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A Powder Neutron Diffraction Study of the Structure of and Oxygen Vacancy Distribution in 6*H* $BaFeO_{2.79}$

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The structure and oxygen vacancy distribution have been determined for 6*H* $BaFeO_{2.79}$. The hexagonally stacked AO_3 layers are found to have composition $BaO_{2.5}$ while the cubic stacked layers are $BaO_{2.835}$. Possible models for the vacancy distribution are discussed in relation to the defect structures of $SrFeO_{2.5}$ and $SrFeO_{2.75}$.

Introduction

The anion deficient perovskite related compounds ABO_{3-x} where A = Sr, Ba and B = Mn, Co, Ni have structures which may be described as close packed AO_3 layers with B cations in octahedral sites (Katz & Ward, 1964). All show extensive non-stoichiometry in the range $0<x<0.5$ but considerable differences are found in the structures and compositions of intermediate phases. Little is known of the detailed distribution of O vacancies.

The $BaFeO_{3-x}$ system is one of the most extensively investigated, in part because of the interesting magnetic properties which result from the presence of both Fe^{3+} and Fe^{4+}. Gallagher, MacChesney & Buchanan (1965) and MacChesney, Potter, Sherwood & Williams (1965) identified two phases; $BaFeO_{2.5}$, thought to be isostructural with brownmillerite and a hexagonal phase $BaFeO_{2.84-2.95}$. Subsequently, Mori (1965, 1966, 1970) reported the phase at $x=0.5$ to be triclinic and in addition prepared a number of other compounds including a second triclinic phase, $BaFeO_{2.67}$, rhombohedral $BaFeO_{2.62-2.64}$, tetragonal $BaFeO_{2.75-2.81}$ and 6*H* hexagonal $BaFeO_{2.63-2.95}$. All compounds other than triclinic *I* and 6*H* were obtained at low temperatures and showed weak superlattice reflexions in their powder X-ray patterns. Zanne & Gleitzer (1971) found that the 6*H* hexagonal phase exists in the range $BaFeO_{2.95}$–$BaFeO_{2.69}$ and in addition reported a 12*R* compound with a BaO_3 stacking sequence *chhc*, prepared at high O_2 pressure. The twelve-layer modification has also been described by Takeda, Shimada, Kanamaru & Koizumi (1973).

Phase relations in nonstoichiometric perovskite related compounds are often complicated by slow diffusion of metal ions which may lead to the formation of metastable phases with respect to the cation distribution. Equilibrium with respect to O is generally attained more rapidly. Ichida (1973) investigated the attainment of equilibrium by using the decomposition of $BaFeO_4$ as a synthetic route in preference to the more usual solid state reaction of Fe_2O_3 with $BaCO_3$ or BaO_2. Triclinic *I* and 6*H* $BaFeO_{2.63-2.95}$ were established as equilibrium phases and in addition to the low-temperature phases of Mori a new $BaFeO_{2.5}$ structure was reported.

In the present work, the structure and O vacancy distribution of 6*H* $BaFeO_{2.79}$ have been determined by powder neutron diffraction. No detailed structures for any of the phases discussed have been reported, unlike the analogous $BaMnO_{3-x}$ system where the structures of the 8*H* compound and the structure and vacancy distribution in 4*H* $Ba_{0.5}Sr_{0.5}MnO_{2.83}$ have been determined (Potoff, Chamberland & Katz, 1973; Jacobson & Horrox, 1976). In the Fe system the effect of a different preferred coordination for the reduced cation is expected to lead to a different vacancy distribution.

Experimental

Sample preparation

The starting materials used were $BaCO_3$ and Fe_2O_3 obtained 'Specpure' from Johnson Matthey Chemicals Ltd. The $BaCO_3$ was fired in CO_2 at 950°C and the Fe_2O_3 at 1000°C in O_2 prior to use. A stoichiometric mixture of the starting materials (30 gm) was hand mixed in an agate mortar and fired in a Pt crucible in air at 1000°C for 48 h. The sample was reground and refired at 800 and 650°C for periods of 96 h. Between the two firings the sample was reground and after both firings examined on a Philips X-ray diffractometer with monochromated Cu *Kα* radiation. After the 800°C firing several weak extra reflexions were present but after the final firing all lines could be indexed on a 6*H* hexagonal cell with $a=5\cdot682$ (3), $c=13\cdot970$ (5) Å in good agreement with Mori (1970).

The average Fe oxidation state was determined by dissolving in HCl containing an excess of KI and titrating the liberated I_2 with $Na_2S_2O_3$. The composition was found to be $BaFeO_{2\cdot79\,(1)}$.

Neutron diffraction

The neutron diffraction data were collected at room temperature on a powder diffractometer at the reactor, PLUTO, UKAEA, Harwell. The sample was contained in a thin-walled V can and the wavelength used was 1·320 Å obtained from the (511) planes of a Ge crystal with a 75° take-off. The counter was stepped at 0·02° intervals and total counts accumulated at 0·1° over the angular range $7° < 2\theta < 91°$.

Structural parameters were refined by the profile analysis method (Rietveld, 1967) based on space group $P6_3/mmc$. The starting parameters were taken as those corresponding to ideal close packing of the BaO_3 layers in the sequence *cch*.* The scattering lengths used were $b_{Ba}=0\cdot52\times10^{-12}$ cm, $b_{Fe}=0\cdot952\times10^{-12}$ cm and $b_O=0\cdot58\times10^{-12}$ cm (Neutron Diffraction Commission, 1972). Background contributions were estimated by hand and 20 parameters including individual isotropic temperature factors and the O occupancies were refined. The O vacancy distribution was initially assumed to be random. The reliability index defined as:

$$R_{\text{profile}}=\frac{100\sum w\,(y_{\text{obs}}-1/c\,.\,y_{\text{calc}})^2}{\sum w y_{\text{obs}}{}^2}$$

where y is the number of counts at a point in 2θ, c is a scale factor and $w=1/\sigma^2$ converged to a value of 12·9% compared with an idealized minimum of 5·2%. *R* based on integrated intensities was 6·0%. The data were refined until all parameter shifts were less than $0\cdot3\sigma$ and there were no composition constraints.

Table 1. *Atomic positional parameters obtained from neutron refinement of* $BaFeO_{2\cdot79}$

$P6_3/mmc$, $a=5\cdot6766$ (3), $c=13\cdot9765$ (11) Å.

		x	y	z	B(Å^2)
2(*b*)	Ba(1)	0	0	$\frac{1}{4}$	0·37 (22)
4(*f*)	Ba(2)	$\frac{1}{3}$	$\frac{1}{3}$	0·5874 (6)	1·34 (20)
2(*a*)	Fe(1)	0	0	0	0·65 (11)
4(*f*)	Fe(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·1523 (3)	0·60 (9)
6(*h*)	O(1)	0·4771 (8)	−0·0458 (16)	$\frac{1}{4}$	1·68 (24)
12(*k*)	O(2)	0·1681 (6)	0·3362 (12)	0·4166 (3)	0·80 (12)

Occupation numbers

O(1)	2·51 (6)
O(2)	5·67 (9)

Composition 2·73 (5)

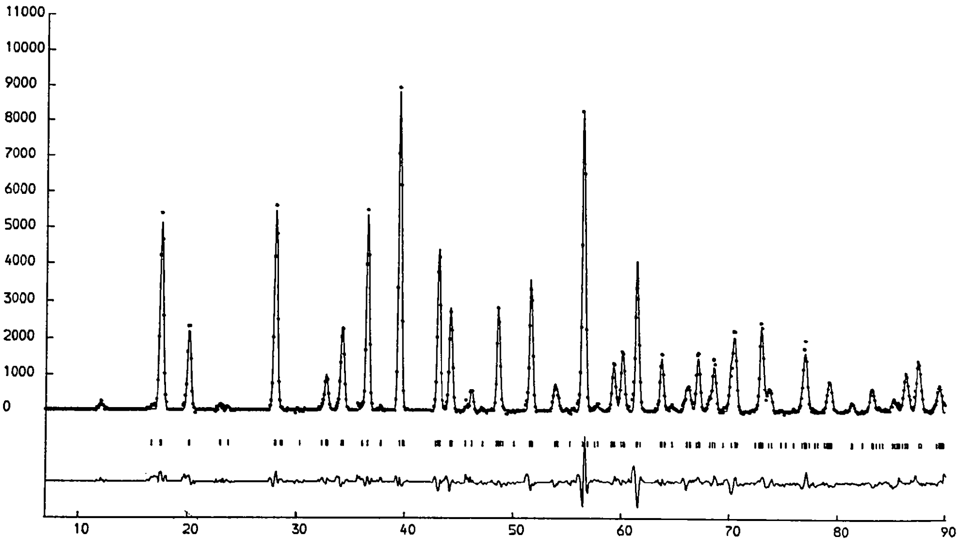

Fig. 1. Powder neutron diffraction profile for $BaFeO_{2\cdot79}$. Small circles are the experimental points, and the continuous line passes through the calculated points. The small vertical lines mark the positions of the Bragg reflexions and the bottom trace is the difference profile.

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* The stacking sequence was confirmed by electron microscopy (Hutchison & Jacobson, 1975).

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $BaFeO_{2\cdot79}$

Ba(1)–O(1)	2·847 (7)	O(1)–Ba(1)–O(1)	50·93 (2)
Ba(2)–O(2)	2·839 (5)	O(1)–Ba(1)–O(1)	69·07 (19)
Fe(1)–O(2)	2·022 (2)	O(2)–Ba(2)–O(2)	59·42 (15)
Fe(2)–O(1)	1·965 (6)	O(2)–Ba(2)–O(2)	60·56 (15)
Fe(2)–O(2)	1·889 (6)	O(2)–Fe(1)–O(2)	90·10 (14)
O(1)–O(1)	2·448 (7)	O(2)–Fe(1)–O(2)	89·90 (19)
O(1)—O(1)	3·228 (11)	O(1)–Fe(2)–O(1)	77·05 (19)
O(2)—O(2)	2·814 (8)	O(2)–Fe(2)–O(2)	96·32 (25)
O(2)—O(2)	2·863 (8)	O(2)–Fe(2)–O(1)	92·57 (20)
Fe(1)–Fe(2)	2·731 (6)	Fe(2)-O(1)—Fe(2)	88·02 (34)
		Fe(1)-O(2)—Fe(2)	175·46 (30)

The atom positions are given in Table 1 and interatomic angles and distances in Table 2. The experimental and calculated profiles are shown in Fig. 1 with the difference plot.

The composition determined from the refinement 2·73 (5) is in reasonable agreement with the chemical analysis 2·79 (1). The lattice parameters obtained from the neutron diffraction were $a=5\cdot677$ (1) and $c=13\cdot977$ (3) Å.

Discussion

In 6*H* $BaFeO_{2\cdot79}$ the O vacancies are found to be distributed unequally between the cubic and hexagonal layers; the hexagonal layers have composition $BaO_{2\cdot5}$ and the cubic layers are $BaO_{2\cdot835}$. The powder neutron diffraction experiment can only give information concerning the average unit cell. However, the average unit-cell contents may be interpreted in terms of a model for vacancy incorporation particularly by analogy with known compounds. In this respect it is of interest to compare $BaFeO_{2\cdot79}$ with the fully reduced phase $SrFeO_{2\cdot5}$ (Greaves, Jacobson, Tofield & Fender, 1975).

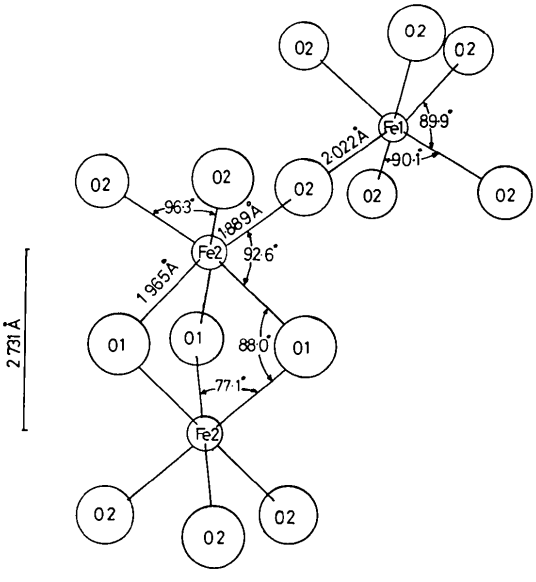

Fig. 2. Iron environment in $BaFeO_{2\cdot79}$.

$SrFeO_{2\cdot5}$ has a structure which is based on cubic stacking of AO_3 layers. Vacancies are found in strings along the ⟨110⟩ simple cubic direction in such a way as to lead to alternate sheets of $Fe^{III}O_6$ octahedra and distorted $Fe^{III}O_4$ tetrahedra. For comparison with $BaFeO_{2\cdot79}$ it is convenient to transform the structure into the corresponding hexagonal cell with the hexagonal *c* axis (the cubic ⟨111⟩ direction) along the direction of close packing. Strings of vacant O sites are now in the hexagonal ⟨110⟩ direction within a SrO_3 layer. One complete string in every four is removed to give every layer a composition $SrO_{2\cdot5}$. This suggests that the $BaO_{2\cdot5}$ layer may be similarly derived. One ⟨110⟩ string in every four is removed and one quarter of the pairs of $Fe^{IV}O_6$ face-shared octahedra are converted to corner-sharing $Fe^{III}O_4$ tetrahedra and one quarter to $Fe^{III}O_6$ octahedra. The removal of alternate O from every other ⟨110⟩ string which gives one half of the Fe atom pairs five coordination, cannot be ruled out and indeed such a model has been suggested to explain the vacancy ordering in $SrFeO_{2\cdot75}$ (Tofield, Greaves & Fender, 1975).

The removal of only the hexagonally stacked O leads to a composition $BaFeO_{2\cdot833}$. Further reduction may then take place by removal of O from corner-shared positions (cubic layers). The lower phase limit $BaFeO_{2\cdot62-2\cdot65}$ suggests that the maximum vacancy concentration allowed in the cubic layers is $BaO_{2\cdot75}$ before transformation to the triclinic *I* phase with complete reduction to Fe^{III} takes place.

The behaviour of the Fe systems may be contrasted with that found for $BaMnO_{3-x}$. In 4*H* $Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot83}$ all the vacancies are found in hexagonal layers (Jacobson & Horrox, 1976) and the distribution can be interpreted in terms of the formation of edge-sharing pairs of trigonal bipyramids containing the Mn^{3+} ions. The phase limits of 6*H* and 10*H* $BaMnO_{3-x}$ (Negas & Roth, 1971) support this model and suggest that O vacancies are incorporated in AO_2 layers in contrast to the $AO_{2\cdot5}$ layers found for both 6*H* $BaFeO_{2\cdot79}$ and $SrFeO_{2\cdot5}$. The difference between the two systems is partly explained by different coordination schemes for the reduced ion. The Mn^{3+} (d^4) ion is stabilized in a trigonal bipyramidal site with a *d* electron configuration, $e_g^2e_g^2a_{1g}^0$. The empty a_{1g} orbital is in the axial direction covalently bonded to two O atoms. This type of coordination is found in, for example, $YMnO_3$ (Yakel, Koehler, Bertaut & Forrat, 1963). High-spin d^5 Fe^{3+}, however, is frequently found in both octahedral and tetrahedral sites, for example in the inverse spinel Fe_3O_4.

The local environment of Fe in $BaFeO_{2\cdot79}$ is shown in Fig. 2. The average Fe–O distances for the face-shared and corner-shared positions are 1·927 and 2·022 Å respectively. The short Fe–O distance in the face-shared octahedra is compatible with a model in which one quarter of these ions are tetrahedrally coordinated (the mean tetrahedral distance in $SrFeO_{2\cdot5}$ is 1·874 Å). The Fe–O distance in the corner-shared octahedra which are thought to be $Fe^{IV}O_6$ is however longer than expected and may be a result of an overall expansion due to the presence of the large Ba^{2+} ions. The O–O distance in the hexagonal layer is short, 2·448 Å. This appears to be a general feature of ABO_{3-x} systems and is found in 4*H* $Ba_{0·5}Sr_{0·5}MnO_{2·83}$ (2·471 Å) and 8*H* $BaMnO_3$ (2·507 Å). The shortest distance corresponds to the highest vacancy concentration.

A further experiment concerning the vacancy distribution in the ABO_{3-x} systems is at present in progress for $BaCoO_{3-x}$.

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The Molecular and Crystal Structure of 5,6-Dihydro-2,4-dithiouridine, $C_9H_{14}N_2O_4S_2$

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5,6-Dihydro-2,4-dithiouridine crystallizes in the space group $P2_1$ with $a=15·393$, $b=7·7509$, $c=4·9850$ Å, $\beta=92·814°$, $Z=2$. The structure was solved by direct methods and refined by full-matrix least-squares techniques to $R=0·035$. The heterocyclic ring displays a twist half-chair conformation with C(5) and C(6) displaced by 0·158 and 0·504 Å on either side of the nucleobase plane. The heterocycle exists in the diketo form. The ribose moiety has C(3′)-*endo* conformation. The glycosidic torsional angle, 23·5°, is *anti*. The conformation about C(4′)–C(5′) is *gauche–trans*. Both S atoms are involved in intermolecular hydrogen bonding; S(2) to O(5′) (3·342 Å) and S(4) to N(3) (3·310 Å). Sugar–sugar interaction is realized through the O(2′)–H···O(3′) (2·724 Å) and O(3′)–H···O(5′) (2·811 Å) hydrogen bonds. There is no base stacking.

Introduction

The occurrence of some S-containing minor nucleosides in t-RNA's has been established. The synthesis of thio-analogues of 5,6-dihydrouridine forms part of a study of possible unusual constituents of t-RNA. These investigations have been undertaken at the 'Ruđer Bošković' Institute by Dr V. Škarić and his coworkers (references in Kojić-Prodić, Liminga, Šljukić & Ružić-Toroš, 1974). Crystals of 5,6-dihydro-2,4-dithiouridine were provided by Dr V. Škarić.

Experimental

Weissenberg photographs recorded with Cu *Kα* radiation indicated $P2_1$ or $P2_1/m$. Since the molecule is optically active, the space group is necessarily $P2_1$.