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CRYSTAL CHEMISTRY OF PEROVSKITE-LIKE LAYER-TYPE FERROELECTRICS

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Résumé. — Le nombre \( m \) de couches monoocahédriques 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 \( t_0 \approx 0.99 \). 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'élèvement et l'abaissement de \( T_c \). \( \text{Bi}_2\text{WO}_6 \) est le premier ferroélectrique à une couche avec \( T_c \approx 950 \) °C.

Les cristaux \( \text{Bi}_2\text{NbO}_6 \) et \( \text{Bi}_3\text{TaO}_6 \) sont aussi des cristaux ferroélectriques à une couche ayant respectivement pour \( T_c \) les valeurs 30 °C et 10 °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 monoocahedral 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 \( t_0 \approx 0.99 \). 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 \( T_c \). \( \text{Bi}_2\text{WO}_6 \) is the first one-layer ferroelectric with \( T_c \approx 950 \) °C. Crystals \( \text{Bi}_2\text{NbO}_6 \) and \( \text{Bi}_3\text{TaO}_6 \) are also one-layer ferroelectrics with \( T_c \approx 30 \) °C and 10 °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 \( A_{m-n+1}B_m\text{O}_{3m+2} \) [1], where \( A \) are large cations occupying usually octahedral emptinesses in perovskite-like packages, \( B \)-small cations, \( m \)- is a number of monoocahedral 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 \( t_0 \approx 0.99 \) and \( t_1 \approx 0.87 \) in the interval of which structures can be formed theoretically with any number of monoocahedral layers in the perovskite-like package. Figure 2 shows the dependence of \( m \) upon \( t \) for

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

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 \( \text{Bi}_2\text{Bi}_4\text{Ti}_3\text{Fe}_3\text{O}_{27} \), \( T_c = 830 \) °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 \([\text{Me}_2\text{O}_4]\) 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.
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, so far as deficiency of cations \( A \) decreases, then character of the change of \( T_c \) will depend upon the magnitude of polarizability of \( A \) cations \( \varkappa_A \) as compared with polarizability of \( O^{2-} \) ion. At \( \varkappa_A > \varkappa_0 \) with increasing of \( m \) decreasing of \( T_c \) will occur.

However in case \( \varkappa_A > \varkappa_0 \) both increasing (when \( A = \text{Bi}^{3+} \)) and decreasing (when \( A \neq \text{Bi}^{3+} \)) of \( T_c \) take place. For example, the first occurs in the following case:

<table>
<thead>
<tr>
<th>( m )</th>
<th>( T_c, ^\circ C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>750</td>
</tr>
<tr>
<td>5</td>
<td>810</td>
</tr>
<tr>
<td>8</td>
<td>830</td>
</tr>
</tbody>
</table>

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 \( \text{Bi}^{3+} \) 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 \( T_c \approx 750 ^\circ C \) of ferroelectrics \( \text{PrBi}_4\text{Ti}_3\text{FeO}_{15} \) [7] and \( \text{Bi}_3\text{Bi}_4\text{Ti}_3\text{Fe}_5\text{O}_{27} \) [2] are explained. Thus, such a kind of increasing of \( T_c \) may be as an indicator of replacing of \( \text{Bi}^{3+} \) 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 \( \text{Bi}^{3+} \) ions. Because of this the peaks of \( \varepsilon \) are sharp if \( A \) ion enters only into the bismuth-oxygen layer (for example, in \( \text{PrBi}_4\text{Ti}_3\text{FeO}_{15} \)) and broadening if it is placed in the perovskite-like unit (as in \( \text{LaBi}_4\text{Ti}_3\text{FeO}_{15} \), Fig. 3). Evidently, this result...
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\(_6\) 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\(_{3d}\)-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\(_{15}\)-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 [11]. Our investigation of \(e(T)\) 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 ant 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 (\(P_r = 4\) µcoul/cm\(^2\)). Thus these crystals are also one-layer ferroelectrics with \(T_c \approx 30\) °C and 10 °C.

References

[1] ISMAILZADE (I. G.), Kristallografiya, 1963, 8, 852