Fluoride Ion Compensated Substitutions of Bivalent Cations

in BaFe₁₂O₁₉ and Other Hexagonal Oxides

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Samples of hexagonal, magnetoplumbite-type oxides were prepared, with bivalent cations and fluoride substituted for tervalent cations and oxygen, having the general formula $BaM_x^{II}M_{12-x}^{III}O_{19-x}F_x$, where $M^{III}=Al^{3+}$, Ga^{3+} , and Fe^{3+} , $and M^{II}=Ni^{2+}$, Co^{2+} , Cu^{2+} and Zn^{2+} . Optical spectra show that the M^{2+} ions preferentially occupy tetrahedral sites in the Al samples, and octahedral (Ni2+) or tetrahedral (Co2+) sites in the Ga samples.

The powdered ferrites of the above series show an apparent increase in magnetization with increasing $(Ni^{2+}+F^{-})$ concentration.

Single crystals of the ferrites were grown from a NaFeO₂ flux, yielding the magnetoplumbite phase for $(Cu^{2+}+F^{-})$ -substituted ferrites. For all $(Ni^{2+}+F^{-})$ and high $(Co^{2+}+F^{-})$ substituted phases, the structure is that of the known W phase. Magnetization data in the easy direction show saturation moments in agreement with the assumption that charge-compensated Ni²⁺ is in tetrahedral sites with moments antiparallel to the net magnetization, while uncompensated Ni2+ is in octahedral positions with parallel moments.

This paper describes an attempt to study the site preferences of bivalent transition metal ions in the magnetoplumbite structure. This structure has five crystallographically nonequivalent positions for the tervalent ions. There are two cations in tetrahedrally coordinated positions $(4f \text{ in } C_6/\text{mmm})$, nine octahedrally coordinated (2a, 12k, 4f) and one surrounded by a trigonal bipyramid of anions (2b), per formula unit, A^{II}B^{III}O₁₉.

The unsubstituted magnetoplumbites studied were BaA1₁₂O₁₉, BaFe₁₂O₁₉ and BaGa₁₂O₁₉. The site preferences of bivalent ions in the A1³⁺ and Ga³⁺ systems were determined by the measurement of diffuse reflectance spectra, using simple crystal field ideas and analogy with known systems for the interpretation of the spectra. In the case of $BaFe_{12}O_{19}$, the site preference was studied by the measurement of the magnetic properties of the substituted ferrites.

When a bivalent ion is substituted for a tervalent ion, another substitution must be effected to maintain electrical neutrality. This was done by the substitution of F⁻ for O²⁻. This type of charge compensation was first reported by Frei, Schieber and Shtrikman1).

In the system BaA1₁₂O₁₉, materials of the general formula $BaM_x^{II}A1_{12-x}O_{19-x}F_x$, where $M_{II} = Ni^{2+}$, Co^{2+} and $x = 0.1 \rightarrow 2.5$, were prepared. These materials were prepared by firing BaF₂, BaCO₃, A1₂O₃, M^{II}O in a dried N_2 atmosphere. The reflection spectra were measured, using pellets pressed from the powder, by means of Beckman and Cary spectrophotometers.

For all materials where $x=0.1\rightarrow 2.0$ the bivalent ion (M^{II}) showed a strong tetrahedral site preference. Samples having the composition $BaZn_2M_{0.5}^{II}A1_{9.5}O_{16.5}F_{2.5}$ were prepared. Where M^{II}=Ni²⁺, the spectra show that the Ni²⁺ was displaced almost entirely by Zn²⁺ from the tetrahedral sites to the octahedral sites. Where MII=Co2+ it was found that Co²⁺ had a stronger tetrahedral



Fig. 1. Diffuse Reflectance. I. BaNi1.5Al10.5O17.5-F1.5 II. BaZn2Ni0.5Al9.5O16.5F2.5 III. BaCo2-Al10O17F2 IV. BaZn2Co0.5Al9.5O16.5F2.5

site preference than Zn2+. Fig. 1, curve 2, shows the appearance of a strong absorption band at 27000 cm⁻¹ which is indicative of octahedral Ni²⁺, with a corresponding decrease in the intensity of bands indicating Ni²⁺ in tetrahedral sites (curve 1). As the intensity of the absorption of tetrahedral nickel is much larger than that of octahedral nickel, curve 2 indicates that only a small amount of Ni²⁺ has remained in the tetrahedral sites. Curve 3 shows the absorption spectrum of the material BaCo₂A1₁₀O₁₇F₂ and indicates the presence of tetrahedral cobalt exclusively. The absorption spectrum of BaZn₂Co_{0.5}- $A1_{9.5}O_{16.5}F_{2.5}$ (curve 4) is identical in form to the spectrum shown in curve 3, indicating a stronger tetrahedral site preference on the part of Co²⁺ than Zn²⁺.

The next system studied involved the replacement (fluoride-compensated) of Ni²⁺ and Co²⁺ for Ga³⁺ in BaGa₁₂O₁₉. Samples of composition BaGa_{11.5} $M_{0.5}^{II}O_{18.5}F_{0.5}$ were prepared by adding the starting materials (Ga₂O₃ instead of A1₂O₈) to a flux composed of equimolar quantities of Na₂CO₃ and Ga₂O₃, heating to 1350°C, and cooling at the rate of 20°C/hr. On leaching the product with acid, hexagonal platelets, up to 1 mm across, were obtained. These crystals were green when nickel was present and blue in the case of

cobalt. X-ray diffractometer traces of these materials showed only the magnetoplumbite phase

The spectra of powdered samples of Ba-Ni_{0.5}Ga_{11.5}O_{18.5}F_{0.5} (Fig. 2, curve 1) showed approximately equal reflectance at the main peaks for octahedral and tetrahedral Ni²⁺. Because of the greater intrinsic intensity of the absorption in the tetrahedral peak, it was concluded that there is more nickel in octahedral than in tetrahedral sites. In the cobalt-substituted gallate, the spectrum is nearly identical to that of Co²⁺ in the aluminate. This indicates a stronger tetrahedral site preference on the part of Co²⁺ than on the part of Ga³⁺. This is almost the same behavior shown by these ions in the zinc substituted aluminates. The stronger tetrahedral site preference of Ga³⁺ over A1³⁺ and Co²⁺ over Ni²⁺ is consistent with their behavior in spinels; the behavior of Co²⁺ relative to Zn²⁺ is not so.

The site preferences of the bivalent ions in the ferrites can be found, although not unequivocally, by the measurement of the magnetization. If the bivalent ion (any bivalent ion except Mn^{2+}) occupies the tetrahedral (4f) sites of the two (4f) octahedral sites, there would be an overall increase in the magnetic moment. Occupation of any



Fig. 2. Diffuse Reflectance I. BaGa11.5Ni0.5O18.5F0.5 II. BaGa11.5C00.5O18.5F0.5

of the remaining sites (7 octahedral, 1 trigonal bipyramid) would cause an overall decrease in the magnetic moment. If Ni²⁺ shows the same site preference that it shows in the spinel ferrites there should occur a decrease in the magnetic moment.

Materials having the composition BaNi_x- $Fe_{12-x}O_{19-x}F_x$ were prepared by firing mixtures of BaF₂, BaCO₃, NiO, Fe₂O₃ in a dry O₂ atmosphere. The mixtures fired correspond to materials having value of x=0.5, 1.0, 2.0. X-ray diffraction indicated only the presence of the magnetoplumbite phase. The unit cell parameters of these samples were the same as those of BaFe₁₂O₁₉, except for very small increases in the "c" axis with increasing values of x. Chemical analysis of these samples indicated that the composition of these materials was essentially unchanged on firing. For example, in the Ni_{0.5} sample, the nickel analysis gave 2.77% Ni, compared to 2.60% added, and the fluorine analysis gave 0.89% compared to 0.85%.

Since it was not possible to saturate the powders (magnetically) with the field strengths which were available, measurements of magnetization were made (field strength ~ 6000 oersteds) and compared with values which were obtained for BaFe₁₂O₁₉ powder²). Fig. 3 (curves 1, 2, 3 and 4) shows the results of these measurements between room temperature and the Curie point. All the samples showed an increase in magnetization over BaFe₁₂O₁₉ in the order x=.5<1.0<2.0 (example—at 160°C $\sigma_{\text{BaFe}_{12}O_{19}}=31$ $\sigma_{(x=1.0)}=35$). Fig. 3 also shows that the Curie temperature decreases with increasing x.

In these powders it is impossible to distinguish how much of the apparent increase in magnetization is due to a tetrahedral site preference on the part of Ni²⁺ and how much is due to a possible decrease in the anisotropy. For this reason attempts were made to grow crystals of these materials. Na₂CO₃ and BaF₂ were both used as fluxes with poor results. A flux composed of an equimolar mixture of Na₂CO₃ and Fe₂O₃ was used³⁾. The starting materials were fired with this flux at 1350-1400°C and cooled at 20°C/hr. The flux was leached out with hot 4 N HC1. Large hexagonally shaped crystals were produced in this manner. Crystals containing Ni²⁺, Co²⁺, Cu²⁺ were grown in this manner. X-ray analysis gave the following results: Ni²⁺ crystals were not magnetoplumbite but were of the Fe₂W type⁴⁾ (BaM₂¹¹Fe₁₆O₂₇ $a_0 = 5.8$, $c_0=32.8$). This phase was formed for all concentrations of Ni²⁺.

 Co^{2+} — for concentrations of $Co \le 0.5$ the magnetoplumbite phase was found, for Co > 0.5 the W-phase. This concentration also seems to correspond with a change in the



Fig. 3. I. $BaFe_{12}O_{19}$ II. $BaFe_{11.5}Ni_{0.5}^{-5}O_{18.5}F_{0.5}$ III. $BaFe_{11}Ni_1O_{18}F$ IV. $BaFe_{10}Ni_2O_{17}F_2$ σ gauss cm³/gm vs T.



Fig. 4. σ_{||} gauss cm³/gm vs T°C. I. BaFe₂^{II}Fe₁₆O₂₇ II. BaFe_{1.98}^{II}Ni_{0.012}Fe_{15.417}Ni_{0.563}O_{26.417}F_{0.583}
III. BaFe_{1.99}^{II}Ni_{0.01}Fe_{14.67}Ni_{1.33}O_{25.67}F_{1.33} IV. BaFe_{1.14}^{II}Ni_{0.86}Fe_{13.67}Ni_{2.33}O_{24.67}F_{2.33}

	Table I.	Composition	from Chemical	Analysis.	
li	% F	Moles Ni	Moles F		Composi

% Ni	% F	Moles Ni	Moles F	Composition
2.23	0.7	.596	.583	BaFe _{1.987} Ni _{.018} Fe _{15.417} Ni _{.563} O _{26.417} F _{0.583}
4.95	1.6	1.34	1.33	BaFe ^{II} _{1.99} Ni _{.01} Fe _{14.67} Ni _{1.33} O _{25.67} F _{1.33}
11.65	2.73	3.21	2.34	$BaFe_{1.14}^{II}Ni_{.86}Fe_{13.67}Ni_{2.33}O_{24.67}F_{2.33}$
	% Ni 2.23 4.95 11.65	% Ni % F 2.23 0.7 4.95 1.6 11.65 2.73	% Ni % F Moles Ni 2.23 0.7 .596 4.95 1.6 1.34 11.65 2.73 3.21	% Ni % F Moles Ni Moles F 2.23 0.7 .596 .583 4.95 1.6 1.34 1.33 11.65 2.73 3.21 2.34

anisotropy (c to a).

 Cu^{2+} —magnetoplumbite for Cu concentrations 0–2.

The saturation magnetization of the nickel substituted W-phases was measured and compared to $BaFe_2^{II}Fe_{16}O_{27}$. These results are summarized in Fig. 4 Tables I and II.

Fig. 4 shows the values of $\sigma_{\text{sat.}}$ vs T of the substituted ferrites as compared to BaFe₂^{II}-Fe₁₆^{III}O₂₇⁴⁾. The results indicate almost all of

Table	II.	Magnetization.

	Sample	σ_0 calc.	σ_0 obs.	μ_B calc.	μ_B obs.
I	Fe ¹¹ ₂ W	98	98	28	28
II		104	101.8	29.73	29.17
III		111	108.5	32.0	31.12
IV		115	113.0	33.27	32.78
		Curi	e Temp (°C)	
		Fe ^{II} W	455		
		NiFeII	520		

of the charge compensated Ni²⁺ preferentially occupies the tetrahedral sites yielding magnetizations which are in good agreement with calculated values. (The error involved in measuring σ is $\pm 5\%$).

It can also be seen from Fig. 4 that the Curie temperature of the substituted ferrites is not very different than the unsubstituted W-phase. This is not consistent with the observation that the W phase with one mole nickel substituted for ferrous has a higher Curie temperature than the unsubstituted W phase.

The calculated values for the magnetizations were obtained by assuming that all the Ni²⁺ not charge-compensated by fluoride replaces the Fe²⁺ in octahedral sites (these sites have spins parallel to the overall magnetic moment) and all the Ni²⁺ compensated by F^- occupies the tetrahedral sites (these sites have spins antiparallel to the overall magnetic moment).

In the Fe₂W structure there are 11 octahedral sites (9 of which contain Fe³⁺, 2 contain Fe²⁺) and 1 trigonal site which adds to the magnetization. There are 4 tetrahedral and two octahedral sites (all containing Fe³⁺) whose spins are aligned antiparallel. The calculation of the predicted magnetic moment was made in the following way:

 $4(2-x)_{\rm Fe^{2+}}+5(10)_{\rm Fe^{3+}}+2(x)-5(6-y)+2(y)=\mu_{B}$

where x = quantity of uncompensated Ni²⁺,

y = quantity of fluoride-compensated Ni²⁺

The magnetic moments of the copper substituted magnetoplumbites are now being measured and are expected to show increases in the magnetic moments as compared to $BaFe_{12}O_{19}$. The copper-substituted samples are being measured now, as they are expected to give the greatest increase in moment of all the bivalent transition metal ions.

References

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DISCUSSION

G. HEIMKE: Did you measure the coercivity of your materials or their anisotropy?

E. BANKS: No. We expect to get an estimate of the anisotropy from the field dependence of the magnetization in the hard direction, as soon as those measurements are completed.