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PEROVSKITE-LIKE LAYER-TYPE
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CRYSTAL CHEMISTRY
OF PEROVSKITE-LIKE LAYER-TYPE FERROELECTRICS
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Résumé. — Le nombre \( m \) de couches monoocataédriques dans les empilements du type perovskite dépend de la valeur du facteur de tolérance \( t \). Les critères limites, supérieur et inférieur, de formation de structures en couches sont \( t_1 \approx 0.87 \) et \( t_u \approx 0.99 \). Dans les couches \([\text{Bi}_2\text{O}_3]^2^+\), seulement un des ions \( \text{Bi}^{3+} \) peut être remplacé, et seulement par un cation trivalent; cela conduit à accroître \( T_c \). L'accroissement de \( m \), dépendant de la polarisabilité des ions A et \( \text{O}^{2-} \) cause à la fois l'élavation et l'abaissement de \( T_c \). \( \text{Bi}_2\text{WO}_6 \) est le premier ferroélectrique à une couche avec \( T_c = 950 \, ^\circ\text{C} \).

Les cristaux \( \text{Bi}_2\text{NbO}_5\text{F} \) et \( \text{Bi}_2\text{TaO}_5\text{F} \) sont aussi des cristaux ferroélectriques à une couche ayant respectivement pour \( T_c \) les valeurs 30 \( ^\circ\text{C} \) et 10 \( ^\circ\text{C} \).

La chimie des cristaux ferroélectriques du type perovskite à couche a été considérablement étudiée, et les points principaux sont donnés dans la présente note.

Abstract. — The number of monoocatahedral layers in the perovskite-like package \( m \) depends on the value of tolerance factor \( t \). The lower and upper criteria of layer structure formation are \( t_1 \approx 0.87 \) and \( t_u \approx 0.99 \). In \([\text{Bi}_2\text{O}_3]^2^+\) layers only one of the \( \text{Bi}^{3+} \) ions may be replaced, and only by trivalent cation; that leads to increasing of \( T_c \). Depending upon the polarizability of A and \( \text{O}^{2-} \) ions increasing of \( m \) causes both raising and lowering of \( T_c \). Crystals \( \text{Bi}_2\text{NbO}_5\text{F} \) and \( \text{Bi}_2\text{TaO}_5\text{F} \) are also one-layer ferroelectrics with \( T_c \approx 30 \, ^\circ\text{C} \) and 10 \( ^\circ\text{C} \).

Crystal chemistry of perovskite-like layer-type ferroelectrics has been considerably developed in [1]-[5] the main points of which are given in the present paper.

1. The general formula of layer-type ferroelectrics is \( A_{m-n+1}\text{Bi}_n\text{B}_{m-2}\text{O}_{3m+3} \) [1], where \( A \) are large cations occupying usually octahedral emptinesses in perovskite-like packages, \( B \)-small cations, \( m \) is a number of monoocatahedral layers in one perovskite-like unit (Fig. 1), \( n = 2 \) or 4.

In the earlier known layer-type ferroelectrics \( m \) was equal only to 2, 3, 4 and 5. In our work [2] it was shown that the value of \( m \) depends on geometry of ions packing in perovskite-like units—upon the magnitude of the tolerance factor \( t \). It was established that the upper and lower criteria favorable for the formation of perovskite-like layer-type structure are \( t_u \approx 0.99 \) and \( t_1 \approx 0.87 \) in the interval of which structures can be formed theoretically with any number of monoocatahedral layers in the perovskite-like package. Figure 2 shows the dependence of \( m \) upon \( t \) for

\[ A = \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Bi}^{3+}, \text{Sr}^{2+} \text{and Ca}^{2+}. \]

For the system \( N\text{ATiO}_3\text{Bi}_4\text{Ti}_3\text{O}_{12} \) (\( A = \text{Pb}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+} \)) and \( N\text{BiFeO}_3\text{Bi}_4\text{Ti}_3\text{O}_{12} \) any number \( m \) is possible. In particular formation of the first eight-layer ferroelectric-anti-ferromagnetic \( \text{Bi}_2\text{Bi}_4\text{Ti}_3\text{Fe}_{2}\text{O}_{27}, \ T_c = 830 \, ^\circ\text{C} \) [2], [3] confirms this conclusion.

In cases when cations \( A \) are different, the concept of an average ionic radius, and consequently the calculated factor \( t \), is applicable if the sizes of these ions do not considerably differ. Otherwise in determining of the possibility of a layer structure formation it is necessary to bear in mind the values of the factor \( t \), separately calculated for each of \( A \) cations.

Satisfaction of the geometrical criteria (on the nominal charges of ions) is necessary but it is not always sufficient for formation of the layer-type structure. The electron configuration of ions in the unit cell and polarizability of the cations \( A \) and \( B \) play an important role. Apparently in some cases a considerable deviation of effective charge of ions from the nominal charges can stipulate the seeming deviation from the established criteria.

2. Possibility of formation of the \([\text{Me}_2\text{O}_3]\) layers predetermines building of the perovskite-like layer structure. In this connection investigation of the substitution of \( \text{Bi}^{3+} \) ions by another ions in the bismuth-oxygen layers is very important. According to Subbarao [4] and Popper et al. [5] \( \text{Bi}^{3+} \) ions in \([\text{Bi}_2\text{O}_3]^3^+\) layers cannot be replaced without destroying the structure. Our investigation show that [3] in the bismuth-oxygen layer the only one of the two \( \text{Bi}^{3+} \) ions can be substituted, and only by trivalent cations. Such a replacement of ions sufficiently effects the value of the Curie temperature of a crystal, what we shall mention later on.
3. Earlier it was adopted that by the given A and B cations with increasing of m the Curie temperature $T_c$ of the layer-type ferroelectrics decreases. Recently we have shown [3] that in the general case increasing of m can lead to decreasing as well as to increasing of $T_c$ of this type ferroelectrics. In comparison with the perovskite structure, perovskite-like packages differ by some surplus of oxygen ions and to the same degree by deficiency of cations $A$. With increasing of $m$ surplus of $O^{2-}$ and deficiency of $A$ gradually are diminished and they strive for mutual compensation, that is the perovskite-like package approaches the perovskite unit. This in general should lead to decreasing of $T_c$. However in case $\alpha_A > \alpha_0$ both increasing (when $A = Bi^3+)$ and decreasing (when $A \neq Bi^3+$) of $T_c$ take place. For example, the first occurs in the following case:

$$
\begin{array}{c|c}
m & T_c, °C \\
\hline
BiBi_4Ti_3FeO_{15} & 4 & 750 \\
Bi_2Bi_4Ti_3Fe_2O_{18} & 5 & 810 \\
Bi_3Bi_4Ti_3Fe_5O_{27} & 8 & 830 \\
\end{array}
$$

Thus the $T_c$ of layer-type ferroelectrics depend upon the nature of A (and B) cations, disposing in the perovskite-like units, and apparently in this the bismuth-oxygen layers at all events do not play a considerable role.

4. The Curie temperature of layer-type ferroelectrics to a great extent depends also upon the fact if the A cations are placed in the perovskite-like units or they enter into the bismuth-oxygen layers. In the last case $Bi^3+$ ion which is replaced by cation $A$, passes to perovskite-like unit that should cause a considerable raising of $T_c$ of crystal. By this, in particular, the equal values $T_c \approx 750 °C$ of ferroelectrics $PrBi_4Ti_3FeO_{15}$ [7] and $BiBi_4Ti_3FeO_{15}$ [2] are explained. Thus, such a kind of increasing of $T_c$ may be as an indicator of replacing of $Bi^3+$ ions in the bismuth-oxygen layers.

For a given B cations the degree of broadening of the ferroelectric phase transition (the width of the dielectric constant peak) is in direct dependence on the size difference of $A$ and $Bi^3+$ ions. Because of this the peaks of $\varepsilon$ are sharp if $A$ ion enters only into the bismuth-oxygen layer (for example, in $PrBi_4Ti_3FeO_{15}$) and broadening if it is placed in the perovskite-like unit (as in $LaBi_4Ti_3FeO_{15}$, Fig. 3). Evidently, this result

![Fig. 1: The unit cell of ferroelectric $Ba_3Bi_4Ti_5O_{18}$ projected on (100).](image1)

![Fig. 2: The dependence $m = \varphi(t)$.](image2)

![Perovskite structure](image3)

![Layer (m=3) + Perovskite](image4)

![Structure](image5)
also may serve as an evidence of replacement of Bi$^{3+}$ ion in the bismuth-oxygen layer by A cation.

5. The chemical formula of possible one-layer perovskite-like layer-type ferroelectrics Bi$_2$BO$_5$ is obtained from the general formula at $m = 1$ and $n = 2$. However up to 1970 the existence of these ferroelectrics was unknown. For the first time on the basis of high temperature X-ray investigation [8] and a non-polar space group $D_{2h}$-Pccn [8] it was concluded by us that, probably, bismuth-tungstat, Bi$_2$WO$_6$, was antiferroelectric with $T_c \approx 950$ °C [9]. However recently for Bi$_2$WO$_6$ a polar group $C_{17}$-B2cb was determined [10]. This allows us to contend that Bi$_2$WO$_6$ is the first discovered one-layer ferroelectric (may be ferrielectric) with $T_c \approx 950$ °C. Other one-layer compounds Bi$_2$NbO$_5$F and Bi$_2$TaO$_5$F were synthetized and structurally studied in [11] and $C_{3v}$, $D_{2d}$, $D_{1h}$ space groups have been determined. Our investigation of $\varepsilon(T)$ in the wide range of temperature (−170 °C, +500 °C) discovered the dielectric constant peak at $\approx 30$ °C for Bi$_2$NbO$_5$F and at $\approx 10$ °C for Bi$_2$TaO$_5$F. On the single crystals of Bi$_2$NbO$_5$F at 15 °C the dielectric hysteresis loop was observed ($P_s = 4$ μcoul/cm$^2$). Thus these crystals are also one-layer ferroelectrics with $T_c \approx 30$ °C and 10 °C.

References

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