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A new anion conductive bismuth–vanadium oxyfluoride

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A new anion conductive oxyfluoride $Bi_2VO_5F_{0.7}$ has been obtained. Its crystal structure, related to the well-known Aurivillius phases, has been determined from powder X-ray and neutron diffraction data combined with a piezo test and magnetic measurements (*I*4*mm*, $a = 3.869(3)$ Å, $c = 15.648(6)$ Å, $R_p = 4.41$, $R_{wp} = 9.50\%$). The transport properties of this compound have been studied as a function of temperature by impedance spectroscopy. The relation of the $Bi_2VO_5F_{0.7}$ crystal structure and anion conductivity with different modifications of $Bi_2VO_{5.5}$ oxide is discussed.

1. Introduction

Recently a new class of material that exhibits high anion conductivity was discovered. These materials are based upon layered bismuth mixed oxides $Bi_2A_{n-1}B_nO_{3n+3}$ with the Aurivillius structure[1] that consists of n perovskite-like layers $[A_{n-1}B_nO_{3n+1}]^{2-}$ sandwiched between fluorite-like bismuth–oxygen sheets $[Bi_2O_2]^{2+}$.

The $Bi_2VO_{5.5}$ phase is of particular interest among them as it has the highest oxide ion conductivity reported. This compound is a one-layer Aurivillius phase with intrinsic oxygen vacancies in the perovskite layer $[Bi_2O_2]^{2+}$-$[VO_{2.5}\square_{0.5}]^{2-}$. It undergoes two structural transitions[1] α-$Bi_2VO_{5.5} \xrightarrow{450\,^{\circ}C} \beta$-$Bi_2VO_{5.5} \xrightarrow{570\,^{\circ}C} \gamma$-$Bi_2VO_{5.5}$ to form three phases: monoclinic α (*C*2/*m*, $a = 5.6120$ Å, $b = 15.2829$ Å, $c = 16.6014$ Å, $\beta = 89.756^{\circ}$),[2] orthorhombic β ($a = 5.543$ Å, $b = 5.615$ Å, $c = 15.321$ Å),[3] tetragonal γ (*I*4/*mmm*, $a = 3.988$ Å, $c = 15.42$ Å).[4]

Details of the $Bi_2VO_{5.5}$ structure are not known precisely. It is considered that at lower temperatures, the oxygen vacancies are associated with the vanadium atoms and form alternating vanadium-centered octahedra and tetrahedra.[1,4] At higher temperatures, the oxygen vacancies are disordered, and the high oxide ionic conductivity exhibited by this material at elevated temperatures (>843 K) is believed to be due to this disorder. From that point of view the concentration of the oxygen vacancies and the defect structure related to it should play an important role (the defect structure is determined by the possible interaction between the defects). The concentration of the vacancies may be changed by partial replacement of the vanadium atoms with metal atoms in a different oxidation state or by filling the vacancies with some other anion, for example, fluorine.

There have already been numerous different investigations conducted on the former,[1] but as for fluoride derivatives of the structure in question, the first reports have appeared only recently.[5,6] In these works the solid solutions (BIMVOXF) $Bi_2V_{1-x}M_xO_{5.5-5x/2}F_{2x}$ (M = Zn,[5] Cu[6]) were found and the influence of the fluorine on their transport properties determined.

At the same time nothing is known on the prospect of fluorination of the non-doped $Bi_2VO_{5.5}$ (BIVOX) and its influence on the ion-conducting properties of this phase. The present article is devoted to this question.

The well-known Bi_2NbO_5F may be taken as the prototype of the initial stoichiometric phase. It has a one-layer Aurivillius structure without anion vacancies.[7] Thus, the composition of the 'model' stoichiometric oxyfluoride may be written as Bi_2VO_5F.

2. Experimental

2.1 Synthesis of materials

The starting materials Bi_2O_3 and V_2O_5 were guaranteed to be better than 99.9% pure. BiF_3 was prepared by boiling Bi_2O_3 with 40% HF, the wet product obtained was further heated at 673 K for 3 h under a flow of anhydrous HF generated by decomposition of dry KHF_2. To obtain BiOF a 1 : 1 mixture of bismuth oxide and fluoride was ground in agate mortars, pressed into tablets and placed into copper tubes (prior testing of the tube material was carried out to ensure it did not react with the sample). After degassing under dynamic vacuum for 2 h and filling with dry argon the tube (80 mm length and 10 mm i.d.) was sealed. The sample was annealed at 673 K for 12 h.

X-Ray powder diffraction (STOE STADI/P, $CuK_{\alpha 1}$, Ge crystal as monochromator) was used for identification of products of the reaction just mentioned.

The bismuth–vanadium oxyfluoride was synthesized using stoichiometric mixtures of initial components in accordance with the equations

$$2BiOF + Bi_2O_3 + V_2O_5 = 2Bi_2VO_5F$$

or

$$2BiF_3 + 5Bi_2O_3 + 3V_2O_5 = 6Bi_2VO_5F$$

The starting charges were ground, then either pressed into pellets and placed in a copper envelope and processed as described above, or placed as powders in an alumina or beryllia crucible sealed in a silica ampoule. The silica ampoules were evacuated (residual pressure was 10^{-2} Torr). The samples were heated at 873 K for 6 days. Sometimes during the heating small regular crystals formed on the pellet surfaces.

2.2. Diagnostics of new phase

X-Ray analysis. Results of X-ray analysis showed that the same product forms in all versions of the bismuth–vanadium

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Table 1 Powder X-ray diffraction data for 'Bi_2VO_5F'

d/Å	I/I_0	h	k	l	Q_{exp}[a]	Q_{calc}
7.8320	19	0	0	2	163	163
3.9221	2	0	0	4	650	653
3.7597	12	1	0	1	707	709
3.1093	100	1	0	3	1034	1035
2.7382	26	1	1	0	1334	1337
2.6083	11	0	0	6	1470	1470
2.4340	10	1	0	5	1688	1689
2.2434	8	1	1	4	1987	1990
1.9356	15	1	0	7	2669	2669
		2	0	0		2668
1.8887	17	1	1	6	2803	2806
1.6427	17	2	1	3	3706	3709
1.5859	10	1	0	9	3976	3975
1.5541	7	2	0	6	4140	4143
1.5124	3	2	1	5	4372	4363
1.3751	2	2	0	8	5288	5287

[a] $Q = 10^4/d^2$.

oxyfluoride synthesis. X-Ray patterns were fully indexed ($F_{15} = 22$, $M_{15} = 48$) in the tetragonal crystal system with unit cell parameters: $a = 3.868(1)$ Å, $c = 15.658(6)$ Å (Table 1). Systematic absences were consistent with *I*-centring.

X-Ray study of a single crystal (CAD-4, Mo K_α radiation) showed that its unit cell parameters ($a = 3.8969(5)$ Å, $c = 15.416(2)$ Å) differ from those obtained from the powder samples. This may be caused by the small difference in the anion stoichiometry in powder and single crystal samples.

Microprobe analysis. The chemical composition of the product annealed in a copper container was clarified by microprobe analysis data (CAMEBAX microanalyzer, SI-Li detector LINK AN10000). Eight spots were used to get reasonable statistics. The following ratio for heavy elements was obtained: Bi : V : F = 2.01(5) : 1.04(7) : 0.67(5). By the same method the absence of copper in the sample was established. The results indicate that the obtained sample has a stoichiometry different from that expected, therefore it will be referred to as 'Bi_2VO_5F'. The same data indicate partial reduction of V(v) to V(iv).

Magnetic measurements. The measurements were carried out by Faraday's method at 293 K in magnetic field 5–10 Oe. The specific spin receptivity was 1.73 μ_B giving evidence for the presence of a system with a lone electron, *e.g.* V^{4+}.

The presence of V^{4+} ions (outer electron shell $3s^23p^63d^1$) was also monitored by electron paramagnetic resonance (EPR) spectroscopy at the X band (about 9 GHz). EPR spectra were recorded on a Varian E-3 EPR Spectrometer at 77 K. The amount of paramagnetic centers in the sample (N_x) was defined as $N_x = N_{st}S_x/S_{st}$, where N_{st} is the amount of paramagnetic centers in the standard sample (single crystal of $CuSO_4 \cdot 2H_2O$), S_{st} and S_x are the areas occupied by the absorption curves of standard and tested samples normalised to the same recording conditions. The relative precision of the determination of the paramagnetic centers concentration was $\approx \pm 10\%$.

According to the EPR spectroscopy results the amount of paramagnetic centers (V^{4+} ions) was 31% of the total amount of vanadium.

DTG. Measurements were carried out on the Paulic Paulic Erdei derivatograph in an Ar atmosphere on a tablet sample placed in a Pt holder. The speed of heating was 10 K min^{-1}. From the DTG data the sample started to lose mass at a temperature near 643 K. According to the X-ray analysis after the heating the sample was a mixture of Bi_2VO_5 and $Bi_2VO_{5.5}$.

Piezotesting. A standard piezotest carried out on a VÊ-16 electrometer showed a considerable piezo-response. The relatively high value of piezo-response indicated that the substance itself and not the adsorbed water was responsible for the piezoelectricity.

2.3. Search for solid solutions based on 'Bi_2VO_5F'

To find oxofluoride phases with different fluorine contents a search for solid solutions based on 'Bi_2VO_5F' was conducted.

First of all we attempted to introduce 'additional' fluorine into the non-stoichiometric 'Bi_2VO_5F' using XeF_2. The initial 'Bi_2VO_5F' was ground in an agate mortar. In a dry camera (dried with P_2O_5) 'Bi_2VO_5F' and XeF_2 were placed into a nickel crucible, which was then closed with a nickel lid and flame-sealed in a copper ampoule. Then the mixture was kept at 523 K for 2 days. According to the X-ray phase analysis the sample did not correlate to the initial phase or belong to any known phase in the Bi–V–O–F system. Obviously, the introduction of fluorine into the compound with preservation of the initial structure is impossible even with such a soft fluorinating agent as XeF_2.

Also, the phase relations in the 'Bi_2VO_5F'–BiOF, $BiVO_4$, $Bi_2VO_{5.5}$ systems were studied. To do so, mixtures of Bi_2O_3, BiF_3, V_2O_5, taken in the required ratios with a 10 molar percent step in each of the above systems were calcined for 6 days at 873 K in copper containers as described above. The samples obtained were studied with X-ray powder diffraction. The formation of an extensive solid solution was not observed in any of the studied systems.

2.4. Structural studies

To determine the crystal structure of the obtained compound three diffraction experiments were performed: X-ray and neutron experiments on powder samples and an X-ray experiment on a single crystal sample. The reasons for such a combination were the following. Firstly, the determination of light atoms' (O, F) co-ordinates is difficult on a sample containing heavy ones (Bi) if only X-ray diffraction is used; neutron diffraction provides better information on lighter atom positions. However, due to the very low neutron scattering length of vanadium it is impossible to detect this using neutron diffraction. On the other hand, as shown above, the single crystal composition was slightly different from the one determined for the powder sample. Hence the structure solution algorithm was as follows: from the single crystal data the heavy atoms were located, with these results the neutron data was treated to determine the light atoms' positions (set as oxygen), their occupancies and thermal parameters. With this model the final structure refinement was confirmed with the X-ray powder data.

2.5. Structure determination

Among the crystals mentioned above we found a single crystal suitable for structural analysis. An X-ray diffraction study of the selected single crystal was carried out on a CAD-4 diffractometer (Ge monochromator, MoK_α radiation). For obtaining diffraction data ω–θ scanning of 1/4 sphere was used at room temperature. Fifteen well-centered reflections were used for accurate cell determination. The X-ray data were corrected by Lorentz and polarization factors, and a semi-emprical absorption correction was used with 6 reflections at χ about 90°. The powder neutron diffraction data were collected at 295 K on the high-flux powder diffractometer Polaris at the ISIS facility, Chilton, UK. Approximately 3 g of powdered sample were contained in a cylindrical vanadium can. The X-ray powder data were obtained on a STOE STADI/P diffractometer in the 2θ range 10–110°. The single crystal data were analysed using the SHELX-97[8] program; the powder data

Table 2 Crystallographic data for 'Bi_2VO_5F'

Sample	Single crystal	Powder	Powder
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	*P*4	*I*4*mm*	*I*4*mm*
Cell constants (298 K)			
a/Å	3.8969(5)	3.86367(5)	3.86042(4)
c/Å	15.416(2)	15.6886(4)	15.6834(2)
Instrument	CAD-4	Polaris	Stoe STADI/P
Radiation	$MoK_{\alpha 1}$; λ = 0.70926 Å	Neutron TOF	$CuK_{\alpha 1}$; λ = 1.54056 Å
θ–ψ, degrees	4.11–21.07		
d-range/Å		0.47–4.2	
2θ-range/deg			10.0–110.0
No. of reflections	113	748	66
No. of reflections with $I > 4\sigma$ [F_0]	111		
R_1, R_p (powder) (%)	5.65	4.41	10.1
wR_2, R_{wp} (powder) (%)	6.62	9.50	13.1

Table 3 Atomic co-ordinates and thermal parameters for 'Bi_2VO_5F' from neutron data

Atom	Wyck-off	Occ.	*x*	*y*	*z*	U_{eq} × 100/Å^2
Bi1	2a	1	0	0	0.323(3)	2.06(7)
Bi2	2a	1	0	0	−0.339(3)	1.54(7)
V	2a	1	0	0	0	1.00
O1	4b	0.5	0	0.5	0.022(3)	4.5(1)
O2	2a	1	0	0	0.102(3)	4.3(1)
O3	4b	1	0	0.5	0.235(3)	0.83(3)
O4	8c	0.25	0.095(2)	0.095(2)	−0.110(3)	6.1(4)
O5	4b	0.5	0	0.5	−0.021(3)	4.5(1)

were analysed using the GSAS suite.[9] Relevant data collection and refinement parameters of these experiments are given in Table 2.

At first the heavy atoms were located with the MULTAN program from the CSD package.[10] The co-ordinates of the light atoms were obtained with difference Fourier synthesis. The final refinement was done with the SHELX-97 program. We were unable to locate one of the oxygen atoms from this single crystal refinement. The best model of the structure (R_F = 5.65%) was found for space group *P*4, which is consistent with the piezoelectric properties we found earlier.

The model obtained was applied to the neutron data, but the solution in the *P*4 space group was unstable. A stable solution was obtained in the *I*4*mm* space group in which 3 versions were tested: 1) with anisotropic refinement for O1/O5 and O2/O4 (Table 3) in the VO_6 octahedron; highly anisotropic values gave good evidence for disordering of these atoms; 2) with fixed U_{iso} for these atoms and refinement of the occupancy—a slightly low value was refined at each site, so conclusive discrimination

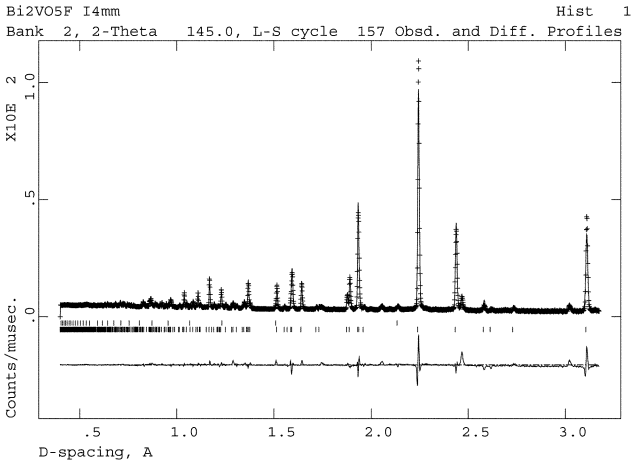

Fig. 1 Final neutron Rietveld refinement plot for 'Bi_2VO_5F', space group *I*4*mm*.

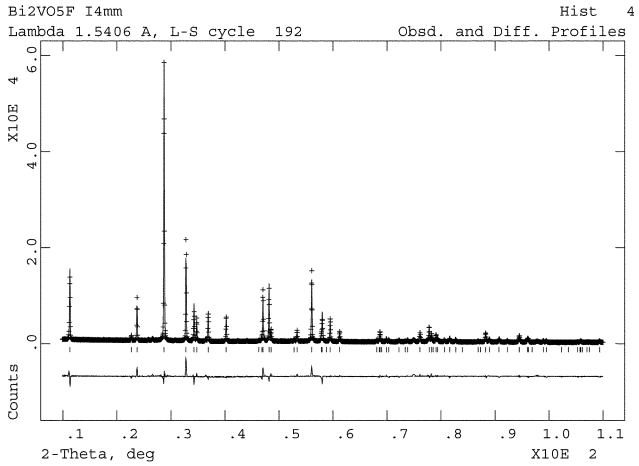

Fig. 2 Final X-ray Rietveld refinement plot for 'Bi_2VO_5F'.

of the possible ordering of anion vacancies cannot be made; 3) with fixed occupancies but disordered positions for atoms O1/O4/O5; this was found to be the best model—perhaps significantly, the two 'apical' sites O2 and O4 display differing behaviour, with O4 appearing significantly more 'disordered'—this may be suggestive of a partial ordering of O vacancies at this site and, perhaps, the driving force for the observed polar space group.

Co-ordinates and thermal parameters of the atoms are given in Table 3, experimental, theoretical and difference profiles are shown in Fig. 1.

As a final check on the validity of this model, the final model from the neutron structure refinement was used to fit the X-ray powder data. Positions of the oxygen atoms were fixed—Bi and V sites were refined. No significant deviations of any of these parameters were observed—moreover, the thermal parameter for V remained at a sensible value, suggesting no significant deviation from the ideal position. The reliability factors for this refinement are given in Table 2, the final Rietveld profiles in Fig. 2. Final interatomic distances from the neutron refinement are presented in Table 4.

Table 4 Interatomic distances for 'Bi_2VO_5F' from the powder neutron refinement

Bond		Distance/Å
Bi1–O3/Bi2–O3	×4	2.365(2)/2.247(2)
V–O1/O5[a]	×4	1.93
V–O2/O4[a]	×2	1.60(5)/1.73

[a]Calculated for the ideal 'ordered' positions of O1/O5 (0,0.5,0) and O4 (0,0,−0.110).

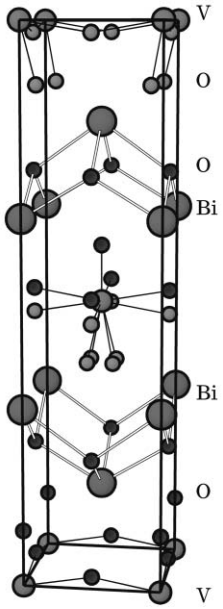

Fig. 3 Model of the unit cell of 'Bi_2VO_5F' (*all* positions of the light atoms are shown).

2.6. Description of structure

The structure was solved under the assumption of the statistical distribution of oxygen and fluorine in the same positions, but all anions were set as 'oxygen' (neutron scattering lengths, $b_O = 5.805 \times 10^{-15}$ m, $b_F = 5.65 \times 10^{-15}$ m).

The obtained solution of the 'Bi_2VO_5F' structure in the non-centrosymmetric *I*4*mm* space group agrees both with the systematic absences in the powder X-ray data and with the results of the piezo-test. The single crystal data, however, suggest a possible very subtle lowering of symmetry to primitive. As there is no evidence for lowering of symmetry to orthorhombic in any of our diffraction data, the polar axis is confirmed as *c*, which may possibly be related to disorder or vacancies around the apical anion sites of the VO_6 octahedron. There is no evidence of an off-centre displacement of the V atom itself. The acceptable values of the reliability factors and crystallographic parameters in our solution indicate that the model adequately describes the structure of the new oxyfluoride.

The compound has a layered structure (Fig. 3) close to that of the Aurivillius phases. One can distinguish a fluorite-like layer formed by the Bi and O3 atoms. The anions around the vanadium atoms form an octahedron-like figure, but each vertex of this octahedron is split into two or four positions statistically filled with anions. In the (*ab*) plane the octahedra connect through their vertices similarly to the way they do in the Aurivillius phases.

2.7. Ionic conductivity measurements

The measurements were performed by the AC method on cylindrical tablets (thickness 0.5–1.5 mm, diameter 8 mm). Silver paste electrodes were placed on a tablet. Silver electrodes were deposited by sputtering metal on both planar faces of the previously sintered sample. Complex impedances were measured using a Solartron 1255 frequency response analyzer with a Solartron 1286 electrochemical interface in the 1–10^6 Hz frequency range. Impedance spectra obtained for each temperature were treated by the equivalent circuit method using complex nonlinear least-squares fitting.

The sample demonstrated quite high ionic conductivity: at 573 K it is as high as 10^{-3} S cm^{-1}. The conductivity–temperature dependence between 300 and 558 K exhibits

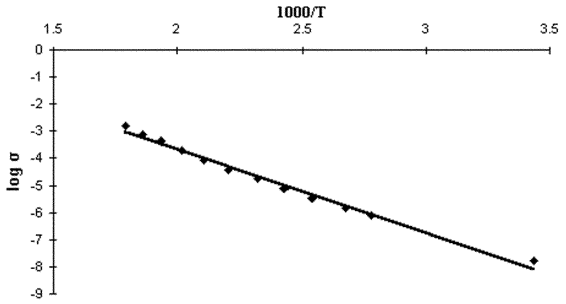

Fig. 4 Arrhenius plot of conductivity for'Bi_2VO_5F'.

Arrhenius-type behaviour (Fig. 4). A linear fit to $\sigma(T) = \sigma(0)\exp(E_a/kT)$ is shown, with a correlation coefficient of 0.97. The activation energy ($E_a = 0.62$ eV) compares well with those determined for BiCuVOF samples with maximum F contents ($E_a = 0.60$ eV).[6] However, in Fig. 4, some degree of curvature may be noted above 495 K. In our opinion this may be due to an ordering phenomenon that is a common feature in both BiMVOX (the γ–γ' transition[11,12]) and BiMVOF[6] phases. For example, in BiZnVOF[6] there is an analogous curvature at a similar temperature. The low temperatures of these anomalies in the F-containing systems testify to the important role of fluorine in these ordering processes.

3. Discussion

During this work the first non-doped bismuth–vanadium oxyfluoride was synthesized. Its stoichiometric formula should be Bi_2VO_5F, but the experimental data indicate that the new phase contains less fluorine, and vanadium in the mixed oxidation state (IV/V). This does not come as a surprise, since V(IV) was also observed in $Bi_2VO_{5.5}$ synthesized in evacuated containers.[13] From the results of microprobe analysis and EPR we can give the formula $Bi_2V^{V}_{0.7}V^{IV}_{0.3}O_5F_{0.7}$ (with the precision shown above), the oxygen content is only derived from the electrical neutrality assumption.

The lattice dimensions of the fluorinated phase are close to those of the γ-modification of $Bi_2VO_{5.5}$, but we suppose the true symmetry of the compound is lower, although none of our attempts to find a superstructure succeeded.

During our solving of the 'Bi_2VO_5F' structure the anion composition was considered to be solely oxygen, because the methods used did not allow us to distinguish between the oxygen and the fluorine atoms. The final values of Bi–O and V–O distances are rather similar to those observed in the oxides. Since the ranges of V–O and V–F bond lengths are similar, the fluorine position could not be located unambiguously.

In the fluorite-like blocks of the fluorinated Sillen and Aurivillius phases the O3 position is never occupied by fluorine atoms. Thus in the compound under discussion it can be considered as occupied exclusively by the oxygen atoms. The nearest neighbours of bismuth—O3—form a square, which together with the O2/O4 square forms a square antiprism around the bismuth atom. However, the Bi–O2/O4 distance is relatively large ($\sim$2.9 Å, calculated from the ideal, ordered position of O(4) at (0,0,−0.110)), obviously because of the influence of the Bi(III) atom lone electron pair which is directed to the O2/O4 layer. Thus, these O atoms should perhaps not be included in the bismuth co-ordination sphere, leaving its polyhedron open. Such a type of co-ordination is common for cations with a lone electron pair. Usually it is described as a square pyramid BiO_4E, where E is a lone electron pair located at one apex.

Consequently, the fluorine atoms are most likely to be located in the vertices of the vanadium polyhedron. The vanadium is coordinated, on average, by an octahedron of O/F anions, but the disorder around O1/O5 and O4 suggests some

degree of local 'tilting' of the vertex-shared octahedra. Due to the disorder, the associated V–O bond lengths in Table 4 have been quoted as mean values, without errors, for idealised O positions. Due to the slight anion deficiency, the 'real' vanadium coordination number probably varies from four to six.

With all the above-discussed experimental data the formula of the new oxyfluoride can be written as $[Bi_2O_2][V^{V}_{0.7}V^{IV}_{0.3}O_3F_{0.7}\square_{0.3}]$ (where $\square$ = anion vacancy).

Thus, the described oxyfluoride is a new representative of the family of one-layer Aurivillius compounds. In this family two types of phases can be distinguished: $[Bi_2O_2][WO_4]$–$[Bi_2O_2][NbO_5F]$–$[Bi_2O_2][TiO_4F_2]$ and $[Bi_2O_2][VO_{5.5}\square_{0.5}]$–$[Bi_2O_2][VO_3F_{0.7}\square_{0.3}]$. Formally, another member may be added to the latter group—$Bi_4V_2O_{10}$. There the vanadium–oxygen layer is formed from semioctahedra (pyramids) of VO_5 linked through basal vertices,[14] *i.e.* the compound may be written as $[Bi_2O_2]_n[VO_3\square]_n$.

The first group mentioned above is composed of stoichiometric phases, the structures from the other contain a certain number of oxygen vacancies. The distribution of the vacancies depends on the temperature. At low temperatures the defects are probably ordered, with increasing temperature the degree of ordering decreases until the transition to complete disorder occurs. This causes the existence of three polymorphic modifications of $Bi_2VO_{5.5}$ and $Bi_4V_2O_{10}$.[1,14] Filling part of the vacancies with fluorine atoms leads as shown above to the disordered structure similar to γ-$Bi_2VO_{5.5}$.

The discussed structural features of different representatives of the Aurivillius phases have a crucial influence on their transport properties. In stoichiometric Bi_2WO_6 single crystals ionic conductivities (as high as 10^{-2} S cm^{-1}) have been observed only at 1173–1223 K.[1] The Aurivillius phase $Bi_2VO_{5.5}$ with oxygen-deficient perovskite layers exhibits significant oxide conductivity (over 10^{-1} S cm^{-1}) and an extremely low activation energy (0.17 eV) at 873 K. We were able to measure transport properties of 'Bi_2VO_5F' only to 573 K because of its low thermal stability. At this temperature its conductivity (10^{-3} S cm^{-1}) is higher than that of α-$Bi_2VO_{5.5}$ (10^{-5} S cm^{-1})[1] at the same temperature and about as high as that of the doped BiMeVOx phases.[1]

Unfortunately, we were unable to make samples with different fluorine contents and could not study the dependence of the conductivity from the concentration for the fluorinated phases. But as mentioned in the introduction fluorination of $Bi_2VO_{5.5}$ should lead not only to a change of the number of the anion vacancies, but also to a change of the defect structure of the phase dependent on the defect concentration. The data of the above mentioned works[5,6] point to that statement indirectly too. In those works $Bi_2V_{1-x}M_xO_{5.5-5x/2}F_{2x}$ (M = Zn, $0 < x < 0.25$,[5] M = Cu, $0.10 \leqslant x \leqslant 0.20$[6]) solid solutions were studied. In the former case small values of x correspond to the α-$Bi_2VO_{5.5}$-type phase, which at $x \approx 0.02$ transforms into the β-modification and at $x \approx 0.07$ to the γ-modification. The other solution exhibits a γ-$Bi_2VO_{5.5}$-type structure for all studied concentrations. In both cases the c parameter of the tetragonal cell increases with x irregularly, while the a parameter changes in different ways: in the Zn system it decreases smoothly when x increases, and in the Cu system it has two minima. This structural dissimilarity probably causes different conductivity dependences from the concentration. At 573 K the dependence for Zn-containing samples has a sinusoidal character, and for Cu it dramatically decreases with x. The maximum amount of F in the doped phases is considerably less than in 'Bi_2VO_5F', therefore it is difficult to compare their transport properties.

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References

1 K. R. Kendall, C. Navas, J. K. Thomas and H.-C. zur Loye, *Chem. Mater.*, 1996, **8**, 642.
2 O. Joubert, A. Jouanneaux and M. Ganne, *Mater. Res. Bull.*, 1994, **29**, 175.
3 K. B. R. Varma, G. N. Subbana, T. N. Guru Row and C. N. R. Rao, *J. Mater. Res.*, 1990, **5**, 2718.
4 F. Abraham, J. C. Boivin, G. Mairesse and G. Nowogrocki, *Solid State Ionics*, 1990, **40**(41), 934.
5 H. Jacobsoone, C. Follet-Houttemane and J. C. Boivin, *Solid State Ionics*, 1998, **113–115**, 607.
6 I. Abrahams, J. A. G. Nelstrop and F. Krok, *Solid State Ionics*, 2000, **136–137**, 61.
7 B. Aurivillius, *Ark. Kemi*, 1952, **5**, 39.
8 G. M. Sheldrick, in *Crystallographic Computing 6*, ed. H. D. Flack, L. Pakanyi and K. Simon, Oxford University Press, Oxford, 1993, pp. 111–122.
9 A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report LA-UR-86-748, 1987.
10 L. G. Akselrud, Yu. N. Grin, P. Yu. Zavalij, V. K. Pecharsky and V. S. Fundamentsky, CSD—a universal program package for single crystal and/or powder structure data treatment. See http://imr.chem.binghamton.edu/zavalij/CSD.html
11 O. Joubert, A. Jouanneaux, M. Ganne, R. N. Vannier and G. Mairesse, *Solid State Ionics*, 1994, **73**, 309.
12 I. Abrahams, F. Krok, D. Bangobango, W. Bogusz and J. A. G. Nestrop, *Solid State Ionics*, 1996, **111**, 37.
13 I. Abrahams, A. J. Bush, F. Krok, G. E. Hawkes, K. D. Sales, P. Thornton and W. Bogusz, *J. Mater. Chem.*, 1998, **8**, 1213.
14 S. Sorokina, R. Enjalbert, P. Baules, A. Castro and J. Galy, *J. Solid State Chem.*, 1996, **125**, 54.