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A Structural Study of a Nonstoichiometric Niobium–Zirconium Oxyfluoride with the ReO_3 Type Structure

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Within the Zr–Nb–O–F quaternary system a nonstoichiometric compound of the ReO_3 structure is formed with composition limits given by $MX_{2.9}$–$MX_{3.14}$. Crystals at the lower end of this range with a composition of $Nb_{0.55}Zr_{0.45}O_{1.1}F_{1.8}$ ($MX_{2.9}$) have been investigated by optical and electron microscopy and by powder and single crystal X-ray diffraction in order to determine the mode by which the nonstoichiometry has been accommodated in the structure. It was found that the material does not contain crystallographic shear planes or have a perovskite bronze type of structure but contains vacancies in the anion lattice. It seems likely that these defects are associated into clusters with a definite structure rather than being isolated from each other.

Introduction

In recent years, much interest has centred upon materials which support nonstoichiometric phase ranges by the introduction of crystallographic shear (*CS*) planes into a parent structure, and this has been reflected in the appearance of a number of review articles on this subject (*1–4*). One of the best known examples of this type of compound is WO_3, which has often been reported to have an oxygen to metal composition range from 3.0 to approximately 2.96. In reality, this variation in composition is accommodated by varying numbers of *CS* planes within the structure. They are distributed more or less at random, but lie along {102} type planes only (referred to an idealized cubic cell unit). At lower compositions these may order to form homologs of the oxide series W_nO_{3n-1}, but more usually another set of *CS* planes, lying on {103} planes form, generating oxides of general formula W_nO_{3n-2}.

It is of some considerable interest to explain why such *CS* phases form, and to this end, experiments have recently been carried out in which WO_3 has been doped with other cations such as Ti (*5*), Zr (*6*), V (*7*), and Cr (*8*). Such studies, however, by placing emphasis upon the cations present in a WO_3 matrix tend to obscure other trends which may be important, particularly the anion involvement in *CS* plane formation and stability.

On looking for alternative compounds to study which may throw light on both the cation and anion contribution to *CS* plane formation in WO_3 one finds very few with a closely related structure. Of the oxides, only ReO_3 presents itself as a possible candidate, but in practice this compound has proved unsuitable because of its low stability and the ease with which it decomposes to lower stoichiometric oxides or the metal itself on heating in a vacuum. There are, however, three fluorides which have the ReO_3 structure NbF_3, TaF_3, and MoF_3. At present little information is available concerning the nonstoichiometry of these materials. In addition, a number of oxyfluorides, notably NbO_2F, TaO_2F, and $TiOF_2$ have the ReO_3 structure, and of these, *CS* formation has been noted in NbO_2F (*9*) and one well-ordered *CS* phase, Nb_3O_7F, has been characterized (*10*). Because of this it seemed likely that oxyfluorides as a group would be likely to support *CS* plane formation and studies of systems in which a material such as NbO_2F is reacted with other oxides or fluorides containing cations with a formal valence of five or less are of obvious interest.

In this context, the recently reported group of ReO_3 type nonstoichiometric oxyfluorides formed in the Zr–*M*–O–F system (where *M* can be Ti, Nb, or Cr) (*11*) make suitable phases for investigation. The cations Ti, Nb, and Cr all prefer octahedral coordination, and are commonly found in *CS* phases, while the presence of fluoride ions seems to stabilize the octahedral coordination around the Zr atoms in these structures. However, nonstoichiometry in oxide systems containing Zr is often accommodated by anion loss, as the Zr ions seem able to tolerate irregular coordination and do not have a strong desire to retain an octahedral coordination in all circumstances. The presence or absence of *CS* in such phases will then give some information on the relative chemical factors which influence nonstoichiometry in ReO_3 type structures.

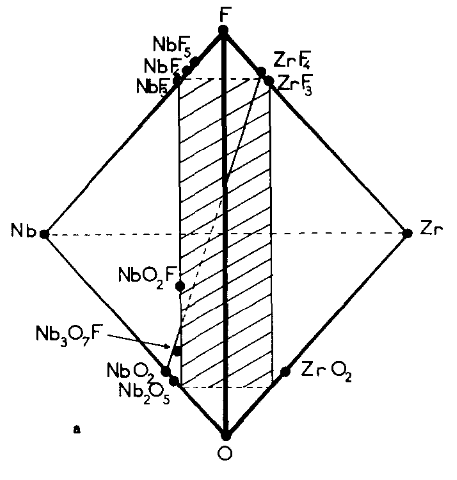

FIG. 1(a). The Zr–Nb–O–F quaternary system, with some ReO_3 related phases indicated.

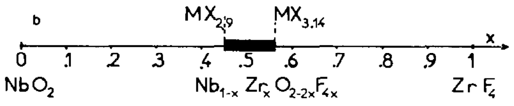

FIG. 1(b). The ZrF_4–NbO_2 line on (a) showing the extent of the ReO_3 phase (Nb, Zr) $X_{3\pm x}$.

In this paper we report a study of one of these phases; that occurring in the Nb–Zr–O–F system between NbO_2 and ZrF_4. A preliminary study by Rannou L'Helgoualch and Lucas (*11*) showed that the cubic phase had a domain of existence from $Nb_{0.55}Zr_{0.45}O_{1.1}F_{1.8}$ ($MX_{2.9}$) to $Nb_{0.43}Zr_{0.57}O_{0.86}F_{2.28}$ ($MX_{3.14}$). A partial phase diagram showing this compound and other ReO_3 related structures in the quaternary Zr–Nb–O–F system is shown in Fig. 1. We have studied samples with the lower anion-to-cation composition by X-ray diffraction and optical and electron microscopy in order to determine how the structure accommodates its anion-to-cation nonstoichiometry. No *CS* planes were found and an anion vacancy type of defect appears to be present in this system.

Experimental

A sample of gross composition $MX_{2.90}$ and of formula $Nb_{0.55}Zr_{0.45}O_{1.1}F_{1.8}$ was obtained by direct reaction between NbO_2 and ZrF_4. The dioxide NbO_2 was prepared by hydrogen reduction of the pentoxide, Nb_2O_5 at 1073°K. The ZrF_4 was a commercial product from Ugine–Kuhlman, purified by successive sublimations under vacuum. The product obtained after heating at 1123°K for 4 days in a sealed nickel tube was black in color and microcrystalline. Numerous crystals suitable for X-ray diffraction studies could be selected by hand.

The material was studied by powder and single crystal X-ray diffraction. Powder photographs were taken using a Guinier–Hägg focusing camera and strictly monochromatic Cu$K\alpha_1$ radiation with KCl added as an internal standard. Single crystal measurements were made with a Nonius CAD-4 automatic diffractometer, using MoK_α radiation. The sample was also examined optically using a Zeiss Ultraphot optical microscope and by electron microscopy using a JEM 100B electron microscope fitted with a goniometer stage and operated at 100 kV. Electron microscope samples were prepared by crushing a small number of crystals in an agate mortar under *n*-butanol. A drop of the resulting suspension was allowed to dry on a netlike perforated carbon film. Only crystal fragments lying over holes in the support film were chosen for examination.

Results

Preliminary Study

Optical microscopy revealed that the sample as prepared was not monophasic but that perhaps three distinct materials were present. Two of these, however, were in very small proportions and the bulk of the preparation consisted of a black well crystalline phase. Much of this latter material had a well-formed cubic habit. The X-ray powder photographs showed a few very weak lines in addition to a strong set which could be indexed in terms of a cubic unit cell with a lattice parameter of 0.394 nm. The weak lines were not identified but serve to confirm the optical microscope results. In all, these observations suggest that the phase range of the cubic compound might be slightly smaller than originally reported and confirms that the crystals chosen for examination are at the lower extreme of the composition range.

Structure Determination

X-ray examination of a single crystal of cubic habit selected from the sample described above confirmed the cubic symmetry of the phase, and revealed the Laüe group to be *m*3*m*. The absence of extinction lead to the assignment of the space group *Pm*3*m* to the phase, which is the same as that of ReO_3. The mean density of the crystals, 3.81 g cm^{-3} is compatible with the presence of one formula unit per unit cell.

Because of the cubic symmetry of the crystals, intensity measurements were restricted to $\frac{1}{8}$ of reciprocal space, that is, to positive values of the indices *hkl*. Of 379 reflections measured, 364 were retained as they complied with the criterion $I > 0.50\sigma(I)$, where

$$\sigma(I) = [|I_M + 4(F_1 + F_2)| \cdot 1/\tau]^{1/2}$$

where I_M is the intensity of the reflection, F_1 and F_2 are measures of the continuous background and τ is the ratio of the maximum velocity to the scanning velocity employed. Taking into account the equivalences

$$I_{hkl} \equiv I_{klh} \equiv I_{lhk} \equiv I_{hkl},$$

92 average intensities were obtained. The relative average variation of the equivalent reflections was 9 % for the group, but fell to 5 % if 22 reflections were rejected for which the variation was greater than 10 %. The greater number of these reflections were not included in the final stage of the structure refinement.

To determine the structure, a preliminary calculation was made assuming an ReO_3 type of unit cell. An average cation (Nb, Zr) was placed at 000, at the origin of the unit cell, and three average anions (O, F) were placed at $\frac{1}{2}$, 0, 0, in the middles of the edges of the cube. Atomic scattering factors were calculated using the data published by Cromer and Weber (*12*). Corrections for anomalous dispersion were also applied, the coefficients $\Delta f'$ and $\Delta f''$ used being those of Cromer (*13*). Because of the similarity between the ions, we have incorporated the Nb^{+4} ions with the Zr^{+4} ions and the O^{-2} ions with the F^- ions. The reliability factor, *R*, calculated for this hypothesis, was found to be

$$R = \frac{\sum|(F_o - Z_K F_c)|}{\sum|F_o|} = 0.13$$

where F_o and F_c are the observed and calculated structure factors and Z_K a scaling constant.

We have attempted to improve this result by refining the value of the isotropic temperature factor and the degree of occupation of the anion sites. For this purpose we have used a general program for structure refinement by the method of least squares. The function minimized is $\sum\omega(|F_o|-Z_K|F_c|)^2$. The weighting factor, calculated following the scheme described by Stout and Jensen (*14*) modified by Grant, Killean and Lawrence (*15*), was taken as

$$1/\omega = \sigma^2(F_o) = K\sigma(\mathrm{I})^2/4\, LP \cdot I + p^2 I.$$

The stability constant *p* was taken to be equal to 0.06 and *K* is a scaling constant. After refinement the values of the parameters

TABLE I

INITIAL VALUES OF PARAMETERS OBTAINED AFTER PARTIAL REFINEMENT OF THE STRUCTURE OF $Nb_{0.55}Zr_{0.45}O_{1.1}F_{1.8}$

Atom	x	y	z	B	No. of atoms on site
(Nb, Zr)	0	0	0	1.72	1
(O, F)	$\frac{1}{2}$	0	0	1.89	2.2

reported in Table I were obtained, corresponding to values of

$$R = 0.092 \text{ and } R_H = \left|\frac{\sum \omega(F_o - Z_K F_c)^2}{\sum \omega(F_o)^2}\right|^2 = 0.093.$$

At this level of refinement one can suppose that only a fraction of the atoms find themselves localized in these two sites, and in particular the 0.7 missing anions occupy another crystallographic site. To check this we have made a three-dimensional Fourier difference projection. All the significant peaks are found in the (110) and equivalent planes. Figure 2 shows the residual electronic density of one of these planes. In this diagram, the density is expressed in units of e/Å^3, and peaks with a value of less than 0.7 e/Å^3 have not been represented. The peaks appear in the neighborhood of the sites normally occupied at (000) and ($\frac{1}{2}$00). The coordinates are described as (x, x, x) with $x = 0.04$ and ($\frac{1}{2}$, x, x) with $x = 0.05$. In particular, no peaks were found at the center of the cell, with coordinates close to ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). It would therefore appear that in such a cell we have a statistical distribution of ions, such that the cations are distributed between the positions (0, 0, 0) and (x, x, x) and the anions between the sites ($\frac{1}{2}$, 0, 0) and ($\frac{1}{2}$, x, x). This suggestion was tested by a further refinement. For this last stage, we have rejected 11 reflections for which the variation relative to the equivalent was greater than 10%. A correction for secondary extinction was also introduced.

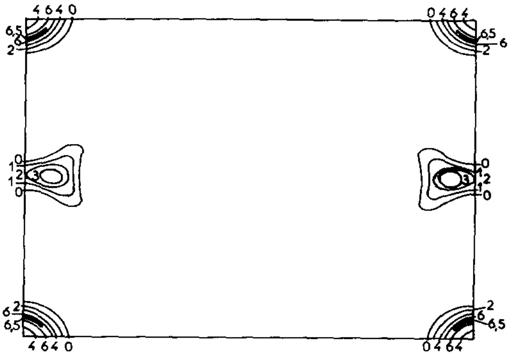

FIG. 2. Residual electron density on the plane (110).

Because of the closeness between the neighboring crystallographic sites the refinable variables are strongly correlated. In this case one can obtain different combinations of the various parameters for comparable values of R and R_H. We reproduce in Table II the group of values corresponding to a solution for which R and R_H are

$$R = 0.026 \quad \text{and} \quad R_H = 0.026.$$

The fractional occupation of the sites 1a and 8g have been fixed at the values indicated after trying several other combinations. The introduction of an anisotropic thermal vibration

TABLE II

FINAL VALUES OF ATOMIC PARAMETERS FOR $Nb_{0.55}Zr_{0.45}O_{1.1}F_{1.8}$

Atom	Site	x	y	z	B_{iso}	No. of atoms on site
(Nb, Zr)	1a	0	0	0	1.61(4)	0.40
(Nb, Zr)	8g	0.029(2)	0.029(2)	0.029(2)	1.04(15)	0.60
(O, F)	3d	0.5	0	0	0.69(7)	0.73(3)
(O, F)	12j	0.5	0.050(2)	0.050(2)	0.90(8)	1.74(4)

parameter did not result in significant improvements in the results. On the other hand, a refinement made under the same conditions, but with 2.9 anions placed between the sites $3d$ and $12j$ resulted in the values

$$R' = 0.044 \text{ and } R'_H = 0.049$$

The ratio of the factors R'_H to R_H was equal to $R'_H/R_H = 1.89$. In this case Hamilton's test (*16*) allows one to conclude that the first suggestion is more likely to be correct, with an uncertainty of less than 0.5%.

The occupation parameters given in Table II reveal that not all the ions occupy the position $(\frac{1}{2}, 0, 0)$ or its close neighbor $(\frac{1}{2}, x, x)$. The contribution of the missing anions (0.4 per unit cell) must, though, be small in view of the low R and R_H values obtained when they are neglected. All further attempts to localize this fraction of the anions has failed. It would seem, therefore, that this missing fraction must be distributed in a nonperiodic fashion over more general positions within the unit cells, resulting in a very small contribution to the diffracted X-ray intensities which is lost in the general background.

Electron Microscopy

The electron microscope study was hampered by the fact that the compound was rather sensitive to the combined effects of electron beam irradiation and vacuum in the microscope column and tended to decompose when observed at high magnification. Low magnification did not seem to have such a serious effect, however, and crystals could be examined for a reasonable period of time under these conditions.

The results of this examination indicated positively that there were no planar faults in the materials. This therefore eliminates the possibility that *CS* is present in the samples and contributes to their nonstoichiometry. The diffraction patterns obtained are quite consistent with the X-ray data and reveal a cubic cell of the ReO_3 type. Some effort was put into a careful examination of the diffraction patterns to check for the presence of diffuse intensities, streaking or superlattice spots. Although many different sections through the reciprocal lattice were taken none revealed such features. As it was possible that beam damage could adversely affect the intensities of such weak scattering in the diffraction pattern, as much of this study as was practicable was carried out using a widely defocused beam and as low a beam intensity as possible.

Finally in order to further check the microstructure of the crystals high resolution lattice images of some fragments were taken. Because of beam damage, this had to be done rapidly, and it was found in practice that fringes from a single row of systematic reflections were more easily observed than the cross-grating pattern from the whole ($hk0$) array. On examination of these images no obvious irregularities in the structures were found.

Discussion

The literature surveyed briefly in the introduction suggests that we can consider these results from two view-points. First we can compare the present compound with others of the type $M_{1+x}X_3$ and thereby assume that additional cations are present in the crystal over and above the stoichiometric ratio. Typical examples of such compounds are the nonstoichiometric phases obtained by reduction of the oxide WO_3 with tungsten or another metal M to yield formulae $WO_{3-\delta}$ (i.e., W_xWO_3) or M_xWO_3. In such phases two structure types have been recorded for compositions similar to that of the $Nb_{0.55}Zr_{0.45}O_{1.1}F_{1.8}$ ($MX_{2.9}$) phase investigated here. These are either *CS* phases, for example WO_{3-x}(*1–4*) and Ti_xWO_3(*5*) or bronzes of the perovskite type, exemplified by Zr_xWO_3(*6*). This latter structure consists of corner sharing WO_6 octahedra and contains the additional M cations in cages formed by the lattice of linked octahedra. As Nb ions are mostly found in octahedral coordination in oxides and oxyfluorides it is likely that the compound we were examining will be similar, so that, if we require a perovskite–bronze type of structure, we need to introduce the Zr ions into the positions between the WO_6 octahedra. In such a case, the formula of the compound would be $Zr_{0.033}Nb_{0.55}Zr_{0.42}O_{1.1}F_{1.8}$ i.e., $Zr_{0.034}$-

MX_3. This is well within the range of composition of the known perovskite bronzes Zr_xWO_3.

The second possibility of accounting for the formula of the compound is to assume that a percentage of the anions are missing and the true formula is then best written as MX_{3-x}. This mode of supporting nonstoichiometry occurs quite commonly in materials related to the fluorite structure, for example, the series of ordered phases formed between ZrO_2 and Sc_2O_3 (*17*).

The electron microscope results are particularly powerful in distinguishing between a *CS* containing structure and the other two, and the present results have shown unequivocally that no *CS* planes are present. The technique is not readily able to distinguish between the other two models, but the fact that no diffuse scattering or streaking was found on the electron diffraction patterns is a clear indication that partial or incomplete long-range ordering or short-range ordering between the structural defects present does not occur under the preparation conditions employed in the present experiments.

The X-ray results have been able to clarify this latter point with some measure of certainty, and it has been shown quite definitely that the material cannot have a perovskite bronze related structure. To prove this we can note that all the electron density in the unit cell is concentrated in the neighborhood of the origin of the cell and the middles of the sides, giving an overall ReO_3 type structure with no evidence for atoms in the cell centre.

Elimination of the *CS* and perovskite models leaves only an anion deficient model of gross formula MX_{3-x}. This is, of course, in accord with the anion site occupation factors recorded in Table II which indicate that less than 3 anions occur per unit cell. However, such a result taken alone is not particularly unequivocal in view of the relatively small weight which is attached to the anion scattering in the refinement. In the present experiments it is supported by the perturbation of the ReO_3 type cell which reflected in the data given in Table II, and which can be explained if one considers anion vacancies to be present in the structure.

At the simplest level, one can consider that the introduction of an anion vacancy will engender a local distortion of the lattice by transforming two MX_6 octahedra into MX_5 polyhedra. These will then relax somewhat so that one can think of several anions in each of these polyhedra migrating towards the vacancy. This relaxation will also be transmitted to the cations, so that locally a fraction of both the anions and cations will be displaced from their normal sites, as indicated by the refined positional parameters of the ions. In general these displacements will depend upon the vacancy concentration and the interaction between vacancies. At the concentration levels implied by the overall formula $MX_{2.90}$ this interaction is likely to be quite substantial. As our results represent an integrated X-ray structure taken over many unit cells it is not possible to specify such relaxations and hence the real structure of such defect clusters in any more detail. Even with the smaller regions examined by electron diffraction, no additional evidence was obtained, and to clarify the structure more closely, other techniques need to be employed.

In conclusion, therefore, we can say that the present study still leaves a number of important questions about the structural nature of these defects unanswered. We can, however, suggest that it seems necessary to attribute a particular role to the Zr^{4+} cation to explain the existence of these phases of high symmetry which contain large concentrations of defects. A preliminary study of the analogous (M, Zr)-X_{3+x} phases which contain an excess of anions with respect to the ideal MX_3 (ReO_3) structure, leads to the same conclusions. In this case we also have an absence of any superlattice reflections in the X-ray diffraction data and structure calculations again reveal that a fraction of the anions and cations are displaced from the normal crystallographic sites. The specific role of the zirconium ions lies in its ability to accept an extreme diversity of coordination polyhedra, which itself results in a great flexibility in the manner of linking of such polyhedra. In the present case, this ability is certainly dominant over the factors which might lead to *CS* formation. Fluorine appears to cause the zirconium ions to lose some of its structural flexibility and to prefer an octahedral coordination. In *CS* structures cations are exclusively found in octahedral coordination and therefore one would perhaps expect that an increase in fluorine concentration would tend to favor the adoption of *CS* as an alternative mode of accommodating the nonstoichiometric deficit found. Further experimental work in other regions of the Zr–Nb–O–F system would be helpful in testing this speculation.

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