

STOICHIOMETRY AND OXYGEN STRUCTURE OF Fe SILLENITE

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The sillenite phase in the $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system has been characterized by X-ray, infrared absorption and magnetic susceptibility measurements. The composition corresponded to a concentration of 3.7 ± 0.2 mol% Fe_2O_3 only compatible with a $\text{Bi}_{25}\text{FeO}_{40}$ stoichiometry. A powder neutron diffraction study provided structural information on the oxygen lattice.

1. Introduction

Sillenites [1,2] are a large group of compounds with interesting physical and chemical properties formed by doping Bi_2O_3 with metal oxides [3]. Their structure-type is bcc (I_{23}) and has been precisely determined for $\text{Bi}_{12}\text{GeO}_{20}$ [4,5]. However, the exact $\text{Bi}_{12}\text{MO}_{20}$ stoichiometry which is found for tetravalent cations is not possible for differently charged ions. Craig and Stephenson [6], and more recently Devalette et al. [7-9], have shown that the structure-type is compatible with a large variety of metal ions if the coupled substitution $(5-n)\text{M}^{4+} = \text{A}^{n+} + (4-n)\text{Bi}^{5+}$ is assumed. In particular, in their X-ray structural study of Fe sillenite, Craig and Stephenson obtained very good agreement with a fully occupied $\text{Bi}_{12}\text{GeO}_{20}$ -type structure assuming an overall composition of $\text{Bi}_{25}\text{FeO}_{40}$ with $\text{Fe}^{3+} + \text{Bi}^{5+}$ substituting for 2Ge^{4+} . The nominal composition of the single crystal used in this case was, however, $19\text{Bi}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and their attempts to chemically analyse for Bi^{5+} proved unsuccessful owing to the extreme insolubility of the material. On the other hand, moreover, different studies [3,10-15] have reported Bi:Fe ratios ranging from 24:1 to 15:1, all below the ideal 25:1 ratio. These compositional dif-

ferences may indicate the existence of anion defect lattices similar to those observed for other closely related phases also based on Bi_2O_3 [16-18]. In order to investigate these possibilities we have examined the $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3$ system in the composition range from 0 to 10 mol% Fe_2O_3 and selected the most likely sillenite stoichiometry for a powder neutron study of the oxygen sublattice.

2. X-ray, IR and magnetic susceptibility characterization of the system

Samples were prepared by mixing precisely weighed amounts of high grade oxides (Bi_2O_3 and Fe_2O_3 , "Specpure" from Johnson Matthey Chemical Ltd.) which were then fired in air at 750°C in Pt crucibles. Powder X-ray analysis of the product (using Cu K α radiation and a Philips PW 1730-1050/80 powder diffractometer with a graphite analyser) agree with previously published diagrams in the range, in that they show only three different phases: Monoclinic $\alpha\text{-Bi}_2\text{O}_3$, the bcc sillenite phase and orthoferrite BiFeO_3 . The lattice parameter of the bcc phase remains constant, independent of Fe_2O_3 concentration, at ≈ 10.18 Å, a value slightly larger than for hydro-

thermally prepared samples [7]. Despite careful analysis and prolonged scanning, no second phases appear in the X-ray diagrams between 3 and 5 mol% Fe_2O_3 .

In order to investigate whether IR spectroscopy is sensitive to changing concentrations of the three phases in the experimental range, infrared absorption spectra (Perkin-Elmer 621 infrared spectrophotometer) were obtained between 1000 and 300 cm^{-1} applying the usual KBr technique. Variations from the spectrum of pure Bi_2O_3 can be observed above 1.5 mol% Fe_2O_3 . There is an absorption peak at 840 cm^{-1} which is observed until 3 mol% Fe_2O_3 but beyond this concentration and up to 8 mol% Fe_2O_3 the spectra

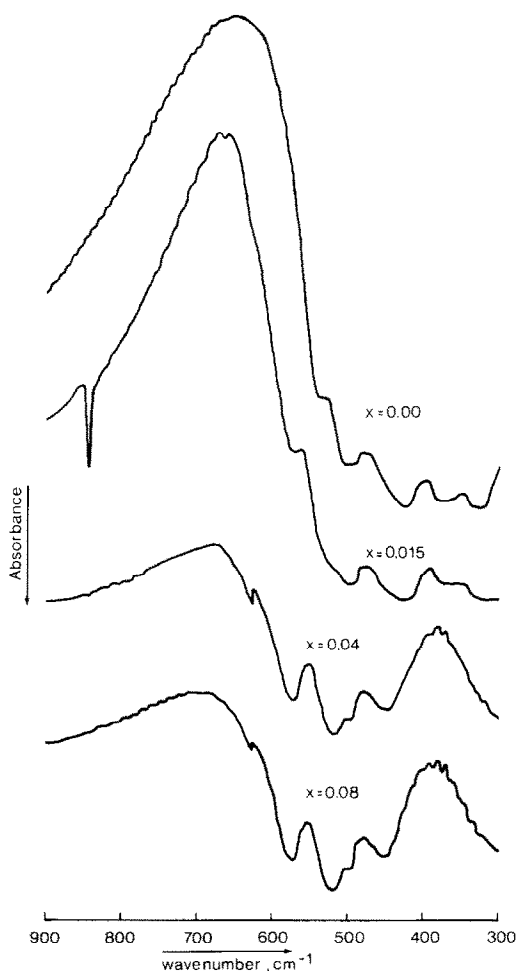


Fig. 1. Infrared absorption spectra for Bi_2O_3 doped with different concentrations of Fe_2O_3 . x indicates Fe_2O_3 molar fraction.

show negligible change with discrete absorption bands at 575, 520 and 450 cm^{-1} and a shoulder at 500 cm^{-1} (fig. 1). The three bands observed characterize the sillenite structure and are observed with only small variations for several other sillenite compounds [9].

A feature of the system which has not been properly exploited, however, is the very different magnetic properties of its three components: α - Bi_2O_3 is diamagnetic, BiFeO_3 is a weakly ferromagnetic antiferromagnet [19] and the bcc phase is paramagnetic [9]. Magnetic susceptibility measurements using the Faraday method (Cahn, Faraday magnetic susceptibility system, calibrated against $\text{HgCo}(\text{CNS})_4$) were carried out at 18°C (a) on homogeneous mixtures of the unreacted pure oxides and (b) on the same material after reaction at high temperatures. Results are shown in fig. 2. The susceptibility of the unreacted oxides shows a variation which is linear on Fe_2O_3 so that a line fitted to the experimental points can be used as an additional control on sample composition. The standard deviation of the samples from their nominal compositions was 0.2 mol% Fe_2O_3 . The susceptibilities of the reacted oxides are clearly divided in two regions: The α - Bi_2O_3 and bcc region (I) and the bcc and BiFeO_3 region (II). Susceptibility curves for both regions

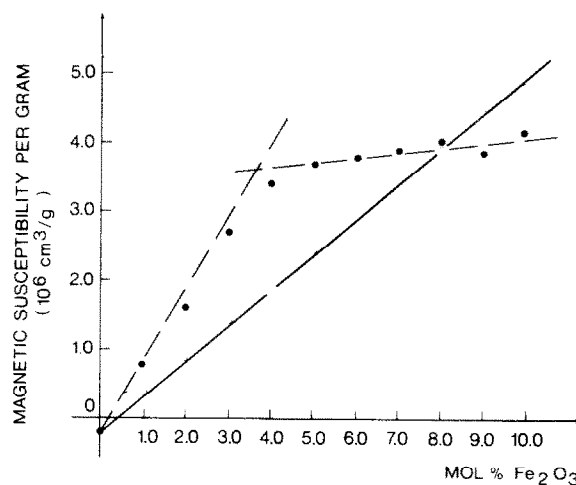


Fig. 2. Magnetic susceptibility per gram as function of Fe_2O_3 concentration. Open circles and the full line correspond to mixtures of the unreacted oxides. Full circles and the broken lines refer to the high-temperature reacted samples.

were calculated by addition of the appropriate molar susceptibilities and by approximating the susceptibility of the bcc phase to that of a paramagnetic dilution of Fe^{3+} in Bi_2O_3 . Using the Fe_2O_3 concentration as an adjustable parameter they were fitted to the experimental points. The intersection of the region I and region II curves occurs at a limiting concentration of 3.7 ± 0.2 mol% Fe_2O_3 which seems only compatible with the $\text{Bi}_{25}\text{FeO}_{40}$ (3.85 mol% Fe_2O_3) stoichiometry suggested by Craig and Stephenson.

3. Neutron diffraction measurement

To check on the oxygen arrangement in the material a much larger sample (46 g) with the ideal 25:1 ratio was prepared for a powder neutron experiment. Neutron diffraction is particularly useful for determining the anion structure of the oxides of metals with high atomic numbers which in most X-ray structural determinations is concealed by the large X-ray scattering amplitude of the metal. An X-ray powder analysis of the sample based on 78 bcc reflections and using a Nelson-Riley correction gave a lattice parameter of $a = 10.1835(3)$ Å. The neutron diffraction experiment was carried out on a two-

Table 1
Atomic coordinates a)

	x	y	z	n
Bi³⁺ in 24 f				
A	0.17635	0.31796	0.01409	1
M in 2a				
	0	0	0	1
O(I) in 24 f				
A	0.6346(10)	0.7521(10)	0.9887(14)	1
B	0.6349(5)	0.7514(5)	0.9866(6)	1
C	0.630	0.750	0.985	36/40
D	0.579(1)	0.762(2)	0.986(2)	39/40
E	0.6404(7)	0.7456(8)	0.9850(10)	1
O(II) in 8 c				
A	0.6885(31)	0.6885(31)	0.6885(31)	1
B	0.6953(7)	0.6953(7)	0.6953(7)	1
C	0.698	0.698	0.698	36/40
D	0.784(2)	0.784(2)	0.784(2)	39/40
E	0.6841(7)	0.6841(7)	0.6841(7)	1
O(III) in 8 c				
A	0.8926(32)	0.8926(32)	0.8926(32)	1
B	0.8998(6)	0.8998(6)	0.8998(6)	1
C	0.902	0.902	0.902	36/40
D	0.852(4)	0.852(4)	0.852(4)	39/40
E	0.8819(12)	0.8819(12)	0.8819(12)	1

- a) A: $\text{Bi}_{25}\text{FeO}_{40}$, X-rays, Craig and Stephenson [6].
 B: $\text{Bi}_{12}\text{GeO}_{20}$, X-rays, Svensson et al. [5]
 C: $(\text{Bi}_6^{3+}\text{M}_8^{2+})(\text{Bi}_2^{3+})\text{O}_{36}$, X-rays, Ramanan et al. [18].
 D: $\text{Bi}_4^{3+}(\text{Bi}_2^{3+})\text{O}_{39}$, neutrons, Harwig [16].
 E: $\text{Bi}_{25}\text{FeO}_{40}$, neutrons, this work.

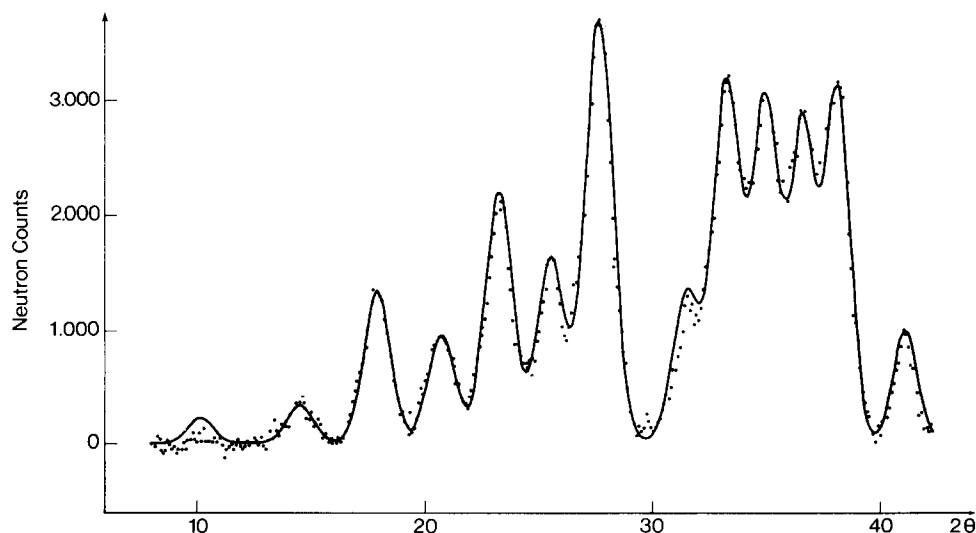


Fig. 3. Powder neutron diffraction profile for $\text{Bi}_{25}\text{FeO}_{40}$. Small circles are the experimental points, and the full curve passes through the calculated points.

axis powder diffractometer at the RECH-1 reactor of the Chilean Nuclear Energy Commission. The mean neutron wavelength of 1.318 Å was calibrated against a Ni standard and sample absorption, measured according to the procedure of Hewat [20], gave a value of $\mu = 0.310 \text{ cm}^{-1}$ which is negligible for the purpose of the experiment. Data were collected in a 2θ range between 8.00° and 41.30° which included 19 nuclear reflections. These were treated using a local version of the original Rietveld profile refinement programme [21]. The refinement of the 5 oxygen positional parameters was carried out in the I_{23} space group using the X-ray values of Craig and Stephenson as starting parameters. The bismuth positions which are well known from X-ray determinations and rather insensitive to changes in dopant ion were kept constant. The experimental and calculated diffraction profiles are shown in fig. 3. The R -factor based on intensities was $R = 5.3\%$ while the weighed profile factor was $R_{\text{pw}} = 10.8\%$ for a statistically expected value $R_e = 8.0\%$. The resulting oxygen coordinates are given in table 1 and compared to those obtained in previous work. Although there are some marked differences with the results for other sillenites, in particular with those for which incomplete oxygen lattices have been assumed, the neutron values for the Fe sillenite agree to about three standard deviations with the Craig and Stephenson coordinates providing, thus, further confirmation of their structural model.

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