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Mössbauer spectroscopy has been used in conjunction with other techniques for studying the crystallization of Basalt Glass (50wt % SiO₂, 14wt % Al₂O₃, 13wt % Fe₂O₃, 10wt % CaO) as a function of heat treatment. First this glass was melted twice at 1500°C for 16 hours and subsequently annealed at 525°C. As such it will be used as a reference ("blank glass"). The crystallization studies were then carried out on samples heat-treated at 600, 650, 700, 800, 900°C for 8 hours respectively.

X-ray diffraction and transmission electron microscopic measurements did not allow to detect the presence of any crystalline phase in the blank glass and in the sample heat-treated at 600°C, while crystallites of magnetite and of some other minor phases such as pyroxene were observed in the other samples. The size of the magnetite clusters was estimated to range between 40 Å and 70 Å. The lower the heat-treatment temperature, the smaller are the magnetite particles.

Mössbauer spectra were recorded at various temperatures between helium and room temperatures on the same samples. Magnetic fields up to 50 kOe were applied at 4.2 K. For each Mössbauer spectrum, the contributions of two iron species have been separated.

- Results and discussion - Some typical spectra, carried out at room temperature are shown in Fig. 1. Each spectrum, except for the 800 and 900°C glass, consists of two superimposed doublets. The less intense one (= 20%), Fe²⁺, has Mössbauer parameters rather similar to that of orthopyroxene [1]. The other one (= 80%) has been assigned to magnetite in a superparamagnetic state [2]. Such an assignment was confirmed by experiments in the presence of an external field. The 800 and 900°C glass consist of the same two doublet spectra as before, superimposed to a diffuse six line magnetic spectrum coming from magnetite below the blocking temperature.

Mössbauer spectra performed at 4 K are represented in Fig. 2. We find the same three contributions: magnetite on each side of the blocking temperature and Fe²⁺ ions (20%).

The superparamagnetic behaviour is typical of small magnetic particles. In several studies [3-4-5] of such grains, it has been reported that the magnetic hyperfine splitting is systematically

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![Fig. 1. Room temperature Mössbauer spectra of blank glass and samples heat-treated at 700 and 900°C for 8 hours. Solid lines are least squares fits.](http://dx.doi.org/10.1051/jphyscol:1980197)
smaller than that found in larger ones. Our experiments on the 800 and 900 glasses at room temperature confirm this observation; for example the largest hyperfine fields (Fe$^{3+}$ tetrahedral sites) were estimated to be 410 and 450 kOe for these two glasses respectively while in the bulk magnetite Mc Nab et al [6] found 486 kOe. According to the model of Morup and Topsoe [4], the hyperfine field for a particle of volume $V$, at a temperature $T$ is written:

$$H_{hf}(V, T) = H_{hf}^{(0)}(T) \left[1 - kT/KV\right]$$

for $kT/KV << 1$. Here $kT$ is the thermal energy and $K$ is related to the anisotropy constant. It should be noted that if $T = 0K$, $H_{hf}$ is independent of the particle size, in agreement with our measurements at 4 K ($H_{hf} = 510$ kOe for all samples except for the blank one). Using the average diameters $D$ of the particles obtained by X-ray diffraction ($D_{800 \text{ glass}} = 64 \AA$, $D_{900 \text{ glass}} = 70 \AA$), we can calculate $K = 10^8 \text{erg cm}^{-3}$. From the magnetic part of the blank glass spectrum at 4 K, the hyperfine field is estimated to be roughly 430 kOe. This value gives an average size of the order of 12 Å for the magnetite particles of the blank glass, below the blocking temperature.

The blocking temperature depends on the particle size. The smaller the particles, the lower the blocking temperature. At 4 K, the percentages of magnetite particles which are above the blocking temperature are approximately 70 %, 0 % and 15 % for the blank, 700 and 900 glasses respectively. We can explain this evolution by taking into account the mobility of the ions in the glass during the thermal treatment. When the temperature of the sample is 600-650° C, the iron ions can move and form microcrystals of magnetite whose size is increasing with temperature. At 700° C, we can assume that all the iron ions belong to small crystals (= 55 Å). Other ions such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$ start moving only when $T = 750°$ C. Then, they could act as a solvent for the surface iron ions. As a consequence, a few iron cations may be isolated again and behave as superparamagnetic particles.

The main feature of the Mössbauer spectra carried out at 4 K, with an external magnetic field of 50 kOe applied parallel to the $\gamma$-direction is the appearance of the lines 2 and 5 of the 650 and 700 glass magnetic spectra. These lines are normally extinguished in a longitudinal configuration when the $\gamma$-ray direction is parallel to the iron magnetic moment. In the 900 glass, we can hardly detect them in the background. The appearance of these lines has been explained by Haneda and Morrish [5] by assuming a non-collinear spin configuration of the surface cations in small particles. The smaller the particles, the greater the proportion of surface cations. Since the average microcrystal size is increasing from the 650 to the 900 glass, the proportion of surface cations is so weak in the 900 glass that they are not detected in the Mössbauer spectrum.

![Fig. 2. Mössbauer spectra of basalt glasses performed at 4 K. Solid lines are least squares fits.](image)

References