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HAL Id: jpa-00218637
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Submitted on 1 Jan 1979

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STRUCTURAL AND MAGNETIC PROPERTIES OF AMORPHOUS BaO-Fe₂O₃-B₂O₃ SYSTEM

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Résumé.— Des verres homogènes du type BaO-Fe₂O₃ (39-63 mol.% Fe₂O₃) avec B₂O₃ 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 Fe³⁺O₄, et qu'il existe un ordre antiferromagnétique à courte distance à basse température.

Abstract.— Homogeneous glasses of the iron-rich BaO-Fe₂O₃ system (39-63 mol.% Fe₂O₃) with a small amount of B₂O₃ are prepared by sputter cooling method. Mössbauer study reveals that the glass mainly consists of tetrahedral network of Fe³⁺O₄ and a short range antiferromagnetic order is formed at low temperatures.

Amorphous specimens of the iron-rich BaO-Fe₂O₃ system with a small amount of B₂O₃ were prepared by sputter cooling method with the aid of laser melting technique. 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 Fe₂O₃/BaO ratio greater and smaller than 1.

Table I : Mössbauer parameters of amorphous BaO-Fe₂O₃-B₂O₃ system

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Composition, mol.%</th>
<th>δ, mm/s</th>
<th>ΔE, mm/s</th>
<th>H_int, kOe</th>
<th>T_N, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-2</td>
<td>39 57 4</td>
<td>0.23</td>
<td>0.84</td>
<td>-</td>
<td>450</td>
</tr>
<tr>
<td>Fe-4</td>
<td>39 48 13</td>
<td>0.24</td>
<td>0.97</td>
<td>-</td>
<td>450</td>
</tr>
<tr>
<td>Fe-9</td>
<td>54 37 9</td>
<td>0.35</td>
<td>0.92</td>
<td>0.41</td>
<td>150</td>
</tr>
<tr>
<td>Fe-10</td>
<td>54 39 7</td>
<td>0.32</td>
<td>0.93</td>
<td>0.42</td>
<td>560</td>
</tr>
<tr>
<td>Fe-11</td>
<td>58 38 4</td>
<td>0.29</td>
<td>0.92</td>
<td>0.32</td>
<td>160</td>
</tr>
<tr>
<td>Fe-14</td>
<td>63 32 5</td>
<td>0.43</td>
<td>0.86</td>
<td>0.37</td>
<td>450</td>
</tr>
<tr>
<td>BaO.5Fe₂O₃</td>
<td>50 50</td>
<td>0.2</td>
<td>0.25</td>
<td>472⁺</td>
<td>880/2/</td>
</tr>
<tr>
<td>BaO.2Fe₂O₃</td>
<td>67 33</td>
<td>0.21</td>
<td>0.23</td>
<td>486⁺</td>
<td>945/3/</td>
</tr>
</tbody>
</table>

δ and ΔE are at room temperature. *Referred to iron metal. H_int is at 4.2 K. *Values at room temperature.

The glass with Fe₂O₃/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 Fe³⁺O₄. The structure around Fe³⁺ ions in the glass is supposed to be very similar to that in the crystalline BaO.₆Fe₂O₃ in which Fe³⁺ 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 Fe³⁺ ions in the glass.

The temperature variation of Mössbauer spectra 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_int, is estimated to be 450 kOe, as expected for Fe³⁺ 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.
The distribution of the internal field is supposed to be narrow, when the quadrupole broadening effect is taken into consideration. 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 Neel temperature of the corresponding crystalline phase, $\text{Ba}_0.2\text{Fe}_3\text{O}_5$.

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 $\text{FePO}_b$ by neutron diffraction.

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


