



'Pseudo-proper' ferroelectric phase transitions in oxyfluoride $K_3WO_3F_3$

M.P. Ivliev, S.V. Misyul, M.S. Molokeev & V.P. Sakhnenko

To cite this article: M.P. Ivliev, S.V. Misyul, M.S. Molokeev & V.P. Sakhnenko (2014) 'Pseudo-proper' ferroelectric phase transitions in oxyfluoride $K_3WO_3F_3$, Phase Transitions, 87:6, 592-602, DOI: [10.1080/01411594.2013.878026](https://doi.org/10.1080/01411594.2013.878026)

To link to this article: <https://doi.org/10.1080/01411594.2013.878026>



Published online: 05 Feb 2014.



[Submit your article to this journal](#) 



Article views: 68



[View related articles](#) 



[View Crossmark data](#) 



Citing articles: 2 [View citing articles](#) 

‘Pseudo-proper’ ferroelectric phase transitions in oxyfluoride $K_3WO_3F_3$

M.P. Ivliev^{a*}, S.V. Misyul^b, M.S. Molokeev^c and V.P. Sakhnenko^a

^aResearch Institute of Physics, Southern Federal University, Rostov-on-Don, Russia; ^bInstitute of Physical Engineering and Radioelectronics, Siberian Federal University, Krasnoyarsk, Russia; ^cKirensky Institute of Physics, Siberian Department RAS, Akademgorodok, Krasnoyarsk, Russia

(Received 28 October 2013; accepted 18 December 2013)

Based on the structural data on the phases of cryolite (ordered perovskite) $K_3WO_3F_3$, we develop a statistical model, which allows to describe the sequence of phase transitions observed in this compound using a unified approach. According to the model, the crystal possesses two structural subsystems: the K cations located in the octahedral positions and the WO_3F_3 octahedra in positions alternating with K cations. In the symmetric (cubic) phase, each subsystem can be found in one of the eight states. At decreasing temperature, an orientational phase transition in the subsystem of octahedra occurs first, followed by a phase transition to the low-temperature phase, caused by the loss of stability with respect to the ordering in the K cation subsystem. We find that the electric polarization occurs as pseudoproper and discuss the mechanisms of formation of the phase states.

Keywords: phase transition; ferroelectric; order–disorder; statistical mechanics

1. Introduction

Oxyfluorides with the general structural formula $A_2A'MO_xF_{6-x}$ ($A, A' = K, Rb, Cs, NH_4$; $M = Ti, Mo, W, x = 1, 2, 3$) belong to the quasi-octahedral crystals with anion sublattice containing mixed ligands, consisting of fluorine and oxygen. Interest in these compounds is due to the presence of acentric blocks forming a frame structure, and due to the possibility of creating various structural types by variation of anions. Such combination of structural features suggests that these compounds may have a wide variety of ferroelectric properties, which makes these crystals promising for creating new functional materials with a wide range of transparency.

Previously,[1,2] it was found that the compounds $A_3MO_3F_3$ ($A = K, Rb, Cs; M = Mo, W$) crystallize in the non-polar (elpasolite-like) kriolite-like cubic structure with a face-centered lattice (space group $Fm-3m, Z = 4$). All compounds in this series exhibit two structural phase transitions (PTs) with decreasing temperature. At the first high-temperature PT the cubic phase is transformed into tetragonal structure, which gives rise to electric polarization. Usually, this transition is characterized as ferroelectric PT. The characteristic feature is that the value of polarization and the dielectric constant at maximum are relatively small.[1–3] This may mean that type of PT differs from ‘proper’ ferroelectric PT. The second PT is accompanied by a multiplication of the cell and the appearance of superstructure. It was found that the lattice parameters for the tungstates and molybdates are very close in magnitude. These results gave reasons to assume that

*Corresponding author: Email: ivlievmp@rambler.ru

the phase states (PSs) and their formation mechanisms are similar for all these compounds.

However, recent studies showed that the thermodynamic properties and the structures of low-symmetry phases of molybdates and tungstates oxyfluorides differ substantially. For example, $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ experiences two ferroelastic PTs at 200 K and 198 K,[4,5] whereas $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ shows ferroelectric and ferroelastic PTs at 297 K and 205 K, respectively.[6] The symmetries of low-temperature phases of $\text{K}_3\text{WO}_3\text{F}_3$ and $\text{K}_3\text{MoO}_3\text{F}_3$ are also different, being Cm (C_s^3) for the former,[7] and Ia for the latter.[8] Thus, it was found that, despite the proximity of crystal-chemical characteristics of Mo and W cations, the thermodynamic properties of compounds based on them may differ substantially. Accordingly, the formation mechanisms of PSs may also be different. In this connection, it is more efficient to consider a particular compound when developing a model. In this paper, we propose a model, which describes all PTs observed in $\text{K}_3\text{WO}_3\text{F}_3$ within a unified approach.

PTs in ferroelectric $\text{K}_3\text{WO}_3\text{F}_3$ were previously studied by calorimetric methods.[2,4] Two first-order structural PTs were found at temperatures $T_1 = 452$ K and $T_2 = 414$ K. In a relatively recent paper,[7] the crystal structures of the three phases of $\text{K}_3\text{WO}_3\text{F}_3$ were determined using X-ray diffraction on powder sample. The critical and non-critical displacements of atoms were identified, which allowed explaining the temperature dependence of the intensity of X-ray reflections. The following sequence of structural changes was found

$$Fm\bar{3}m \xrightarrow[(p, 0, 0)]{11 - 10(\Gamma_4^-)} I4mm \xrightarrow[(p_1, p_2, 0)]{11 - 10(\Gamma_4^-)} Cm,$$

where the symbols under the arrows indicate the phenomenological order parameter (OP), which is electric polarization in this case, and the symbols over the arrows give the critical irreducible representation of space group $Fm\bar{3}m$, according to which this OP transforms. All PTs occur without changes in unit cell volume. In this paper, the terms ‘critical representation’ and ‘OP’ are used according to the definition given,[9], whereas the designations of irreducible representations are used according to [10].

In a somewhat simplified description,[7] the PSs of $\text{K}_3\text{WO}_3\text{F}_3$ are as follows. In the high-temperature cubic phase G_0 , the crystal possesses a cryolite structure, which is an ordered perovskite structure. The unit cell contains one W and two independent (i.e., located in different crystallographic positions) K atoms, whereas the fluorine and oxygen atoms occupy position 24e with site occupancy of 0.5. Graphically, the structure of the crystal in the high-symmetry phase can be represented as two interpenetrating cubic sublattices whose nodes alternate along three directions of the [001] type. The nodes of one of the sublattices are W cations, whereas K cations constitute the nodes of the other sublattice. These cations are located inside octahedra, the vertices of which are occupied by fluorine and oxygen anions with equal occupation numbers. Two neighboring octahedra have one common vertex (Figure 1(a)). According to Ref. [7] the W ion is shifted from the center of the octahedron toward the center of the octahedron faces, i.e., in the direction [111]. The bond distance W–O is slightly smaller than that of W–F. Thus, in the cubic phase the W cation may be found with equal probabilities in one of the eight crystallographically equivalent positions (CEP).

In the tetragonal phase G_1 of $\text{K}_3\text{WO}_3\text{F}_3$, the unit cell contains one W, two inequivalent K atoms, two inequivalent F atoms, and two inequivalent atoms O. This phase appears due to the ordering of the atoms along one of the fourth order axes. In this case, the chains of O–W–F–K–O type appear, the W cation shifts toward oxygen, the K cation toward fluorine, and a charge ordering occurs in the anion subsystem. As a result, electric polarization appears along the fourth order axis and the crystal becomes ferroelectric.

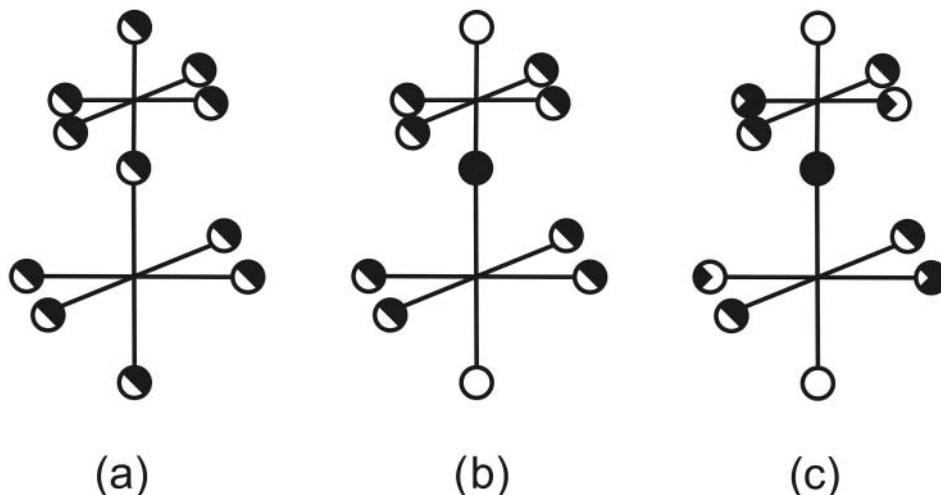


Figure 1. The arrangements of anions in octahedra. The small and large octahedra represent WO_3F_3 and KO_3F_3 , respectively. Filled and open circles represent fluorine and oxygen, respectively. Half-filled circles give 50% fluorine and 50% oxygen occupancy. The degree of filling corresponds to the occupancy of the site by fluorine: the darker the circle the higher the fluorine occupancy and the lower the oxygen occupancy: (a) cubic phase; (b) tetragonal phase; and (c) monoclinic phase.

The vertices in the equatorial plane of the octahedra are occupied by fluorine and oxygen anions with equal probability (Figure 1(b)).

The primitive cell of the low temperature monoclinic phase G_2 contains one W, two inequivalent K atoms, three inequivalent F atoms, and three inequivalent O atoms. In this phase, besides the charge ordering along z corresponding to the tetragonal phase, the ordering of the same type in the equatorial plane of the octahedra along the y -axis additionally occurs, but the disorder along the x -axis remains (the axes x , y , and z are defined along the cubic cell edges) (Figure 1(c)). In this case, in addition to the polarization along the z -axis, polarization along the y -axis appears.

From the analysis of experimental data, it was concluded [7] that PTs in this oxyfluoride have order–disorder type and are apparently due to the ordering of the W cation among eight positions. The validity of this model is confirmed by X-ray diffraction studies of other isostructural compounds $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ and $(\text{NH}_4)_3\text{WO}_3\text{F}_3$. [5,11] In contrast to X-ray diffraction experiment of [7], which was performed on the powder sample $\text{K}_3\text{WO}_3\text{F}_3$, the experiment of [11] was conducted using single-crystal samples of $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ and $(\text{NH}_4)_3\text{WO}_3\text{F}_3$. This allowed establishing with high reliability the presence of disorder of cations in octahedral centers.

According to the above data, the theoretical description of PSs in $\text{K}_3\text{WO}_3\text{F}_3$ requires an eight-minima model. The statistical properties of this model over a broad range of thermodynamic and model parameters were investigated in [12]. However, one can see from this study that without substantial modification it is impossible to obtain a sequence of PSs similar to that observed in $\text{K}_3\text{WO}_3\text{F}_3$ using this eight-minima model. This indicates that the real picture of the PSs formation is more complex than just disordering among the eight positions.

In this paper, we propose a statistical model that allows describing within a unified approach the set of PTs observed in $\text{K}_3\text{WO}_3\text{F}_3$. It was shown that PS responsible for the monoclinic phase is formed by an unusual mechanism.

2. Description of the model

According to the refined structural data,[7] three oxygen atoms form one of the WO_3F_3 octahedron faces, whereas the opposite face is formed by the fluorine atoms. At the same time, one of the octahedron faces is slightly compressed with respect to the regular shape of octahedron, whereas the opposite face is stretched. The W ion is shifted toward the center of the ‘oxygen’ face along the $[111]$ direction. The symmetry of the distorted octahedron is C_{3v} . In the symmetric phase the ‘oxygen’ octahedral faces are orientationally disordered.[7] As a consequence, both the fluorine and the oxygen atoms possess four positions of the type $[a_L, \varepsilon_L, \varepsilon_L]$ ($a_L - 24e$ Wyckoff positions for $L = \text{F}, \text{O}$; $a_F \approx a_O, \varepsilon_L \ll a_L$) in the vicinity of each of the six positions $24e$. That is, an octahedron with slightly ‘diffused’ vertices is actually obtained.

The K cation in the octahedral cavity is also shifted from the centrosymmetric position toward the fluorine atoms.[7] The distribution of anions around the K cation was not investigated; however, similar to the WO_3F_3 octahedron one can assume that the anions of the same kind prefer to be positioned on the same face in the octahedral coordination of the K cation. In this case, the K cation should also have eight CEP of the $[111]$ type in the symmetric phase. However, in contrast to the W cation, K is much weaker bound to the fluoride anions. According to [1,2] the effect of the cations, located in the cuboctahedral cavities, in cryolites is reduced to a relatively small change in temperatures of PTs, while the sequence of PTs does not change. This means that the aforementioned cations do not exert significant impact on the PTs and, therefore, their presence in the approximate model can be ignored.

Thus, in a first approximation, the following model is realistic. We consider a cubic crystal (space group $Fm-3m$) consisting of two interpenetrating sublattices. One of the sublattices is formed by the WO_3F_3 octahedra, whereas the other by K cations. The K cation can be found in one of the eight CEPs slightly shifted in the $[111]$ direction from the inversion center of the octahedral cavity. The arrangement and numbering of CEPs are shown in Figure 2.

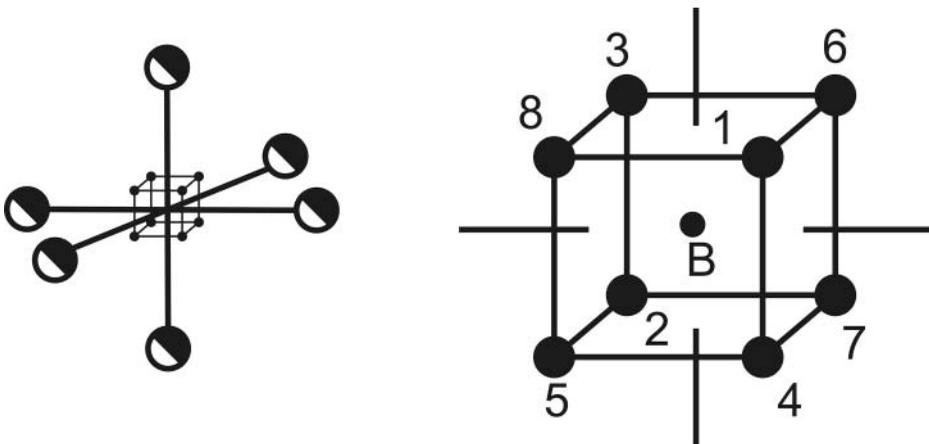


Figure 2. Arrangement and numbering of CEPs in the octahedron. Thin solid lines show the two axes of the fourth order. Point B is the inversion center of the octahedron.

The functions that characterize the probabilities of occupation of CEPs can be written as

$$\begin{aligned}
 p_{1,2} &= 1/8(1 + e_1 + e_2 + e_3 \pm (\zeta + \varphi_1 + \varphi_2 + \varphi_3)), \\
 p_{3,4} &= 1/8(1 + e_1 - e_2 - e_3 \pm (\zeta + \varphi_1 - \varphi_2 - \varphi_3)), \\
 p_{5,6} &= 1/8(1 - e_1 + e_2 - e_3 \pm (\zeta - \varphi_1 + \varphi_2 - \varphi_3)), \\
 p_{7,8} &= 1/8(1 - e_1 - e_2 + e_3 \pm (\zeta - \varphi_1 - \varphi_2 + \varphi_3)),
 \end{aligned}
 \tag{1}$$

where p_j characterize the probability of occupation of j th CEP. The sign ‘+’ refers to the odd numbers and the sign ‘-’ to even. The functions φ , ζ , and e act as OPs. The parameter φ transforms according to the irreducible representation T_{1U} similar to the polarization vector, $e \in T_{2g}$ and transforms as the shear deformation tensor components, $\zeta \in A_{2U}$ and transforms as a third-rank tensor of xyz form. From Equation (1), one can see that OPs φ and ζ characterize the difference, whereas OP e characterizes the homogeneous component in the probability of CEP occupation with numbers $2i-1$ and $2i$ ($i = 1, \dots, 4$).

The ‘oxygen’ face and the cation W associated with it may also have eight CEPs in the octahedron. The arrangement of centers of the octahedron faces (i.e., CEPs) and their numbering are the same as in Figure 2. Let us now introduce the functions that characterize the probabilities that the three oxygen anions constitute the respective face of the octahedron:

$$\begin{aligned}
 n_{1,2} &= 1/8 [1 \pm (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)], & n_{3,4} &= 1/8 [1 \pm (\varepsilon_1 - \varepsilon_2 - \varepsilon_3)], \\
 n_{5,6} &= 1/8 [1 \pm (-\varepsilon_1 + \varepsilon_2 - \varepsilon_3)], & n_{7,8} &= 1/8 [1 \pm (-\varepsilon_1 - \varepsilon_2 + \varepsilon_3)].
 \end{aligned}
 \tag{2}$$

The configurational space of the model contains only one three-component OP that transforms according to the irreducible representation T_{1U} , i.e., similar to the polarization vector. The absence of OP of type e is due to the fact that if the two opposite faces of the octahedron have equal numbers of oxygen, then it has the shape of a regular undistorted octahedron, i.e., OPs of type e are zero. For the same reason, the OP of type ζ is also absent. In this case, a degenerate eight-minima model (8_d -min) is realized. Thus, in the crystal under consideration the existence of two subsystems of ‘particles’ with eight minima is taken into account. Accordingly, for the description of phase transformations it is necessary to use two eight-minima ($8_d + 8$ -min) models.

The nonequilibrium thermodynamic potential for the pair of particles of the $8_d + 8$ -min model in the Gorsky–Bragg–Williams approximation [12–14] has the form

$$F_0 = F_W(\varepsilon) + F_K(\varphi, \zeta, e) - H \left(\sum_{i=1}^3 \varepsilon_i \phi_i \right),
 \tag{3}$$

The last term in Equation (3) describes the interaction of the subsystems with each other:

$$F_L = E_L - TS_L (L = W, K),$$

where F_L is the thermodynamic potential and S_L is the entropy of the subsystem of 'particles' W and K .

$$-S_K = \sum_{i=1}^8 p_i \ln p_i \quad -S_W = \sum_{i=1}^8 n_i \ln n_i. \quad (4)$$

E_L is the average energy

$$E_K(\varphi, \zeta, e) = \sum_{k,l=1}^8 Q_{kl} p_k(\phi, \zeta, e) p_l(\phi, \zeta, e) \quad E_W(\varepsilon) = \sum_{k,l=1}^8 V_{kl} n_k(\varepsilon) n_l(\varepsilon), \quad (5)$$

where Q_{ik} and V_{jl} characterize the pair interaction energy of the particles ('active' particles), located at the minima of different types. In the general case, they include both the direct interaction between the 'active' particles and the indirect interaction through the subsystem of other 'non-active' particles.

Substituting the expressions (1) and (2) (without the factors 1/8) into (4) and (5) and retaining only the terms that depend on the OP, we obtain

$$\begin{aligned} F_W(\varepsilon) &= A_W \left(\sum_{i=1}^3 \varepsilon_i^2 \right) + T \{ [1 \pm (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)] \ln [1 \pm (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)] \\ &\quad + [1 \pm (\varepsilon_1 - \varepsilon_2 - \varepsilon_3)] \ln [1 \pm (\varepsilon_1 - \varepsilon_2 - \varepsilon_3)] \\ &\quad + [1 \pm (-\varepsilon_1 + \varepsilon_2 - \varepsilon_3)] \ln [1 \pm (-\varepsilon_1 + \varepsilon_2 - \varepsilon_3)] \\ &\quad + [1 \pm (-\varepsilon_1 - \varepsilon_2 + \varepsilon_3)] \ln [1 \pm (-\varepsilon_1 - \varepsilon_2 + \varepsilon_3)] \}, \\ F_K(\varphi, \zeta, e) &= A_K \left(\sum_{i=1}^3 \phi_i^2 \right) + D \left(\sum_{k=1}^3 e_k^2 \right) + C \zeta^2 \\ &\quad + T \{ (1 + e_1 + e_2 + e_3 \pm (\zeta + \varphi_1 + \varphi_2 + \varphi_3)) \ln (1 + e_1 + e_2 + e_3 \pm (\zeta + \varphi_1 + \varphi_2 + \varphi_3)) \\ &\quad + (1 + e_1 - e_2 - e_3 \pm (\zeta + \varphi_1 - \varphi_2 - \varphi_3)) \ln (1 + e_1 - e_2 - e_3 \pm (\zeta + \varphi_1 - \varphi_2 - \varphi_3)) \\ &\quad + (1 - e_1 + e_2 - e_3 \pm (\zeta - \varphi_1 + \varphi_2 - \varphi_3)) \ln (1 - e_1 + e_2 - e_3 \pm (\zeta - \varphi_1 + \varphi_2 - \varphi_3)) \\ &\quad + (1 - e_1 - e_2 + e_3 \pm (\zeta - \varphi_1 - \varphi_2 + \varphi_3)) \ln (1 - e_1 - e_2 + e_3 \pm (\zeta - \varphi_1 - \varphi_2 + \varphi_3)) \}. \end{aligned}$$

The ' \pm ' sign suggests the summation of expressions first with the '+' and then with the '-' sign. A , D and C are functions of the constants Q_{ik} and V_{jl} and are actually the phenomenological parameters of the theory. The condition $A < 0$ means that there is an attraction between the particles in CEPs with the same numbers. The condition $D < 0$ ($D > 0$) means that there is attraction (repulsion) between similarly oriented 'quadrupole' moments of the nodes (OP e). Thus, A_W characterizes the corresponding interaction in the WO_3F_3 octahedra subsystem (subsystem I), whereas A_K in the subsystem of K cations (subsystem II). The absence of the factor 1/8 does not affect the quality and generality of the results.

Let us explore the possibility of appearance of the ordering sequence:

$$\begin{aligned} Fm-3m (O_h^5) - |\varepsilon| = |\varphi| = |e| = 0; I4mm (C_{4v}^9) - \varepsilon_1, \varepsilon_2 = \varepsilon_3 = 0, \varphi_1, \\ \varphi_2 = \varphi_3 = 0, |e| = 0, \zeta = 0; Cm (C_s^3)(I) - \varepsilon_1, \varepsilon_2, \\ \varepsilon_3 = 0, \varphi_1, \varphi_2, \varphi_3 = 0, e_1 = e_2 = 0, e_3, \zeta = 0. \end{aligned}$$

The thermodynamic potential F_W with $A_W < 0$ describes a single ordered phase ($\varepsilon_1, \varepsilon_2 = \varepsilon_3 = 0$) of C_{4v} symmetry, arising as a result of the second-order PT. The diagram of PSs of the thermodynamic potential F_K is given in Ref. [12]. In the region $A_K < 0, D > 0$, and $C \geq 0$ along the thermodynamic paths $D = -k A_K (k > 0)$, the following ordering sequences may occur: $O_h^5 - C_{4v}^9, O_h^5 - C_{3v}^5, O_h^5 - C_{3v}^5 - C_{2v}^{20}$. The phases C_{3v}^5 and C_{2v}^{20} are characterized by the sets of OPs $\varepsilon_1 = \varepsilon_2 = \varepsilon_3, \varphi_1 = \varphi_2 = \varphi_3, e_1 = e_2 = e_3, \zeta$ and $\varepsilon_1 = \varepsilon_2, \varepsilon_3 = 0, \varphi_1 = \varphi_2, \varphi_3 = 0, e_1 = e_2 = 0, e_3, \zeta = 0$, respectively. Since the symmetry of the cubic phase is O_h^5 and not O_h^1 , the superscripts of the space groups differ from those given in [12]. All of the transitions from the cubic phase are second-order PTs.

We further assume that $A_W < A_K < 0$, i.e., the interactions in the subsystem I are more intense compared to those in the subsystem II. This means that both subsystems are potentially unstable with respect to appearing of OPs ε and φ , whereas the subsystem I is unstable to a greater extent.

Combining the tetragonal and rhombohedral orderings, one can obtain a sequence of phases $O_h^5 - C_{4v}^9 - C_s^3(II)$ using TP Equation (3). However, the type of ordering in the phase $C_s^3(II)$, described by the set of OPs $\varepsilon_1, \varepsilon_2 = \varepsilon_3, \varphi_1, \varphi_2 = \varphi_3, e_1, e_2 = e_3$, and ζ , has an anisotropy character of ordered states different from that in the phase $C_s^3(I)$, which is observed in $K_3WO_3F_3$. Therefore, in order for the phase $C_s^3(I)$ to occur instead of $C_s^3(II)$ it is necessary to modify the model in such a way as to encourage the instability of the system with respect to $\varphi_2, \varphi_3 = 0$, and not $\varphi_2 = \varphi_3$.

In our opinion, the most realistic is the following scenario of the phase state formation of symmetry $C_s^3(I)$. The OPs ε_1 and φ_1 appear due to orientational ordering in the subsystem of octahedra. Due to striction interaction their appearance should be accompanied by elongation of the respective anion octahedra. However, since the neighboring octahedra have a common vertex, the extension of one of them will lead to a contraction of the other. Indeed, according to [7], at the transition from the cubic to the tetragonal phase the distances O_1-W-F_1 increase, whereas the distances $O_1-K_1-F_1$ decrease. As the OPs ε_1 and φ_1 increase, these interactions are enhanced, creating in the subsystem of compressed octahedra the conditions for the emergence of OP component φ in the plane orthogonal to the fourth-order axis C_4 . But it is necessary the $\varphi_2, \varphi_3 = 0$ order to appear. For that the elongation, which will accompany the appearance of the aforementioned order, should be directed along the axe 2 (Figure 3). To implement this scenario, it is sufficient to consider striction interactions of OPs ε and φ with uniaxial strain. In addition it will make all the PTs first order.

The striction interaction of OP with the parameters characterizing the uniaxial strain can be written as

$$\begin{aligned} c_W(\eta_{W1}^2 + \eta_{W2}^2) + c_K(\eta_{K1}^2 + \eta_{K2}^2) + m(\eta_{W1}\eta_{K1} + \eta_{W2}\eta_{K2}) \\ - g_W(\eta_{W1}U_{W1} + \eta_{W2}U_{W2}) - g_K(\eta_{K1}U_{K1} + \eta_{K2}U_{K2}), \end{aligned}$$

where $\eta_{W(K)1} = \frac{1}{\sqrt{6}}(2u_{W(K)zz} - u_{W(K)yy} - u_{W(K)xx})$, $\eta_{W(K)2} = \frac{1}{\sqrt{2}}(u_{W(K)yy} - u_{W(K)xx})$, and $u_{W(K)ii}$ are components of the deformation tensor of octahedra W and K , respectively, $c_{W(K)}$

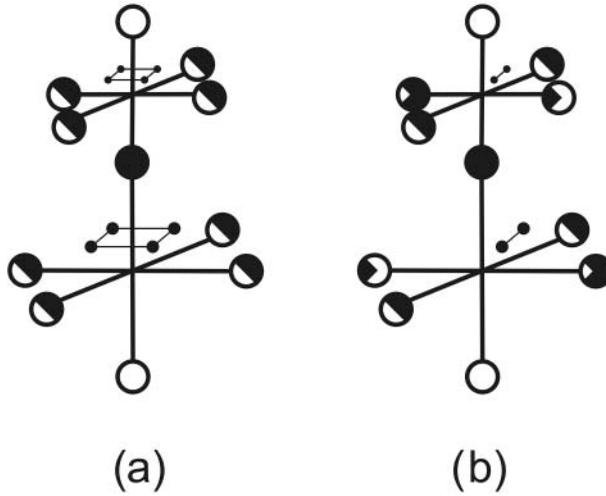


Figure 3. The antiferrodistortive interaction, which results in ‘hard’ elongated octahedron WO_3F_3 compressing the relatively ‘soft’ octahedron KO_3F_3 : (a) tetragonal phase and (b) monoclinic phase. The notation is the same as in Figures 1 and 2.

are elastic modules of W and K octahedra subsystems, respectively, and

$$U_{W1} = \frac{1}{\sqrt{6}} (2\varepsilon_1^2 - \varepsilon_2^2 - \varepsilon_3^2) \quad U_{W2} = \frac{1}{\sqrt{2}} (\varepsilon_2^2 - \varepsilon_3^2).$$

$U_{K1,2}$ will have a similar form after replacing ε_i by φ_i .

Minimizing TP with respect to parameters η_{Wi} and η_{Ki} , we find

$$\eta_{W(K)j} = (2c_{K(W)}g_{W(K)}U_{W(K)j} - mg_{K(W)}U_{K(W)j}) (4c_Wc_K - m^2)^{-1}.$$

Eliminating the variables η_{Wj} and η_{Kj} from TP one can obtain F_{eff} , which depends only on OPs of the model

$$F_{\text{eff}} = F_W(\varepsilon) + F_K(\varphi, \zeta, e) - H \left(\sum_{i=1}^3 \varepsilon_i \phi_i \right) + B \left(\sum_{i=1}^2 \sum_{j=2, i < j}^3 \varepsilon_i^2 \varepsilon_j^2 \right) - \frac{B}{3} \left(\sum_{j=1}^3 \varepsilon_j^2 \right)^2 \\ + G \left(\sum_{i=1}^2 \sum_{j=2, i < j}^3 \phi_i^2 \phi_j^2 \right) - \frac{G}{3} \left(\sum_{j=1}^3 \phi_j^2 \right)^2 + M \left(\sum_{i=1}^3 \varepsilon_i^2 \phi_i^2 \right) - \frac{M}{3} \left(\sum_{j=1}^3 \phi_j^2 \right) \left(\sum_{j=1}^3 \varepsilon_j^2 \right).$$

Since it is practically impossible to estimate the constants H , B , G , and M in the following, they will be considered as phenomenological parameters of the theory. The constant H characterizes the bilinear interaction between the octahedra subsystems and K cations; we assume $H > 0$. Simplifying the situation, one can state the following: the condition $B > 0$ contributes to the fact that PT $O_h - C_{4v}$ is of first order; the condition $M > 0$ favors the appearance of OPs φ_2 and φ_3 in the plane orthogonal to ε_1 and φ_1 ; the condition $G > 0$ results in the appearance of the ordering $\varphi_2, \varphi_3 = 0$, whereas PT $C_{4v} - C_s$ also becomes a first-order PT. This set of conditions allows choosing the constants of the

model so that the set of PSs, their appearance sequence, as well as the main parameters of PTs are qualitatively consistent with what is observed in $K_3WO_3F_3$.

Supposing $A_K = 0.7A_W$, $H = -0.3A_W$, $D = -0.6A_W$, $M = -0.8A_W$, $B = -A_W$, $G = -0.4A_W$, and $A_W < 0$, we obtain

- (1) There is a first-order PT $O_h^5 - C_{4v}^9$ at $T_{c1} = -A_W/3.686$, accompanied by a ‘jump’ of OPs from zero to $\varepsilon_1 \sim 0.71$ and $\phi_1 \sim 0.16$;
- (2) The tetragonal phase ($\varepsilon_1 \sim 0.92$, $\phi_1 \sim 0.2$) at $T_2 = -A_W/4.401$ becomes unstable with respect to the appearance of OPs ε_2 , ϕ_2 , and e_3 , which results in a first-order PT at $T_{c2} = -A_W/4.39999$ to the monoclinic phase $C_s^3(I)$ ($\varepsilon_1 \sim 0.924$, $\varepsilon_2 \sim 0.005$, $\phi_1 \sim 0.2$, $\phi_2 \sim 0.2$, $e_3 \sim 0.025$), which remains stable down to $T \sim 0$;
- (3) At $T \rightarrow 0$ in the phase $C_s^3(I)$ we obtain $\varepsilon_1 \rightarrow 1$, $\varepsilon_2 \rightarrow 0$, $\phi_2 \rightarrow 1$, $\phi_1 > \sim e_3$, $\phi_1 - e_3 \rightarrow 0$, and $\varphi_1 \rightarrow 0.27$.

By ‘at $T \rightarrow 0$ ’, we mean that we consider the area in which OPs are close to saturation and depend weakly on T .

3. Discussion of results

The results indicate that $A_W \sim -3.7kT_{c1}$ (k is the Boltzmann constant) and $T_{c2} \sim 0.84 T_{c1}$. Although the difference $T_{c1} - T_{c2}$ exceeds the experimentally observed value, but is much smaller than T_{c1} . Qualitatively the ratio between the calculated and the experimentally observed PT temperatures is quite satisfactory.

The main structural motif of the ferroelectric monoclinic phase is the ordering of anti-ferrodistortive type. Its special feature is that at low temperatures the orientation of elongated octahedra of subsystem I approaches the C_4 axis, whereas the K cation subsystem is ordered predominantly in orthogonal plane.

The dipole moment of the WO_3F_3 octahedron (d_{oct}) is equal to the vector sum of the moments of the oxygen and fluorine anions, and tungsten cations relative to the geometric center of the octahedron. It is directed from the geometric center of the octahedron to the center of the face formed by fluoride anions. The dipole moment of the K cation (d_K), which is displaced from the centrosymmetric position, is also directed toward fluoride anions. Therefore, in both the tetragonal and the monoclinic phases, the dipole moments of the octahedra subsystems and of the K cations are directed in opposite directions partially compensating each other. Accordingly, in these phases the i th component of the polarization per particle is equal to

$$p_i(T) = \frac{1}{2\sqrt{3}}[\kappa_1 d_{oct} \varepsilon_i(T) - \kappa_2 d_K \phi_i(T)],$$

where κ_i are coefficients of proportionality between OPs ε and φ , the dipole moments and polarization.

From the considerations above, it follows that in the $K_3WO_3F_3$ crystal there is a competition of interactions responsible for the orientational ordering with the electrostatic dipole–dipole interactions. The crystal remains stable with respect to the appearance of polarization under the orientational PT and ‘turned off’ bilinear interaction of polarization with OPs ε and φ . Polarization appears only due to bilinear interaction with orientational

OPs ε and φ , i.e., like ‘pseudo-proper’. Such PT is characterized as ‘pseudo-proper’ ferroelectric PT.

At such PT, the appearance of orientational ordering is accompanied by the appearance of polarization as well as the appearance of a maximum in the temperature dependence of the permittivity. However, their values are significantly smaller than those observed in ‘proper’ ferroelectric PT. A similar pattern is observed in the number of crystals of this type [1–3]. Unfortunately, there is no data on the temperature dependence of the polarization and dielectric constant of $K_3WO_3F_3$ crystal. However, it can be argued that temperature dependence of polarization and the permittivity in this crystal will be similar.

Under the proposed model, the formation of PSs in $K_3WO_3F_3$ is as follows. As the temperature is lowered an orientational PT takes place in the subsystem of WO_3F_3 octahedra connected with the appearance of order in the arrangement of the fluorine and oxygen anions. This PT is accompanied by appearance of a small polarization of the crystal as well as by charge ordering in the subsystem of anions. PT to the low-temperature phase is due to the loss of stability with respect to the ordering in the subsystem of potassium cations located in the octahedral sites. This model is consistent with the data on the temperatures of PTs in cryolites $A_3MO_3F_3$ ($A = K, Rb, Cs; M = W, Mo$). [1,2] Depending on the cation A the temperatures of PTs from the cubic to the tetragonal phase for $A_3WO_3F_3$ and $A_3MoO_3F_3$ differ by $\sim 60^\circ \div 80^\circ$, whereas the temperatures of PTs from the tetragonal to the monoclinic phase differ by $15^\circ \div 30^\circ$. In all the cases, the temperatures of PTs in $A_3MoO_3F_3$ are higher. Since different octahedra result in different PT temperatures, it indicates that the high-temperature PT is due to the ordering of the octahedral subsystem. On the contrary, a slight difference in temperatures of the low-temperature PT indicates that the PT is due to the ordering of nearly identical subsystems. The most suitable for this role is a subsystem of cations A, located in the octahedral sites.

4. Conclusion

This paper discusses one of the possible mechanisms of formation of the phase states in the crystal $K_3WO_3F_3$. For its implementation, it is essential to have at least two structural subsystems, one of which is soft (i.e., easily deformed), whereas the other is rigid. Furthermore, the two subsystems should be potentially unstable with respect to the appearance of certain ordering (orientational, dipole, etc.). These conditions, with appropriate selection of components, can meet the crystals with the structure of ordered perovskites: elpasolites, cryolites, and others.

One of the main causes of the orientational order is the tendency to create order in the arrangement of anions and charge accordingly. In turn, the appearance of the monoclinic phase along with the mentioned reason is also due to the presence of a significant antiferrodistortive interaction between subsystem building blocks.

Despite the fact that the proposed model is only a first approximation, it is capable of reproducing a number of specific features of the thermodynamic behavior of the given crystal. In order to improve and generalize the model we believe it is necessary to (i) determine the actual shape of the MO_3F_3 ($M = K, Rb, Cs, Mo, W$) octahedral, (ii) estimate the probability of the existence of octahedra with symmetry C_{2v} , (iii) take into account the impact of the subsystem of cations located in the cuboctahedral cavities. The fact is that if the MO_3F_3 ($M = Mo, W$) octahedra with the C_{3v} symmetry differ considerably in shape from the regular octahedron, it necessary to use the conventional eight-minima model instead of the eight-minima degenerate model. This increases the probability

of a transition from the cubic to the rhombohedral phase. In turn, T-shaped configurations in the arrangement of oxygen anions at the vertices of an octahedron (of C_{2v} symmetry) can be realized around the cation K. In this case, its potential energy besides eight minima will contain six less deep ones. The presence of six additional minima will create more favorable conditions for the emergence of the monoclinic phase $C_s^3(I)$. Accounting for the effects of cation subsystem located in the cuboctahedral cavities is important for understanding the causes of significant changes in the thermodynamic properties of the compounds at the transition from cryolite to elpasolite.

Funding

This study was supported by the of the President of the Russian Federation for the Support of Leading Scientific Schools [Grant NSh-924.2014.2].

References

- [1] Peraudeau G, Ravez J, Hagenmuller P, Arend H. Study of phase transitions in $A_3MO_3F_3$ compounds ($A = K, Rb, Cs; M = Mo, W$). *Solid State Commun.* 1978;27:591–593.
- [2] Ravez J, Peraudeau G, Arend H, Abrahams SC, Hagenmuller P. A new family of ferroelectric materials with composition $A_2BMO_3F_3$ ($A, B = K, Rb, Cs$, for $rA+>rB+$ and $M = Mo, W$). *Ferroelectrics.* 1980;26:767–769.
- [3] Peraudeau G, Ravez J, Tressaud A, Hagenmuller P, Arend H, Chanussot G. Les transitions de phase de l'oxyfluorure $Rb_3MoO_3F_3$ [Phase transitions of the oxyfluoride $Rb_3MoO_3F_3$]. *Solid State Commun.* 1977;23:543–546. French.
- [4] Fokina VD, Flerov IN, Gorev MV, Molokeev MS, Vasiliev AD, Laptash NM. Effect of cationic substitution on ferroelectric and ferroelastic phase transitions in oxyfluorides $A_2A'WO_3F_3$ ($A, A': K, NH_4, Cs$). *Ferroelectrics.* 2007;347:60–64.
- [5] Molokeev MS, Misyul SV. Processes of ordering of structural elements, critical and noncritical parameters of phase transitions in the $(NH_4)_3WO_3F_3$ crystal. *Phys Solid State.* 2012;54:155–165.
- [6] Flerov IN, Fokina VD, Bovina AF, Bogdanov EV, Molokeev MS, Kocharova AG, Pogorel'tsev EI, Laptash NM. Mechanism and nature of phase transitions in the $(NH_4)_3MoO_3F_3$ oxyfluoride. *Phys Solid State.* 2008;50:515–524.
- [7] Molokeev MS, Misyul' SV, Fokina VD, Kocharova AG, Aleksandrov KS. Structure transformations during phase transitions in the $K_3WO_3F_3$ oxyfluoride. *Phys Solid State.* 2011;53:834–839.
- [8] Brink FJ, Withers RL, Friese K, Madariaga G, Noren L. An Electron diffraction and XRPD study of superlattice ordering in the elpasolite-related oxyfluoride $K_3MoO_3F_3$. *J Solid State Chem.* 2002;163:267–274.
- [9] Sakhnenko VP, Talanov VM, Chechin GM. Theoretical group analysis of complete condensation occurring at structural phase transitions. *Fiz Metallov i Metallovedenie.* 1986;62:847–856. Russian.
- [10] Kovalev OV. Representations of the crystallographic space groups: irreducible representations, induced representations and corepresentations. Amsterdam: Gordon and Breach; 1993.
- [11] Udovenko AA, Laptash NM. Orientation disorder and crystal structures of $(NH_4)_3MoO_3F_3$ and $(NH_4)_3WO_3F_3$. *Acta Cryst B.* 2008;64:305–311.
- [12] Ivliev MP, Raevskaya SI, Raevskii IP, Shuvaeva VA, Pirog IV. Formation of ferroelectric phases in $KNbO_3$ and other niobates with perovskite structure. *Phys Solid State.* 2007;49:769–779.
- [13] Gorsky W. Röntgenographische Untersuchung von Umwandlungen in der Leigerung CuAu [X-ray investigation of transformation in the alloy CuAu]. *Z Physik.* 1928;50:64–81. German.
- [14] Bragg WL, Williams EJ. The effect of thermal agitation on atomic arrangement in alloys. *Proc R Soc A.* 1934;145:699–730.