



**HAL**  
open science

# STRUCTURAL AND MAGNETIC PROPERTIES OF AMORPHOUS BaO-Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> SYSTEM

Y. Syono, A. Ito

► **To cite this version:**

Y. Syono, A. Ito. STRUCTURAL AND MAGNETIC PROPERTIES OF AMORPHOUS BaO-Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> SYSTEM. Journal de Physique Colloques, 1979, 40 (C2), pp.C2-115-C2-117. 10.1051/jphyscol:1979239 . jpa-00218637

**HAL Id: jpa-00218637**

**<https://hal.science/jpa-00218637>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

STRUCTURAL AND MAGNETIC PROPERTIES OF AMORPHOUS BaO-Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> SYSTEM

Y. Syono and A. Ito\*

The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan

\*Department of Physics, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan

Résumé.- Des verres homogènes du type BaO-Fe<sub>2</sub>O<sub>3</sub> (39-63 mol.% Fe<sub>2</sub>O<sub>3</sub>) avec B<sub>2</sub>O<sub>3</sub> en petite quantité ont été obtenus par trempe à partir de l'état liquide. L'étude Mössbauer montre que le verre comporte essentiellement des mailles tétraédriques de Fe<sup>3+</sup>O<sub>4</sub> et qu'il existe un ordre antiferromagnétique à courte distance à basse température.

Abstract.- Homogeneous glasses of the iron-rich BaO-Fe<sub>2</sub>O<sub>3</sub> system (39-63 mol.% Fe<sub>2</sub>O<sub>3</sub>) with a small amount of B<sub>2</sub>O<sub>3</sub> are prepared by splat cooling method. Mössbauer study reveals that the glass mainly consists of tetrahedral network of Fe<sup>3+</sup>O<sub>4</sub> and a short range antiferromagnetic order is formed at low temperatures.

Amorphous specimens of the iron-rich BaO-Fe<sub>2</sub>O<sub>3</sub> system with a small amount of B<sub>2</sub>O<sub>3</sub> were prepared by splat cooling method with the aid of laser melting technique /1/. Mössbauer spectrum was measured from room temperature to 4.2 K and analyzed using an electronic computer. Mössbauer parameters determined are summarized in table I. The glasses presently prepared are classified into two groups with the Fe<sub>2</sub>O<sub>3</sub>/BaO ratio greater and smaller than 1.

around Fe<sup>3+</sup> ions in the glass is supposed to be very similar to that in the crystalline BaO.Fe<sub>2</sub>O<sub>3</sub> in which Fe<sup>3+</sup> ions occupy only tetrahedral sites /2/. A relatively large quadrupole splitting, ΔE, is observed in the glass. The width of the spectrum is 0.47 mm/s, only twice as broad as that of the innermost peak of iron, 0.23 mm/s, corroborating rather uniform tetrahedral environment around Fe<sup>3+</sup> ions in the glass.

The temperature variation of Mössbauer spectra

Table I : Mössbauer parameters of amorphous BaO-Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system

Specimen	Composition, mol%			δ <sup>*</sup> , mm/s			ΔE, mm/s			H <sub>int</sub> , kOe		T <sub>N</sub> , K
	Fe <sub>2</sub> O <sub>3</sub>	BaO	B <sub>2</sub> O <sub>3</sub>	Fe <sup>3+</sup> (t)	Fe <sup>3+</sup> (o)	"Fe <sup>2+</sup> "	Fe <sup>3+</sup> (t)	Fe <sup>3+</sup> (o)	"Fe <sup>2+</sup> "	Fe <sup>3+</sup> (t)	Fe <sup>3+</sup> (o)	
Amorphous	Fe- 2	39	57	4	0.23	-	-	0.84	-	-		
	Fe- 4	39	48	13	0.24	-	-	0.97	-	-	450	-
	Fe- 9	54	37	9	0.35	0.37	0.51	0.92	0.41	1.56		
	Fe-10	54	39	7	0.32	0.38	0.53	0.93	0.42	1.62	460	500
	Fe-11	58	38	4	0.29	0.38	0.50	0.92	0.32	1.66		
	Fe-14	63	32	5	0.43	0.45	0.55	0.86	0.37	1.55	450	490
X <sup>tal</sup>	BaO.Fe <sub>2</sub> O <sub>3</sub>	50	50	-	0.2	-	-	0.25	-	-	472 <sup>†</sup>	-
	BaO.2Fe <sub>2</sub> O <sub>3</sub>	67	33	-	0.21	0.41	-	0.23	0.08	-	486 <sup>†</sup>	516 <sup>†</sup>

δ and ΔE are at room temperature. - \*Referred to iron metal. - H<sub>int</sub> is at 4.2 K. - † Values at room temperature.

The glass with Fe<sub>2</sub>O<sub>3</sub>/BaO < 1 is proved to have a rather simple structure. Figure 1 (upper curve) shows the Mössbauer spectrum of the specimen Fe-2 measured at room temperature. The spectrum is fitted by a single doublet with the Lorentzian profile by the least square method. The value of the isomer shift, δ = 0.23 mm/s, indicates that the glass is formed by tetrahedral network of Fe<sup>3+</sup>O<sub>4</sub>. The structure

of the specimen, Fe-4, is shown in figure 2. At 4.2 K a well resolved hyperfine sextet is observed. The internal field, H<sub>int</sub>, is estimated to be 450 kOe, as expected for Fe<sup>3+</sup> ions in tetrahedral environments. The spectrum is very nearly symmetric, revealing an apparent disappearance of quadrupole shift in the magnetically ordered state, in spite of the large quadrupole splitting observed in the room temperature

spectrum.

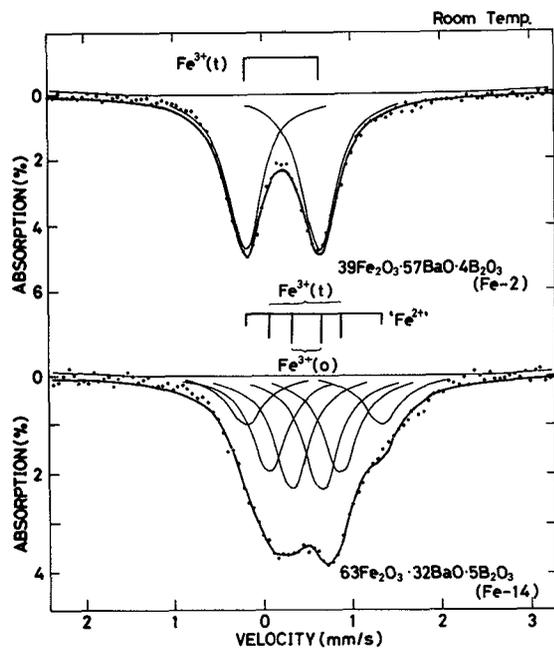


Fig. 1 : Demonstration of computer curve fitting for paramagnetic spectra of the glasses measured at room temperature.

Upper curve : Fe-2 ( $\text{Fe}_2\text{O}_3/\text{BaO} < 1$ ).

Lower curve : Fe-14 ( $\text{Fe}_2\text{O}_3/\text{BaO} > 1$ ).

The distribution of the internal field is supposed to be narrow, when the quadrupole broadening effect is taken into consideration /1/. The temperature dependence of the internal field approximately follows a Brillouin function with  $S = 5/2$ , yielding a magnetic ordering temperature of 70 K. This value is by an order of magnitude smaller than the Néel temperature of the corresponding crystalline phase,  $\text{BaO} \cdot \text{Fe}_2\text{O}_3$  /2/. This decrease is attributed to weakened superexchange interaction due to randomness of bond angles in the glass.

The iron-rich glass ( $\text{Fe}_2\text{O}_3/\text{BaO} > 1$ ) shows complex paramagnetic spectra at room temperature. An example of computer curve fitting is demonstrated in figure 1 (lower curve). In the analysis, the width of each line is fixed to be 0.47 mm/s, the same as that obtained for the spectrum of Fe-2. The spectrum is successfully explained by superposition of two doublets due to tetrahedral and octahedral  $\text{Fe}^{3+}$  ions plus an additional weak doublet which is tentatively assigned to be due to " $\text{Fe}^{2+}$ " ions. The glass structure of this group seems to correspond to the  $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$  crystal hydrothermally synthesized /3/, in which  $\text{Fe}^{3+}$  ions are equally distributed among the tetrahedral and octahedral site. The hyperfine spectrum at low temperatures is also interpreted to

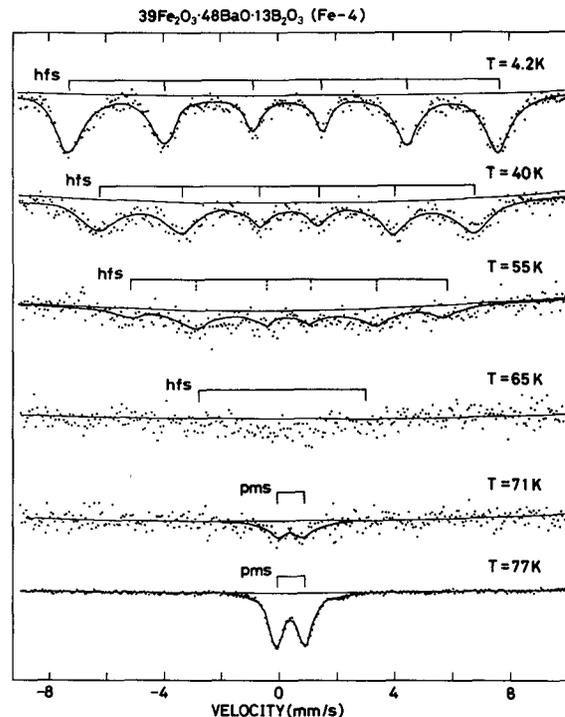


Fig. 2 : Temperature variation of Mössbauer spectra of the glass, Fe-4 (hfs : hyperfine spectrum - pms : paramagnetic spectrum).

consist of two sextets with the internal field of 450 and 500 kOe, corresponding to the tetrahedral and octahedral  $\text{Fe}^{3+}$  ions respectively. The magnetic ordering temperature determined from temperature variation of the internal field is only 140 K in the most iron-rich specimen /1/.

Preliminary magnetic measurements reveal that the magnetic susceptibility shows a broad maximum around the magnetic ordering temperature, obeying Curie-Weiss law in higher temperatures. No evidence for superparamagnetic behavior is found in harmony with Mössbauer measurements. Summarizing, the magnetic ordering achieved in the present amorphous system is of the short range antiferromagnetism, similar to that found in  $\text{FePO}_4$  by neutron diffraction /4/.

**Acknowledgments.**— The authors are indebted to Mr. O. Horie and Dr. K. Okamura for their collaboration in the early stage of this work. Their thanks are due to Professors Y. Nakagawa and S. Yajima for warm encouragements. They are grateful to Professor Y. Matsui who kindly wrote and offered the computer program. The computer analysis was done at the Computer Center, Tohoku University.

References

- /1/ Horie, O., Syono, Y., Nakagawa, Y., Ito, A., Okamura, K. and Yajima, S., Solid State Commun. 25 (1978) 423.
- /2/ Do-Dinh, C., Bertaut, E.F. and Chappert, J., J. Physique 30 (1969) 566.
- /3/ Okamoto, S., Sekizawa, H. and Okamoto, S.I., J. Phys. Chem. Solids 36 (1975) 591.
- /4/ Wedgwood, F.A. and Wright, A.C., J. Non-Cryst. Solids 21 (1976) 95.