TABLE I[a]

Compound	T (°C.)	ϵCCl_4	$\Delta d/\Delta N$	$\Delta\epsilon/\Delta N$	$\Delta(n_D^2)/\Delta N$	P (cc.)	R_D (cc.)
$VOCl_3$	25	2.2283	0.226	0.660	0.524	38.5 ± 0.5	35.0 ± 0.5
$VOCl_3$	35	2.2077	.229	.624	...	38.0 ± .5	....
VCl_4	25	2.2275	.246	.878	0.642	45.2 ± .5	40.0 ± 0.5
VCl_4	35	2.2078	.250	.908	...	45.9 ± .5	....

[a] Solvent was CCl_4, d^{25}_4 1.5858, d^{35}_4 1.5666, n^{25}_D 1.4587.

Discussion and Results

On the basis of cryoscopic measurements in CCl_4, VCl_4 has been postulated to form a dimer.[10] This is probably erroneous due to the formation of a solid solution between CCl_4 and VCl_4.[11] Infrared and Raman studies of liquid $VOCl_3$ indicate the molecule to have a C_{3v} symmetry, which is in agreement with the structure of the vapor as determined by electron diffraction.[16] It seems probable that both compounds are monomeric in dilute solutions, and monomeric molecular weights were used in calculations. Total polarizations and molar refractions were calculated using the extrapolation formula of Hedestrand.[17] The results of the calculations are summarized in Table I.

Because of the tetrahedral structure and general covalent properties, the small difference between P and R_D for VCl_4 probably is due only to atomic polarization. Therefore, as expected the electric moment is zero.

The uncertainty in the total polarization (P) and molar refraction (R_D) is estimated to be about 0.5 cc. A crude estimate of the atomic polarization of $VOCl_3$ can be made from Smyth's data.[18] P_a for $VOCl_3$ (estimated) is 2 cc. Using this value for the atomic polarization (P_a) the electric moment of $VOCl_3$ is calculated to be 0.31 debye unit. Since the difference between the total polarization and the sum of electronic and atomic polarization, *i.e.*, the orientation polarization, is then only 2.5 cc., and the uncertainty is possibly 1 cc., the uncertainty in the electric moment must be ± 0.1–0.2 debye unit. Therefore, the electric moment of $VOCl_3$ is small, being probably between 0.1 and 0.4 debye unit.

This is a low value compared with the large (2.4 debyes) moment of $POCl_3$. However a similar compound, CrO_2Cl_2, has been shown to have a similar small value.[19] It is tempting to postulate a dimer to account for this value, and our cryoscopic data taken in CCl_4 support this. However, our inability to show the absence of a solid solution, and the infrared and Raman studies make a dimer unlikely. We conclude that the V–Cl and the V–O bond moments are similar and that the approximate tetrahedral structure accounts for the low moment.

In order to provide an independent check, the dielectric constant and refractive index of $VOCl_3$ were measured and used in Onsager's equation.[20] This gave a moment of 0.39 debye unit, which is in agreement with our value. Our measured value for the dielectric constant of $VOCl_3$ differed from the previous value of Loomis and Schlundt[8] by −0.5 unit. We are unable to explain the discrepancy, since the work of Loomis and Schlundt appeared to have been carefully done.

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(16) K. J. Palmer, THIS JOURNAL, **60**, 2360 (1938).

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BOZEMAN, MONTANA

[CONTRIBUTION FROM THE PIGMENTS DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Preparation of the Ferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ in Transparent Form[1]

BY LOTHAR H. BRIXNER

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The ferrites $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ have been prepared by the interaction of ferric oxide and the corresponding alkaline earth fluoride or chloride under oxygen. The crystals obtained by this technique are small transparent platelets, up to 1 mm. in diameter and approximately 50 μ thick, which are essentially free of strain, thus permitting directly the observation and study of the internal magnetic domain structure by transmitted polarized light without delicate grinding and polishing procedures. X-Ray diffraction patterns taken on of single crystals gave these parameters: $a_0 \approx 5.88$ Å., $c_0 = 23.20$ Å. for $BaFe_{12}O_{19}$; and $a_0 = 5.86$ Å., $c_0 = 23.00$ Å. for $SrFe_{12}O_{19}$. Pycnometric and X-ray densities are in excellent agreement. Other compounds prepared in transparent form by this technique were: $CaFe_2O_4$, $Ca_2Fe_{10}O_{17}$, $LiFe_5O_8$ and α-Fe_2O_3.

Introduction

Adelsköld[2] first characterized $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ by their corresponding X-ray powder patterns as belonging to a group of compounds which crystallize in the hexagonal magnetoplumbite structure with the space group D^4_{6h} ($P\,6_3/mmc$). Went, *et al.*,[3] investigated the magnetic properties

(1) Part of this paper was presented at the American Chemical Society Meeting, September 12, 1958.

(2) V. Adelsköld, *Ark. Kem. Mineral. Geol.*, **12** [a] (1938) Nr. 29, 9S.

(3) J. J. Went, G. W. Rathenau, E. W. Gorter and G. W. van Oosterhout, *Philips Tech. Rev.*, **13**, [7], 194 (1952).

of these compounds and established their usefulness as permanent ceramic magnets. Very recently Kooy[4] reported that by cooling a "nearly eutectic melt" extremely thin crystal plates of $BaFe_{12}O_{19}$ were obtained, which are suitable for the direct observation of Weiss domains by means of the Faraday effect. In this paper a detailed description and explanation of the internal magnet domain pattern is given, whereas preparative details are not disclosed. While the first transparent magnetoplumbite-type ferrite, $PbFe_{11}Al_1O_{19}$, was prepared from a lead oxide melt by Sherwood, Remeika and Williams,[5] Kooy's $BaFe_{12}O_{19}$ is the first hexagonal alkaline earth ferrite to be reported in transparent form. We can now add the transparent $SrFe_{12}O_{19}$ to this series, which originated with the investigations of Dillon[6] on the transparent yttrium and rare earth garnets. A number of other transparent ferrimagnetic oxides have been found since.[5,7] Generally, the technique used for the preparation of these crystals is the growing of large single crystals from a lead oxide flux and subsequent sectioning and polishing of thin plates.

In the present paper, a different and new technique, which generally involves the interaction of ferric oxide with a halide, is described. The slow conversion of the appropriate halide into the corresponding oxide and the subsequent interaction with Fe_2O_3 may account for the growth of the small monocrystalline platelets. Although limited to a rather small selection of halides, the technique is of somewhat general applicability. Under "Experimental" the solid state reaction between BaF_2 and Fe_2O_3 and the reaction of Fe_2O_3 in a barium and strontium chloride melt will be described in detail. The interaction of Fe_2O_3 with other halide melts will be summarized briefly below. These halides should not have too low a melting point, preferably between 800 and 1000°, have not too high a vapor pressure at 1250° and be thermodynamically stable with respect to oxygen at this temperature.

The reaction of Fe_2O_3 with both $BaCl_2$ and $SrCl_2$ melts under oxygen, resulted in $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ as the only phase. Two phases were obtained, in roughly equal distribution, when Fe_2O_3 was reacted in a $CaCl_2$ melt. They were both in transparent, single-crystalline form and showed a distinctly different crystalline habit. One portion crystallized in red-brown, weakly ferromagnetic needles and prisms; analysis and single crystal X-ray diffraction showed that it was $CaFe_2O_4$. (*Anal.* Found: Ca, 17.76; Fe, 52.34; $a_0 = 3.00 \pm 0.03$ Å., $b_0 = 10.60 \pm 0.03$ Å., $c_0 = 9.20 \pm 0.03$ Å.; space group D^{16}_{2h}; calcd. for $CaFe_2O_4$: Ca, 18.57; Fe, 51.76. The second portion crystallized in hexagonal, transparent platelets and was strongly enough ferromagnetic to be separated magnetically from the first fraction. According to chemical analysis, the compound is $Ca_2Fe_{10}O_{17}$. (*Anal.* Found: Ca, 9.01, Fe, 60.95. Calcd. for $Ca_2Fe_{10}O_{17}$: Ca, 8.80; Fe, 61.33.) The only reference to such a compound was found in Gmelin[8], where it is mentioned under calcium ferrites with "doubtful composition." There $2CaO \cdot 5Fe_2O_3$ is said to have been obtained by chance during the preparation of Fe(III) silicates in the melt of a mixture of CaO, Fe_2O_3 and $2SiO_2$ with great excess $CaCl_2$ as a very fine dark black powder of metallic luster. The crystal habit of this compound is described as poorly defined octahedra. The compound we obtained was hexagonal (a_0 = 6.01 Å. and c_0 = 22.40 Å.) and very similar to magnetoplumbite. Since $KFe_{11}O_{17}$ also crystallizes in this structure, we suggest writing $Ca_2Fe_{10}O_{17}$ as $Ca(CaFe_{10})O_{17}$, with one calcium occupying an iron lattice site.

Magnesium chloride was thermodynamically too unstable under the reaction conditions and completely converted into MgO. A LiCl melt yielded transparent $LiFe_5O_8$; and from a NaCl melt, transparent α-Fe_2O_3 was obtained rather than a sodium compound. Lead chloride had too high a vapor pressure at 1250° to be used.

Experimental

In the course of an investigation directed toward new ferromagnetic materials, BaF_2 and Fe_2O_3 reacted in a 1:6 mole ratio at 1300° under oxygen. During the reaction, considerable weight losses were observed and the X-ray diffraction pattern of the reaction product indicated $BaFe_{12}O_{19}$ or an isomorphous compound as the only phase. Part of the reaction product, contained in a platinum boat, was obtained in form of transparent, red single crystalline platelets 10–100 μ thick and up to 2 mm. in diameter. The mass of the product was polycrystalline. Since the analysis indicated that the reaction product was essentially F-free, reaction (I) is suggested as the most likely mechanism

$$BaF_2 + 6Fe_2O_3 + H_2O = BaFe_{12}O_{19} + 2HF \quad (I)$$

Weight loss data, as summarized in Table I, also substantiate this suggestion.

TABLE I

WEIGHT LOSSES ENCOUNTERED DURING THE INTERACTION OF $6Fe_2O_3 + BaF_2$ UNDER OXYGEN

Expt.	Total amt. of $BaF_2 + Fe_2O_3$ reacted, g.	Wt. loss found, g.	Wt. loss calcd. according to reaction I
1	19.392	0.380	0.3763
2	19.392	0.375	
3	19.392	0.374	
4	59.145	1.135	1.1476
5	59.145	1.140	
6	118.290	2.301	2.295
7	129.280	2.500	2.508

Experiments 1, 2 and 3 from Table I were carried out in a baked out recrystallized Al_2O_3 tube and reproducibly yielded a small quantity of transparent crystals of $BaFe_{12}O_{19}$. In order to substantiate reaction I, a plug of silica wool was placed in the tube, downstream from the boat. The exit gases, after passing the silica wool, were bubbled through a water trap. In this trap a precipitate of SiO_2, resulting from hydrolysis of SiF_4, formed during the reaction. In the filtrate of this precipitate $CaCl_2$ also precipitated CaF_2. While in this experiment the CaF_2 did not account quantitatively for the lost fluorine, an analogous reaction between Fe_2O_3 and $BaCl_2$ allowed the quantitative determination of the chlorine loss during the reaction. *Anal.* Found: Ba, 12.32; Fe, 60.21; $Cl_{(\text{released as gas})}$ 6.04; $Cl_{(\text{retained in reaction product})}$ 0.01. Calcd. for $BaFe_{12}O_{19}$ (from $BaCl_2 + 6Fe_2O_3$): Ba, 12.36; Fe, 60.29; $Cl_{(\text{released as gas})}$, 6.06; $Cl_{(\text{retained in reaction product})}$, 0.00.

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(4) C. Kooy, *Philips Tech. Rev.*, **19** [10], 286 (1958).

(5) R. C. Sherwood, T. P. Remeika and H. T. Williams, *Bull. Am. Phys. Soc.*, [II] **3**, 42 (1958).

(6) J. F. Dillon, *J. Applied Phys.*, **29**, Nr. 9, 1286 (1958).

(7) P. A. Miles, Prog. Rept. (XXI) Lab. for Insulation Research, Massachusetts Institute of Technology, p. 19.

(8) Z. Weyberg, *C. Mineral*, 649 (1906).

Experiments 4–7 were carried out in open platinum dishes and produced only polycrystalline $BaFe_{12}O_{19}$. *Anal.* Found: Ba, 12.35; Fe, 60.23; F, 0.02. Calcd. for $BaFe_{12}O_{19}$: Ba, 12.36; Fe, 60.29; F, 0.00.

Finally, Fe_2O_3 was introduced under completely nonstoichiometric conditions into a great excess of molten barium chloride. Exactly 300 g. of anhydrous barium chloride was melted in a platinum dish and oxygen was bubbled through a perforated platinum tube into the melt. At 1250°, 10.0 g. of Fe_2O_3 was introduced into the melt and reacted for 3 hr. The furnace then was cooled at a rate of 50° per hour. The cold reaction mixture was leached with water and 0.1 *N* HCl. The product consisted of lustrous platelets, most of which were transparent. Again it was shown, by means of an X-ray diffraction powder pattern, that even under these conditions $BaFe_{12}O_{19}$ was obtained as the only phase, which is further an indication for the high crystal energy of this particular barium ferrite. Finally, 10.00 g. of Fe_2O_3 reacted in 300.00 g. of molten $SrCl_2$ under conditions identical to those described above. As before, shiny, mostly transparent platelets of $SrFe_{12}O_{19}$ were obtained. (*Anal.* Found: Sr, 8.17; Fe, 62.89. Calcd. for $SrFe_{12}O_{19}$: Sr, 8.25; Fe, 63.12.) The *d*-spacings of the X-ray powder diffraction pattern of $BaFe_{12}O_{19}$ were in perfect agreement with ASTM File Card 7-276 and those of the isomorphous $SrFe_{12}O_{19}$ showed the same intensity variations with a correspondingly small shift in *d*-spacings.

X-Ray Analyses.—Powder samples of $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ were sealed in 0.3 mm. Lindemann glass capillaries and were mounted in a 114.6 mm. camera. Exposure times to copper K-alpha (λ 1.5418 Å.) radiation varied between 8 and 10 hr. Aluminum foil was placed over the film to minimize fluorescence effects.

Single crystal data were obtained by precession about the *c*-axis in a precession camera. 0 and 1 level photographs were taken with copper radiation and the elementary hexagonal cell dimensions were found to be a_0 = 5.88 Å., c_0 = 23.20 A. for $BaFe_{12}O_{19}$; and a_0 = 5.86 Å., c_0 = 23.00 Å. for $SrFe_{12}O_{19}$. The space group is D_{6h}^4 (P 6_3/mmc.) With two formula weights per unit cell, the X-ray densities are 5.31 g. cc.$^{-1}$ for $BaFe_{12}O_{19}$ and 5.15 g. cc.$^{-1}$ for $SrFe_{12}O_{19}$ in excellent agreement with the pycnometric densities of 5.22 and 4.98 g. cc.$^{-1}$, respectively.

Domain Pattern.—The particular interest of the compounds prepared by the technique described lies in the fact that they are transparent at visible wave lengths. It must be assumed that for this special form of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ *all* iron ions are 3-valent, since the presence of even small amounts of 2-valent iron would cause a significant absorption of light and make the crystal opaque.

In his paper, "Direct Observation of Weiss Domains by Means of the Faraday Effect," Kooy (ref. 4) shows pictures of internal domain patterns and also gives an explanation as to how these pictures come about. Figure 1 shows a virgin state domain pattern of a single crystalline platelet of $SrFe_{12}O_{19}$ as obtained by the interaction of $SrCl_2$ and Fe_2O_3. Transparent strontium–ferrite has not yet been reported in the literature. This pattern is practically identical with the pattern for $BaFe_{12}O_{19}$ as obtained by Kooy. Qualitatively, we also noticed that the domain pattern assumes a much more ordered form if it is observed after the crystal has been magnetized. With crystals of varying thicknesses, we furthermore found that the width of the domains depends on the thickness and that the domain size increases with temperature, which is in accordance with the decreasing crystal anisotropy with increasing temperature.

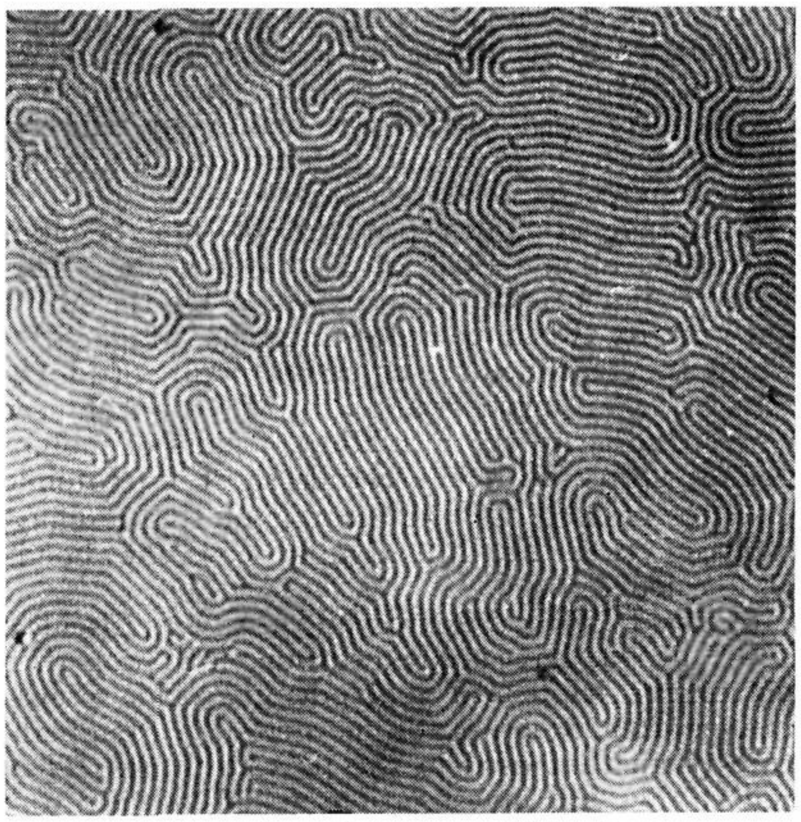
Fig. 1.—Domain pattern of $SrFe_{12}O_{19}$.

Quantitative observations on the domain pattern and its behavior in magnetic fields will be the subject of a forthcoming publication of F. J. Baum, H. S. Jarrett and M. S. Sadler.

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WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE HALDOR TOPSØE RESEARCH LABORATORY]

A Magnetic Investigation on Supported Molybdenum Dioxide

BY ERLING RØST[1]

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The magnetic susceptibilities of a series of precipitated molybdenum oxide–alumina preparations have been measured in a hydrogen atmosphere after hydrogen reduction at 440–450°. Crystalline MoO_2 shows a temperature independent susceptibility of $+0.33 \times 10^{-6}$ per gram. By dilution of the molybdenum oxide on the alumina support, the susceptibility of MoO_2 increases considerably. For the highest diluted compound, with an atomic ratio of Mo/Al = 1/99, the MoO_2 susceptibility was determined as 27×10^{-6} at 78°K., 9.8×10^{-6} at 195°K. and 6.5×10^{-6} at 295°K. The increase in paramagnetism on dilution probably is caused by an increasing number of unpaired electrons due to the decrease in number of Mo–Mo bonds present in the crystal lattice of MoO_2. The susceptibility of the dispersed MoO_2 decreases considerably after exposure to air at room temperature, possibly due to chemisorption of oxygen. The investigation indicates close relationships between degree of dispersion and chemisorption efficiency of the supported MoO_2.

Introduction

A number of transition metal oxides show an increase in magnetic susceptibility by dilution on a high-area diamagnetic support, such as γ-Al_2O_3. The usual explanation of this phenomenon is that exchange interaction covalent bonds exist between adjacent metal atoms in the crystal lattice. By

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[1] Chemical Institute A, University of Oslo, Blindern, Norway.