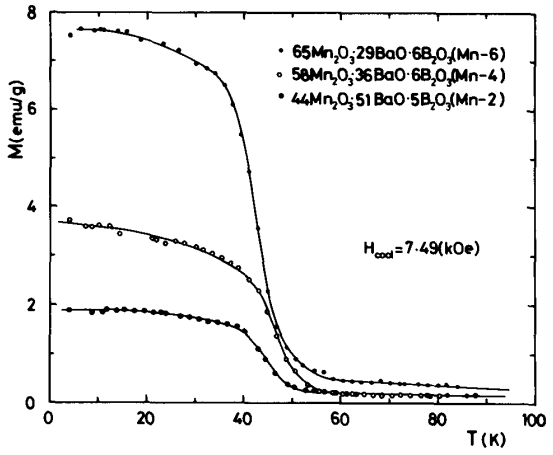



Fig. 5. Temperature dependence of the magnetization with measuring field of 4.0 kOe for the Mn-series glasses field-cooled in a magnetic field of 7.49 kOe.

Table I Magnetic properties of amorphous $BaO-Mn_2O_3-B_2O_3$ system.

| Specimen | Chemical Composition, mol % | | | $T_C$ | $\theta_p$ | $P_{eff}$ |
|---|---|---|---|---|---|---|
| | $Mn_2O_3$ | BaO | $B_2O_3$ | K | K | |
| Mn-2 | 44 | 51 | 5 | 50 | | |
| Mn-4 | 58 | 36 | 6 | 51 | -270 | 5.0 |
| Mn-6 | 65 | 29 | 6 | 48 | -280 | 5.0 |

3 emu/g and vanishes rather steeply around 50 K (This temperature is called $T_C$ hereafter.), after passing through a broad maximum around 30 K. Ferromagnetic components are enhanced by field cooling across $T_C$. The magnetization in 4.0 kOe reaches the value of about 10 emu/g at 4.2 K when cooled in 7.49 kOe.

Above $T_C$, magnetic susceptibility obeys the Curie-Weiss law with the effective Bohr magneton number of 5.0 and the paramagnetic Curie temperature of -280 K. This suggests that prevailing interactions are antiferromagnetic and most manganese ions are in the trivalent state.

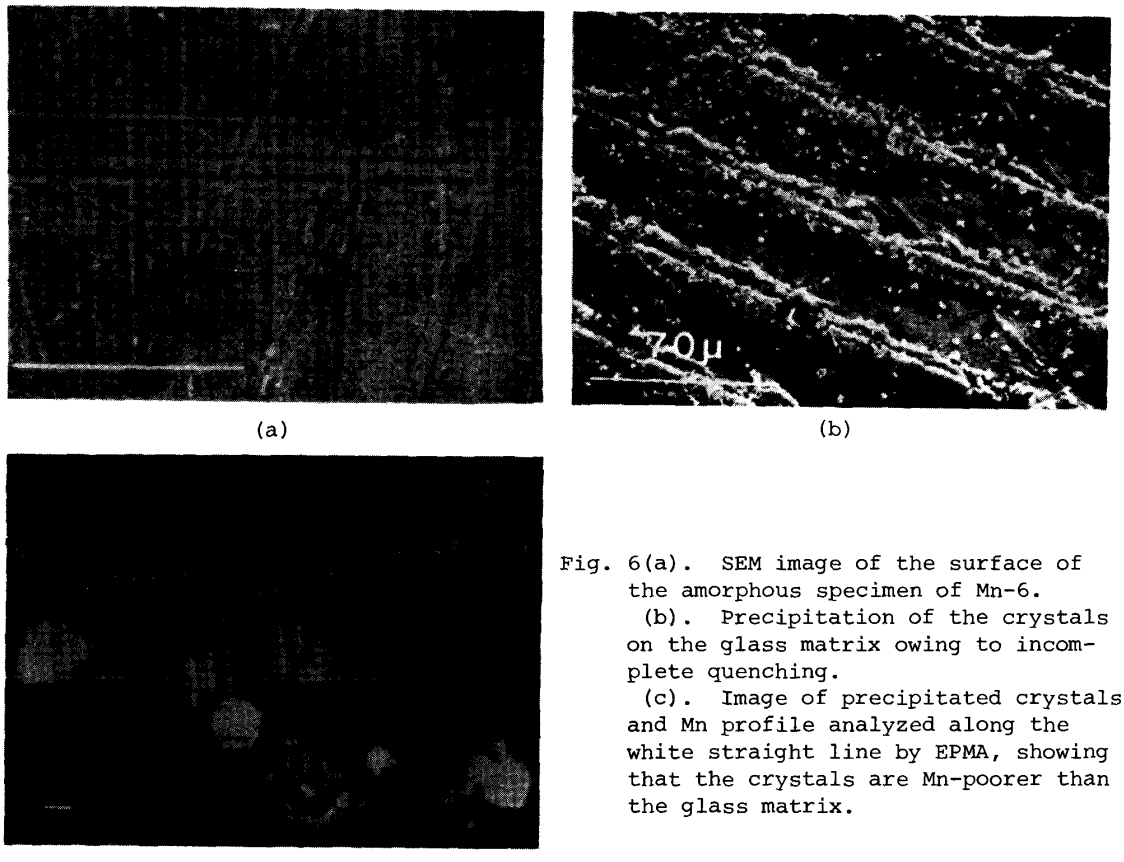
Hysteresis curves of the specimen Mn-6 at 4.2 K are shown in Fig. 4 for the various cooling fields. Notable shift of hysteresis curve in the positive direction is observed with increasing cooling field. For low cooling field, a large hysteresis is observed, indicating the presence of magnetically hard components. For higher cooling field, magnetization measurements show that the acquired remanence is not destroyed by applying measuring field of 7.49 kOe in the opposite direction of the remanence.

Similar ferromagnetic components are also found in the other less Mn-concentrated glasses. Fig. 5 shows the temperature variation of the magnetization measured in 4.0 kOe for the specimen field-cooled in 7.49 kOe. Although the ferromagnetic moment decreases with decreasing Mn-concentration in the glass, the magnetic ordering temperature remains almost constant.

## IV. SEM observation and EPMA analysis of Mn-series

The ferromagnetic Curie temperatures observed in Mn-series glasses are slightly higher than that of hausmanite ($Mn_3O_4$), $T_C$ = 42 K.[10-12] The ferromagnetic components observed in the glass could be attributed to the precipitated hausmanite crystals. However, ferromagnetic moments observed in the Mn-glass reach about 10 emu/g at 4.2 K. In order to explain this value, at least 30 wt% hausmanite must be present in the glass, since the ferromagnetic moment of hausmanite is about 30 emu/g at 4.2 K. This amount of precipitated $Mn_3O_4$ is rather unlikely from the consideration that almost no crystalline phases are detectable in the X-ray diffraction pattern of the glass.

In order to settle this point, observation of the surface of the




(a) (b)

(c)

Fig. 6(a). SEM image of the surface of the amorphous specimen of Mn-6.
(b). Precipitation of the crystals on the glass matrix owing to incomplete quenching.
(c). Image of precipitated crystals and Mn profile analyzed along the white straight line by EPMA, showing that the crystals are Mn-poorer than the glass matrix.

glass by means of scanning electron microscopy (SEM) and the analysis by electron probe microanalyzer (EPMA) were carried out. Fig. 6(a) shows a typical SEM image of the glass surface. No appreciable precipitates within the resolution limits of SEM (about 0.01 μm) are observed in the case of well-quenched glass. No concentration fluctuation on this scale is also detectable. On the other hand, the specimen which could not be completely quenched into the glass shows a lot of precipitated crystals as shown in Fig. 6(b). The chemical analysis by EPMA shows that the precipitates are richer in Ba and poorer in Mn than the matrix (Fig. 6(c)). Considering the fact that the ferromagnetic component increases with increasing Mn-concentration in the glass, we may conclude that the ferromagnetic component observed in the glass is not due to ferromagnetism of the crystalline $Mn_3O_4$.

However, there remains some possibility that microcrystalline $Mn_3O_4$ present below the resolution limit of SEM may explain the ferromagnetic components. This is rather a likely explanation since crystalline $Mn_3O_4$ is clearly observed during the course of crystallization experiments of the glass, as shown in Fig. 7.

The other possibility may be sought in the coexistence of different valence states of manganese ions in the Mn-series glasses. It is to be noted that the double exchange mechanism leads to the appearance of ferromagnetism in the (La, Sr) $MnO_3$ perovskite solid solution series in which $Mn^{3+}$ and $Mn^{4+}$ ions coexist.

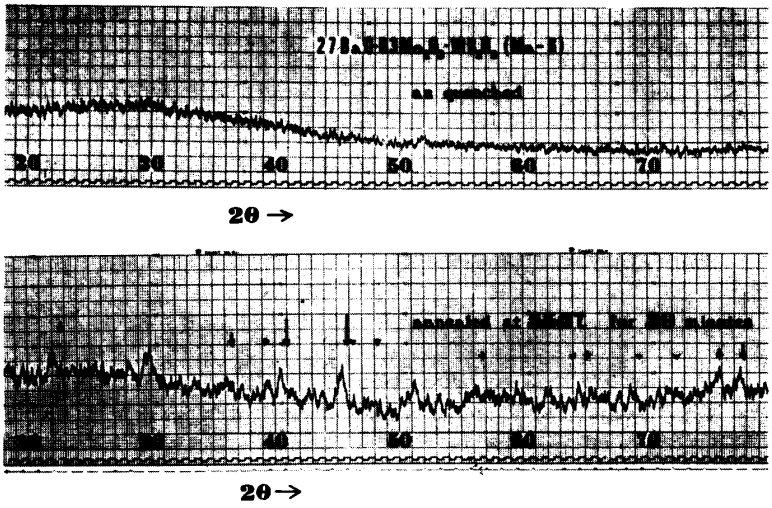



Fig. 7. X-ray diffraction pattern of as-quenched specimen, Mn-6 glass (top) and of annealed specimen at 550°C for 30 minutes (bottom). Fe $K_\alpha$ radiation is used. Arrows indicate expected diffraction angles from hausmanite crystal ($Mn_3O_4$).

V. Comparison of field-cooling experiments in Fe- and Mn-glasses.

Magnetic properties of glasses of Fe- and Mn-series show marked contrast; Fe-glasses are characterized by a typical example of spero-magnetism in which antiferromagnetic order in a short range is formed while Mn-glasses seem to be of the inhomogeneous magnetism. Both features are particularly well demonstrated in the field dependence of thermoremanent magnetization (TRM) as summarized in Fig. 8. TRM of Fe-series glass is very weak, only 0.15 emu/g, showing that about 0.1 % of magnetic moment of $Fe^{3+}$ ions is statistically aligned in the direction of cooling field, and this value compares favorably with what is expected from the perpendicular susceptibility of antiferromagnets, i. e. the ratio of the cooling field to the molecular field.

On the other hand, TRM of Mn-series glasses is very remarkable. The field dependence of TRM may be interpreted to consist of two parts: the major part is readily saturated in a relatively weak field of 100 Oe while the other part shows a less remarkable field dependence. This lends support to the suggestion that the glass is rather inhomogeneous with large concentration fluctuations. Most probably superparamagnetic clusters may exist around the magnetic ordering temperature. Hausmanite-like clusters may explain the ferromagnetic character of the glass at low temperatures.

The discrepancy between the TRM behavior of these two systems is also demonstrated in their relaxation effect. Fig. 9 shows the variation of magnetization with time with an applied field of 7.49 kOe in

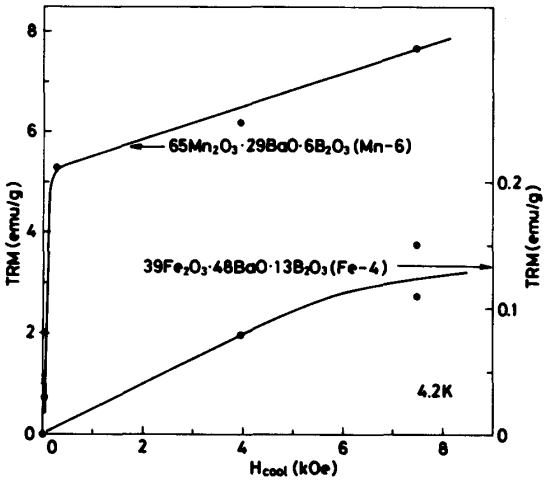



Fig. 8. Field dependence of TRM of amorphous specimens of Mn-6 and Fe-4, measured at 4.2 K.

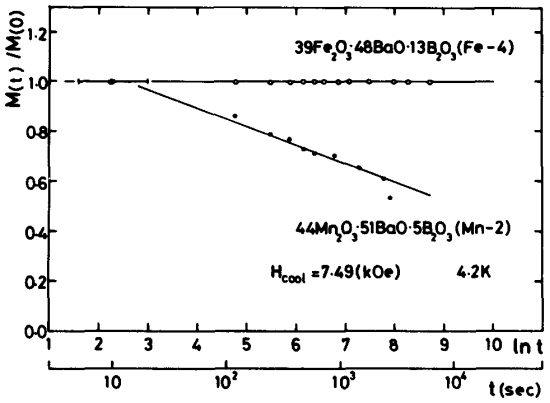



Fig. 9. Time variation of magnetization induced by field cooling in the amorphous specimens of Fe-4 and Mn-2, when the external field is applied at 4.2 K in the opposite direction to that of the cooling field.

the opposite direction to the direction of cooling field in which TRM was acquired. The magnetization of Mn-series glass decreases very rapidly with lapse of time while no appreciable change is detectable in the magnetization of Fe-series glass within the experimental time.

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