

Hexagonal Ferrimagnetic Compound Containing Fluorine†

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A partial substitution of the oxygen ions by fluorine in $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ is reported. The new compound with a formula near to $\text{BaF}_2 \cdot 2\text{FeO} \cdot 5\text{Fe}_2\text{O}_3$ has at room temperature a magnetization saturation of 72 cgs units/gram compared to 67 cgs units/gram for $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$. The specific gravity, Curie temperature, and unit cell dimensions are practically the same for both compounds.

MANY cation substitutions have been carried out in various ferrimagnetic oxides. Oxygen substitutions, on the other hand, were reported only in spinels.¹ A partial replacement of oxygen by fluorine² in several compounds was tried in our laboratory. The fluorine ion was chosen because its ionic size is similar to that of the oxygen. The compound analogous to $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ shall be described here.

Samples with differing ratios of BaF_2 to Fe_2O_3 were prepared in the usual ceramic way. The final firing was carried out at a temperature of 1250°C for 20 hours in an atmosphere of thoroughly dry oxygen. As BaF_2 is volatile at this high temperature, single phase samples are difficult to obtain. After washing the powdered samples in HCl, a pure magnetoplumbite phase was obtained as shown by x-ray powder diagrams. It should be noted that the pure sample is much less soluble in HCl than $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$. The specific gravity of the purified material, measured by the powder picnometric method, is 5.25. The same value was obtained for $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$. Weissenberg diffraction patterns of single crystals³ of both compounds show intensity differences in some reflections. These differences can be explained

by changes in the anions but not in the number of cations.⁴ Chemical analysis of the purified compound suggests a formula near to $\text{BaF}_2 \cdot 2\text{FeO} \cdot 5\text{Fe}_2\text{O}_3$. This formula is in agreement with specific-gravity and x-ray data. This means that two fluorine ions replaced oxygen ones in $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ and two trivalent iron ions were reduced to divalent without changing the crystallographic structure.

Saturation magnetization measured by the ponderometer technique⁵ on oriented samples of the purified fluorine compound at room temperature is 72 cgs units/g. Nonpurified samples had lower saturation magnetization. The room temperature value obtained by us for oriented $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ both for various commercial samples and for samples synthesized in our laboratory is 67 cgs units/g, in agreement with Henry.⁶ The higher magnetization of the fluorine compound suggests, accepting the magnetic structure of $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ given by Went *et al.*,⁷ that the divalent iron ions are in the $4f_2$ sites.⁸ The fluorine ions, according to this picture, are near the barium ions.

Work is now being done on Pb and Sr homologs of this compound and in the ternary system $\text{BaF}_2\text{--CoO--Fe}_2\text{O}_3$.

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¹ F. K. Lotgering, thesis, Utrecht, 1956 (unpublished).

² Magnetic fluorides which do not contain any oxygen ions were reported by E. Gruner and W. Klemm, *Naturwissenschaften* **25**, 59 (1937), and by K. Knox and S. Geller, *Phys. Rev.* **110**, 771 (1958).

³ Small single crystals were grown in cavities bored in a pressed prefired sample after a slow cooling from 1300°C.

⁴ The authors wish to thank Dr. S. Hirschfeld for this suggestion.

⁵ G. W. Rathenau and J. L. Snoek, *Philips Research Repts.* **1**, 239 (1948).

⁶ W. E. Henry, *Phys. Rev.* **112**, 326 (1958).

⁷ Went, Rathenau, Gorter, and van Oosterhaut, *Philips Tech. Rev.* **13**, 194 (1952).

⁸ V. Adskjöld, *Ark. Kemi Min. Geol.* **12A**, 1 (1938).