Tribochemical Synthesis and Structure of K_2BiF_5

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The synthesis of K_2BiF_5 by a tribochemical reaction is reported. This compound crystallises in a K_2SmF_5-type arrangement with the lattice parameters $a = 11.3862(2)$, $b = 7.5480(1)$, $c = 6.6008(1)$ Å and space group *Pnma*. The effect of substituting Bi into the K_2SmF_5-type structure is discussed in comparison with other compounds considering the effect of the lone-pair activity of Bi^{3+}.

Key words: Fluorobismutates, Lone-pair Effects, Deformation Tensor

Introduction

In an attempt to synthesise fluorovanadates we have studied the reactions of vanadates with various fluorides in high-temperature reactions. When trying to react $BiVO_4$ with KHF_2 we noticed that a chemical reaction already takes place during the mixing procedure of the powders. The detailed analysis of the products – as discussed below – showed that grinding the powders resulted in the formation of new compounds according to the equation

$$BiVO_4 + 4\,KHF_2 \rightarrow K_2BiF_5 + K_2VO_2F_3 + 2\,H_2O.$$

This fluorobismutate was hitherto unknown, and only d values taken from a powder diagram of a compound were reported, whose composition was postulated from the study of the KF-BiF_3 phase diagram by thermoanalysis [1]. Due to the similarity of the diagrams the authors conjectured that there is a close structural relationship to ternary fluorides of the rare earth elements having the composition A_2LnF_5 (A = alkali ions, Ln = rare earth cations). We therefore extended our studies to other ways of preparation and to the determination of the structure of this compound. The structure of the second product was known before [7]. $K_2VO_2F_3$ crystallises in another A_2BF_5-type arrangement (B = trivalent cation; Rb_2CrF_5 type), and it was important to know whether these two structures play a role in this reaction.

Experimental Section

The reaction mentioned above was carried out in the following way: Powders of $BiVO_4$ and KHF_2 in a molar ratio of 1 : 4 were ground in diethyl ether in an agate mortar using agate balls for 5 h. The ether was then let to evaporate, and the resultant powder was dried for 15 h at 100 °C in air.

To make clear whether solid solutions of the type $K_2(BiF_2)_{1-x}(VO_2)_xF_3$ exist, K_2BiF_5 had to be prepared independently.

For the synthesis of pure K_2BiF_5 we have used the following procedure: BiF_3 was milled together with KHF_2 in a molar ratio of 1 : 2 under argon and then heated to 200 °C in air in a platinum crucible in a dry box. Powder samples were mounted into the cavity of a steel disk for the use as flat specimens in reflecting geometry, and XRD scans were taken at the ANKA synchrotron of the Karlsruhe facility using a wavelength of 1.0882 Å. The measured range was 10 – 70° in 2θ with a step width of 0.0025° using 2 multi-element monochromators together with X-ray mirrors on the primary side and a Si monochromator as analysator on the secondary side for high resolution and lasted for about 8 h for a total scan. Rietveld refinements were done with the program TOPAS (version 2.1, Bruker AXS).

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-418777.

Results

Structure determination and refinement

Grinding KHF_2 with $BiVO_4$ as described above yields the compounds K_2BiF_5 and $K_2VO_2F_3$ in a tribochemical reaction at ambient temperature, the latter compound being clearly identified as the only second

Table 1. Structural parameters of K_2BiF_5 (a = 11.3862(2), b = 7.5480(1), c = 6.6008(1) Å, R_{Bragg} = 4.86, R_{wp} = 17.76, space group *Pnma*, B_{eq} = 1.77(2) for all sites).

Atom	Wyckoff position	x/a	y/b	z/c
Bi	4*c*	0.0468(1)	1/4	0.0660(1)
K	8*d*	0.1666(3)	0.4986(7)	0.5104(4)
F1	4*c*	0.9919(8)	1/4	0.3973(14)
F2	4*c*	0.1722(8)	1/4	0.8142(15)
F3	4*c*	0.2128(9)	1/4	0.2248(17)
F4	8*d*	0.9046(7)	0.4594(8)	0.8797(12)

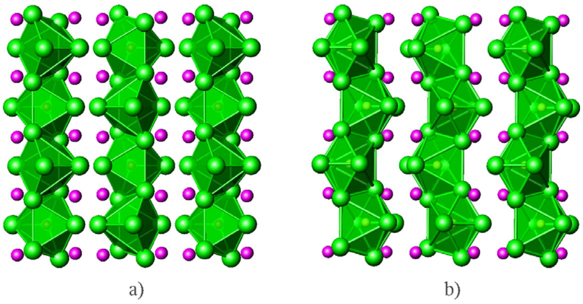
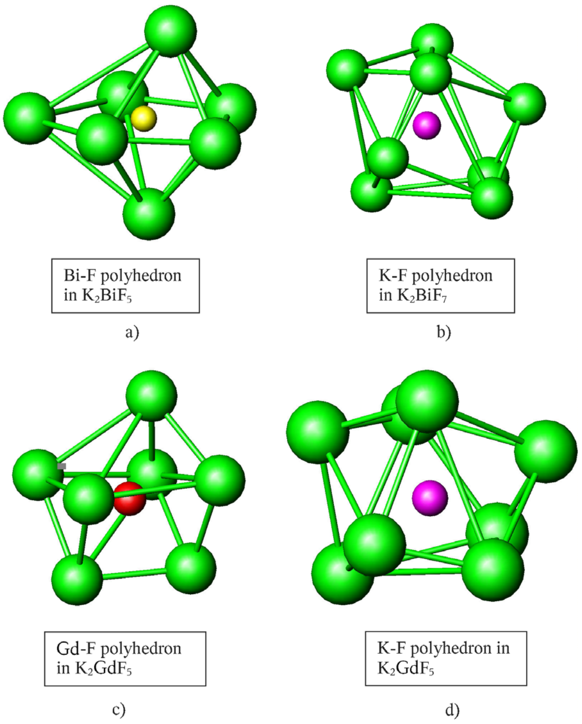

a) b)

Fig. 1. Comparison of the structure of K_2BiF_5 (a) with that of K_2GdF_5 (b) in a view along [001]; the chains of edge-sharing BF_7 polyhedra and the K ions are shown.

phase in the powder diagram. This compound crystallises in the Rb_2CrF_5 type [2] and may therefore also be classified as an A_2BX_5-type structure. (A refinement of the lattice parameters yielded the values a = 7.3948(1), b = 5.6505(1), c = 11.4210(2) Å).

This structural arrangement is realised in compounds with fairly small B-type cations. For compounds with larger cations other structures are known. In the series of lanthanide compounds of the type K_2LnF_5 (*Ln*: Sm–Yb; one of the two modifications of the Nd compound also belongs to this type [3]) the so called K_2SmF_5 type occurs. Compounds having this structure in most cases are described in the space group $Pn2_1a$ [4] and its centro-symmetric variant *Pnma* [3].

The powder diagram of K_2BiF_5 as prepared tribochemically – and also by the second variant starting from BiF_3 and KHF_2, where only minute traces of BiOF could be detected as a second phase – could be indexed on the basis of an orthorhombic cell. The lattice parameters were refined to a = 11.3862(2), b = 7.5480(1), c = 6.6008(1) Å (R_{Bragg} = 6.35), values fitting very well those observed for the K_2SmF_5-type compounds. Using the positional parameters of this structure as a starting set, the data could be refined to the values given in Table 1 for K_2BiF_5 when using the centro-symmetric space group *Pnma*. Attempts to use space group $Pn2_1a$ did not result in better residuals. From the published parameters of the rare earth compounds the pseudo-symmetry is obvious, however, the deviations from the higher symmetry are quite distinct. On the other hand, a later structure determination of K_2GdF_5 with single crystals has clearly shown the higher symmetry [3], so the existence of examples with polar symmetry is not proven. For a comparison of the structures we will therefore use the data of K_2GdF_5, the structure of which has been determined with single crystal data.



a) b) c) d)

Fig. 2. Comparison of coordination polyhedra in K_2BiF_5 (a, b) and K_2GdF_5 (c, d).

Discussion

In Fig. 1 the structure of K_2BiF_5 is compared with that of K_2GdF_5 in corresponding projections. In both cases we see strands of edge-sharing BF_7 polyhedra along [010] with the K atoms in between coordinated by 8 fluorine atoms. The overall coordination may be given as $K_2^{[8]}B^{[7]}F_3^{[5]}F_2^{[4]}$ showing that fluorine participates in two different coordination patterns. The geometry of the coordination polyhedra is slightly different; Fig. 2 gives a comparison. The sevenfold coordination around Gd can be described as a capped trigonal prism or a triangle over a square, whereas in the case of Bi it is closer to a pentagonal bipyramid. The average distance Bi–F is 2.34 Å spreading from 2.16 to 2.60 Å, for Gd–F it is 2.29 Å with a smaller spread from 2.22 to 2.44 Å. With two of the equatorial F ligands having the largest distances, one may conjecture that there is a certain $6s^2$ lone-pair activity of Bi^{3+}, which causes the structural differences between the two types of structure.

However, this stereochemical effect is quite small, especially when comparing it with the lone pair effect in K_2SbF_5 [5] where we find a pronounced ψ-octahedral co-ordination of Sb by F. The observation thus confirms the general rule that the stereochemical effect of lone pairs is reduced when moving to higher homologues in the same group of the periodic system.

The polyhedra around K in both compounds are rather asymmetric and could be approximated by a bicapped trigonal prism, the mean K–F distance being 2.41 Å in K_2BiF_5 (spreading from 2.69 to 2.83 Å) and 2.76 Å in K_2GdF_5 (spreading from 2.65 to 2.86 Å).

Apart from the local distortions it is interesting to see how the larger cation Bi and its stereochemistry affect the macroscopic parameters of the structure, *i. e.* the cell parameters. For a more profound discussion it is useful to compare the changes in lattice parameters along the line of isotypic rare earth compounds with the effects of the Bi substitution.

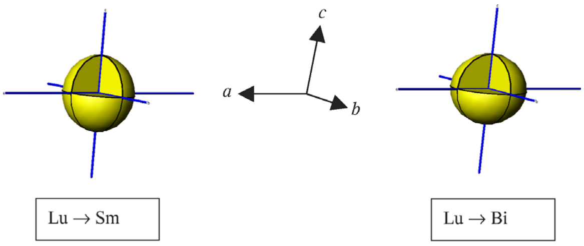
To quantify and/or describe these changes we propose to define a deformation tensor which may be defined as follows. The metrics of the compounds to compare are represented by the lattice parameters in the form of the fundamental metric tensor $\mathbf{G_{ik}} = \mathbf{a_i a_j}$. The deformation of the lattice by the change of the B-type cation can then be discussed as a “transformation” to another $\mathbf{G_{ik}}'$. The transition may be represented by the transformation matrix $\mathbf{M}$ which transforms the axes according to $\mathbf{a_i} = \mathbf{M} \bullet \mathbf{a_j}$. The metric tensor will then be transformed [6] according to:

$$\mathbf{G_{ik}}' = \mathbf{M} \bullet \mathbf{G_{ik}} \bullet \mathbf{M}^{\mathbf{T}}$$

For this simple orthogonal case $\mathbf{M}$ is defined as

$$\mathbf{M} \equiv \begin{matrix} k_1 & 0 & 0 \\ 0 & k_2 & 0 \\ 0 & 0 & k_3 \end{matrix} \equiv \mathbf{M}^{\mathbf{T}}$$

where $\mathbf{M}$ is symmetric and k_i represent the ratios between the corresponding axes. Since this is not necessarily true for lower cases of symmetry one would rather prefer to use the product $\mathbf{M} \bullet \mathbf{M}^{\mathbf{T}}$ just as it appears in the relation between $\mathbf{G_{ik}}$ and $\mathbf{G_{ik}}'$. (In our case the matrix then contains the squares of these relations, while in other cases possible rotations of the cell will also be incorporated in the off-diagonal elements). The result can now be used like a tensor, and its square can be plotted like displacement ellipsoids giving a pictorial presentation and not only numbers to show the changes in the geometry of the cell.



a) b)

Fig. 3. Deformation ellipsoids a) $K_2LuF_5 \rightarrow K_2SmF_5$, b) $K_2LuF_5 \rightarrow K_2BiF_5$ (see text) (a points to the left, c upwards).

Each of the ellipsoids in Fig. 3 therefore gives a pictorial comparison between two structures which is a representative for a certain type of deformation by substitution. The pairs are chosen from the end members of the isotypic rare earth compounds K_2LuF_5 and K_2SmF_5, together with K_2BiF_5.

Substituting Sm for Lu in the series K_2LnF_5 will increase the cell volume preferentially in c direction (Fig. 3a) and expand it least along [100], the diagonal terms of the transformation matrix being 1.017, 1.043 and 1.061. When looking at the structure one can see that the $^1_\infty[\mathrm{BiF}_{4/2}\mathrm{F}_3]$ chains are closer to each other in c direction. The increase in their waist size will therefore be reflected in such a deformation. The volume increase on substituting Sm for Bi even leads to a slight contraction along [001] which is balanced by a stronger dilatation along the other two axes (Fig. 3b, diagonal terms 1.103, 1.063 and 0.972; the increase along b is smaller than along a). The cross-section of the chains is now more asymmetric and upon being turned slightly they can fit even better to each other, thereby compensating the increase in size of the central cation.

As stated above, the chemical reaction of KHF_2 with $BiVO_4$ yields also $K_2VO_2F_3$ which is known to crystallise in the space group $Pnma$ with quite similar lattice parameters. The question arises whether a mixed crystal system of the type $K_2(BiF_2)_{1-x}(VO_2)_xF_3$ exists which can also influence the cell size. However, the compound $K_2VO_2F_3$ has a Rb_2CrF_5-type arrangement containing zig-zag chains of octahedra sharing two corners, $^1_\infty[CrF_4F_{2/2}]$, around the transition metal cations. The size relation $r_V/r_{O,F}$ does not fit into the structure of K_2BiF_5, and therefore a mixed crystal system is highly improbable. The refinement of the lattice parameters of the product of the reaction between KHF_2 and BiF_3 – *i. e.* without any vanadate present – gave no other values.

Conclusion

K_2BiF_5 may easily be prepared from the binary constituents. It has a K_2SmF_5-type structure which reflects the size of the Bi^{3+} cation and a minor lone-pair activity in characteristic deformations of the structure which, however, are quite small especially when compared with the corresponding Sb compound.

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