MÖSSBAUER SPECTROSCOPY OF STRONTIUM FERRITES RELATED TO PERMANENT MAGNET MATERIALS
R. Vogel, B. Evans

To cite this version:
R. Vogel, B. Evans. MÖSSBAUER SPECTROSCOPY OF STRONTIUM FERRITES RELATED TO PERMANENT MAGNET MATERIALS. Journal de Physique Colloques, 1979, 40 (C2), pp.C2-277-C2-279. <10.1051/jphyscol:1979298>. <jpa-00218689>

HAL Id: jpa-00218689
https://hal.archives-ouvertes.fr/jpa-00218689
Submitted on 1 Jan 1979

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.
MÖSSBAUER SPECTROSCOPY OF STRONTIUM FERRITES RELATED TO PERMANENT MAGNET MATERIALS

R. Vogel and B.J. Evans

Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109 U.S.A.

Abstract.- In the synthesis of SrFe\textsubscript{12}O\textsubscript{19} from SrCO\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3}, SrFe\textsubscript{0.5} is formed as the only intermediate phase, which reacts subsequently with Fe\textsubscript{2}O\textsubscript{3} to form SrFe\textsubscript{12}O\textsubscript{19}. Nonstoichiometric hexaferrites, i.e. with SrO/Fe\textsubscript{2}O\textsubscript{3} ratios from 1/5.5 to 1/5.0, contain Sr\textsubscript{0.5}Fe\textsubscript{0.5} as a second phase. The degree of resolution of the spectra from the five magnetic sublattices of SrFe\textsubscript{12}O\textsubscript{19} depends upon the concentration of Sr\textsubscript{0.5}Fe\textsubscript{0.5}. The superior magnetic properties of nonstoichiometric Sr-hexaferrites appear to be related to the coexistence of the two magnetically ordered phases SrFe\textsubscript{12}O\textsubscript{19} and Sr\textsubscript{0.5}Fe\textsubscript{0.5}.

1. Introduction.- Current interests in the synthesis and magnetic properties of SrFe\textsubscript{12}O\textsubscript{19} are directed toward (1) the reaction mechanism, which is known to be different from that for BaFe\textsubscript{12}O\textsubscript{19}, but is otherwise controversial and not well understood /1/, especially for the technologically important nonstoichiometric compositions; and (2) the physical and chemical basis for the superior magnetic properties of the nonstoichiometric materials compared to those of stoichiometric SrFe\textsubscript{12}O\textsubscript{19} /2/. The optimal compositions for nonstoichiometric hexaferrites correspond to Sr\textsubscript{0.5}Fe\textsubscript{0.5} ratios in the reactants between 1/5 and 1/5.5.

We report here on our investigation of two aspects of the above concerns: First, we have sought to determine the existence of an intermediate phase, its crystal chemical characteristics and role in the formation of SrFe\textsubscript{12}O\textsubscript{19}; and secondly, we have attempted to establish the nature of the nonstoichiometry in the hexaferrites with excess strontium, i.e. whether single-phase or multi-phase and if multi-phase, the magnetic character of each phase.

2. Experimental.- Sample preparation and the acquisition of the Mössbauer spectra were as described previously /3/, except for the use of ultra-high purity (99.99 % pure) SrCO\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3}.

3. Results and discussion.- SrFe\textsubscript{12}O\textsubscript{19} does not form directly from SrO and Fe\textsubscript{2}O\textsubscript{3}; SrFe\textsubscript{2}O\textsubscript{5} and Sr\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} had been reported /4/ as the intermediate phases.

first appearing at 925 K and reacting at 1025 K and above with Fe\textsubscript{2}O\textsubscript{3} to give SrFe\textsubscript{12}O\textsubscript{19}. This reaction scheme has been questioned recently /1/ and the following reaction sequence has been proposed for the formation of SrFe\textsubscript{12}O\textsubscript{19} from SrCO\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3}.

\[
\text{SrCO}_3 + 6\text{Fe}_2\text{O}_3 + \left(\frac{1 - 2x}{4}\right)\text{O}_2 = \text{SrFe}_{12-x}\text{O}_{19} + 5.5\text{Fe}_2\text{O}_3 + \text{CO}_2
\]

(1)

\[
\text{SrFe}_{12-x}\text{O}_{19} + 5.5\text{Fe}_2\text{O}_3 = \text{SrFe}_{12}\text{O}_{19} + \left(\frac{1 - 2x}{4}\right)\text{O}_2
\]

(2)

This reaction sequence is clearly confirmed by the \textsuperscript{57}Fe Mössbauer spectra in figure 1. Below 990 K, the reaction mixture consists of hematite, SrO and a small quantity of SrFe\textsubscript{0.5}O\textsubscript{0.5}, as indicated by the weak absorption near 0.2 mm/s. At 1073 K, the concentration of SrFe\textsubscript{0.5}O\textsubscript{0.5} has increased substantially and SrFe\textsubscript{12}O\textsubscript{19} is also present. At 1178 K, SrFe\textsubscript{0.5}O\textsubscript{0.5} is no longer present and the resulting material is single phase SrFe\textsubscript{12}O\textsubscript{19}. No evidence exists for the presence of SrFe\textsubscript{2}O\textsubscript{4} or Sr\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5}.

For reaction mixtures with excess strontium, the reaction mechanism is apparently more complicated than that given by equations (1) and (2). First, SrFe\textsubscript{0.5}O\textsubscript{0.5} is not present among the reaction products as might be expected on the basis of equations (1) and (2) /1/. Before this investigation, it was not certain whether these two latter formulae represented two distinct phases; however, during the process of annealing SrFe\textsubscript{2}O\textsubscript{5} at 1473 K, it was observed that the Mössbauer spectrum approached that of Sr\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{3} for long annealing times.
We, therefore, conclude that the correct composition for the phase in question is $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ for which the $^{57}\text{Fe}$ Mössbauer spectrum is shown in figure 2. The spectrum of this material is quite different from that of $\text{Sr}_6\text{Fe}_{12}\text{O}_{19}$ and it is therefore surprising that $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ has not been observed in the Mössbauer spectra of non-stoichiometric Sr-hexaferrites. To determine the detectability of $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ in a mixture of $\text{Sr}_6\text{Fe}_{12}\text{O}_{19}$, a highly non-stoichiometric composition, i.e. $\text{SrO}/\text{Fe}_2\text{O}_3 = 1/3$, was fired to give a product in which the intensity of the X-ray diffraction lines of $\text{Sr}_6\text{Fe}_{12}\text{O}_{19}$ was comparable to that of $\text{Sr}_6\text{Fe}_{12}\text{O}_{19}$ and a mechanical mixture of 28 mole percent $\text{Sr}_6\text{Fe}_{12}\text{O}_{19}$ and 72 mole percent $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ was also prepared. As seen from figure 2, the spectra of these two phase mixtures can be accounted for within the usual goodness-of-fit criterion on the assumption that $\text{Sr}_6\text{Fe}_{12}\text{O}_{19}$, alone, is present. $^{57}\text{Fe}$ Mössbauer spectra of the sample with the 1/3 $\text{SrO}/\text{Fe}_2\text{O}_3$ ratio taken above the Néel temperature of $\text{Sr}_6\text{Fe}_{12}\text{O}_{19}$ clearly demonstrates the presence of this phase. Consequently, it is entirely possible that $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ is present in nonstoichiometric Sr-hexaferrites but goes undetected in the Mössbauer spectra. Indeed a reconsideration of the spectra presented in an earlier study /3/ shows that the resolution of the spectra between 6.7 mm.s$^{-1}$ and 9.3 mm.s$^{-1}$ depends sensitively on the $\text{SrO}/\text{Fe}_2\text{O}_3$ stoichiometry. For highly stoichiometric materials all five magnetic sublattices can be observed in the 298 K spectrum in the absence of an applied magnetic field. As the $\text{SrO}/\text{Fe}_2\text{O}_3$ ratio varies from 1/6 to 1/3, the five, well-resolved lines between 6.7 mm.s$^{-1}$ and 9.3 mm.s$^{-1}$ degenerate into three, highly-broadened absorption lines. Thus, even though the presence of $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ in nonstoichiometric hexaferrites is not obvious, there are some features which can be definitively associated with the existence of this phase and which can, in principle, be put on a quantitative basis.

It is noteworthy that strontium hexaferrites having unusually large values for the remanent magnetization and coercive force /3/ exhibit poorly-resolved
lines in the 6.7 mm.s\(^{-1}\) to 9.3 mm.s\(^{-1}\) region of their Mössbauer spectra. This result suggests that Sr\(_4\)Fe\(_6\)O\(_{13}\) may have a significant beneficial effect on the bulk magnetic properties of ceramic compacts of nonstoichiometric Sr-hexaferrites. Whether this beneficial influence is effected through texture control or a direct superposition of the magnetic properties of the two phases must await further experimentation.

In summary, the present investigation has shown the following: (1) SrFe\(_{0,3-x}\) is an intermediate phase in the formation of SrFe\(_{1,3}O_{19}\) from SrCO\(_3\) and Fe\(_2\)O\(_3\); (2) high purity, stoichiometric SrFe\(_{1,3}O_{19}\) exhibits a 298 K Mössbauer spectrum in which all five magnetic sublattices are obvious; (3) nonstoichiometric Sr-hexaferrites contain Sr\(_3\)Fe\(_6\)O\(_{13}\); and (4) Sr\(_3\)Fe\(_6\)O\(_{13}\) among the final products of nonstoichiometric materials has a beneficial influence on the bulk magnetic properties compared to materials resulting from stoichiometric starting compositions.

Partial support of this investigation by the Alexander von Humboldt Foundation (West Germany) and the warm hospitality and provision of facilities by S.S. Hafner and his co-workers at the University of Marburg are gratefully acknowledged.

References