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I. Ismailzade

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CRYSTAL CHEMISTRY OF PEROVSKITE-LIKE LAYER-TYPE FERROELECTRICS

I. H. ISMAILZADE

The Institute of Theoretical Problems of Chemical Technology
of the Academy of Sciences of the Azerbaijan S. S. R., Baku, U. S. S. R.

Résumé. — Le nombre m de couches monooctaédriques 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 $[\text{Bi}_2\text{O}_2]^{2+}$, seulement un des ions 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 O^{2-} cause à la fois l'élévation et l'abaissement de T_c . Bi_2WO_6 est le premier ferroélectrique à une couche avec $T_c \approx 950^\circ\text{C}$.

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°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 monooctahedral 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 $[\text{Bi}_2\text{O}_2]^{2+}$ layers only one of the 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 O^{2-} ions increasing of m causes both raising and lowering of T_c . Bi_2WO_6 is the first one-layer ferroelectric with $T_c \approx 950^\circ\text{C}$. 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°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 $A_{m-n+1}\text{Bi}_n\text{B}_m\text{O}_{3m+3}$ [1], where A are large cations occupying usually octahedral emptinesses in perovskite-like packages, B-small cations, m - is a number of monooctahedral 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 monooctahedral layers in the perovskite-like package. Figure 2 shows the dependence of m upon t for

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

For the system $\text{N A TiO}_3\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ ($A = \text{Pb}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}$) and $\text{N BiFeO}_3\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ any number m is possible. In particular formation of the first eight-layer ferroelectric-anti-ferromagnetic $\text{Bi}_5\text{Bi}_4\text{-Ti}_3\text{Fe}_5\text{O}_{27}$, $T_c = 830^\circ\text{C}$ [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 $[\text{Me}_2\text{O}_2]$ layers predetermines building of the perovskite-like layer structure. In this connection investigation of the substitution of Bi^{3+} ions by another ions in the bismuth-oxygen layers is very important. According to Subbarao [4] and Popper *et al.* [5] Bi^{3+} ions in $[\text{Bi}_2\text{O}_2]^{2+}$ layers cannot be replaced without destroying the structure. Our investigation show that [3] in the bismuth-oxygen layer the only one of the two 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.

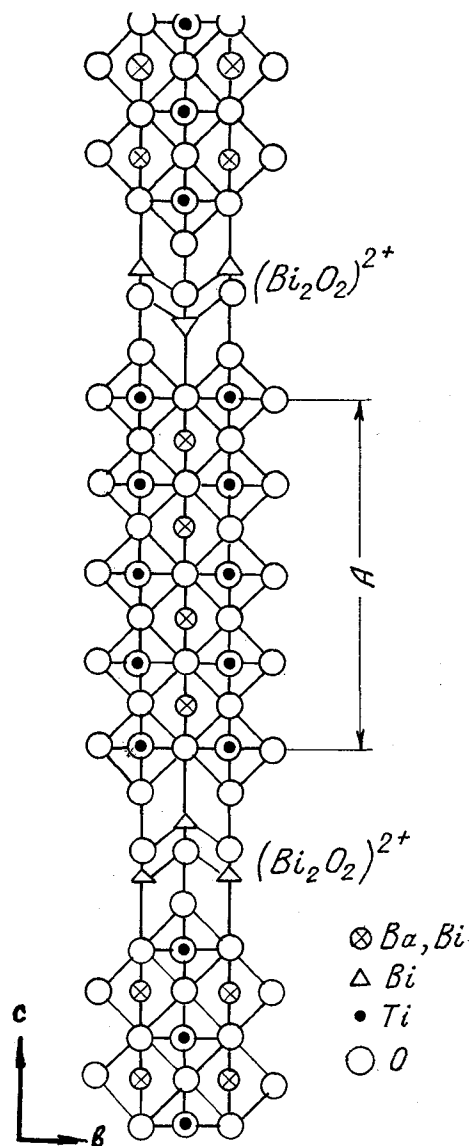


FIG. 1. — The unit cell of ferroelectric $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ projected on (100).

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 led 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 α_A as compared with polarizability of O^{2-} ion. At $\alpha_A < \alpha_0$ with increasing of m decreasing of T_c will occur.

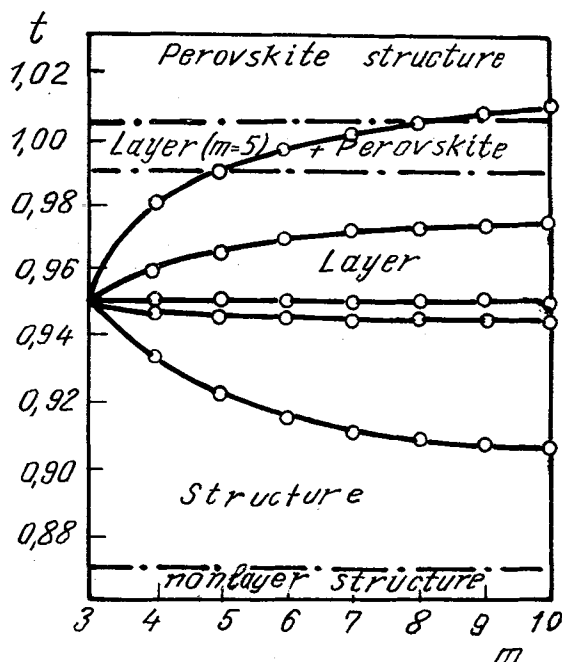


FIG. 2. — The dependence $m = \varphi(t)$.

However in case $\alpha_A > \alpha_0$ 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 :

	m	$T_c, ^\circ\text{C}$
$\text{BiBi}_4\text{Ti}_3\text{FeO}_{15}$	4	750
$\text{Bi}_2\text{Bi}_4\text{Ti}_3\text{Fe}_2\text{O}_{18}$	5	810
$\text{Bi}_5\text{Bi}_4\text{Ti}_3\text{Fe}_5\text{O}_{27}$	8	830

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 $T_c \approx 750^\circ\text{C}$ of ferroelectrics $\text{PrBi}_4\text{Ti}_3\text{FeO}_{15}$ [7] and $\text{BiBi}_4\text{Ti}_3\text{FeO}_{15}$ [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 ϵ 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

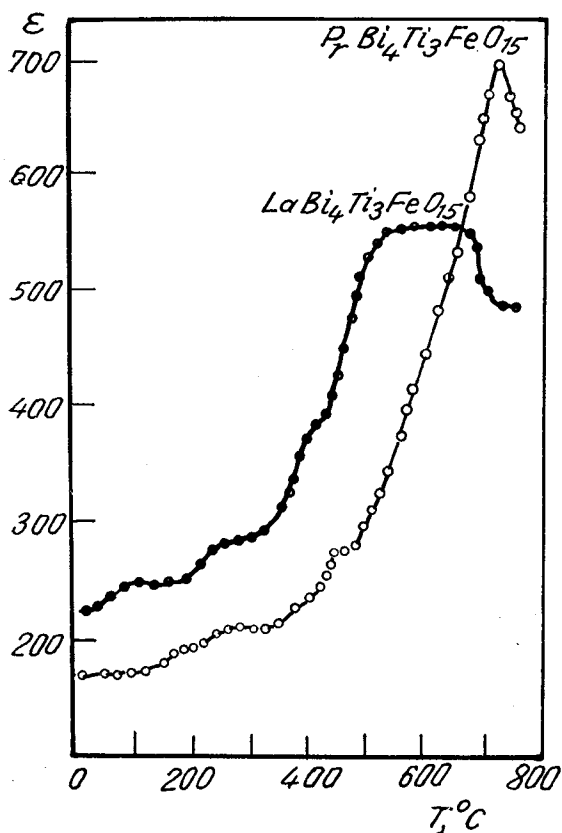


FIG. 3. — The dependence $\varepsilon(T)$ of $\text{PrBi}_4\text{Ti}_3\text{FeO}_{15}$ and $\text{LaBi}_4\text{Ti}_3\text{FeO}_{15}$.

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_2BO_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 $\text{D}_{2h}^{10}\text{-Pccn}$ [8] it was concluded

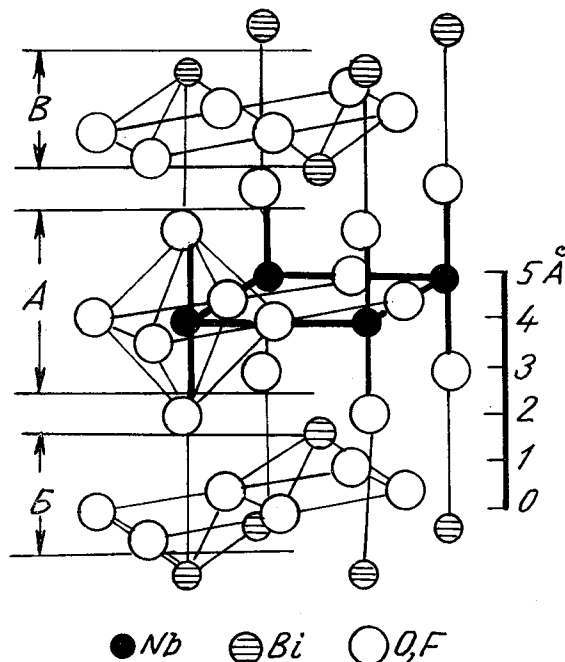


FIG. 4. — One half of the unit cell of $\text{Bi}_2\text{NbO}_5\text{F}$ [11].

by us that, probably, bismuth-tungstat, Bi_2WO_6 , was antiferroelectric with $T_c \approx 950^\circ\text{C}$ [9]. However, recently for Bi_2WO_6 a polar group $\text{C}_{2v}^{17}\text{-B2cb}$ was determined [10]. This allows us to contend that Bi_2WO_6 is the first discovered one-layer ferroelectric (may be ferroelectric) with $T_c \approx 950^\circ\text{C}$. Other one-layer compounds $\text{Bi}_2\text{NbO}_5\text{F}$ and $\text{Bi}_2\text{TaO}_5\text{F}$ were synthesized and structurally studied in [11] and C_{4v}^9 , D_{2d}^9 , D_{2d}^{11} space groups have been determined. Our investigation of $\varepsilon(T)$ in the wide range of temperature (-170°C , $+500^\circ\text{C}$) discovered the dielectric constant peak at $\approx 30^\circ\text{C}$ for $\text{Bi}_2\text{NbO}_5\text{F}$ and at $\approx 10^\circ\text{C}$ for $\text{Bi}_2\text{TaO}_5\text{F}$. On the single crystals of $\text{Bi}_2\text{NbO}_5\text{F}$ at 15°C the dielectric hysteresis loop was observed ($P_s = 4 \mu\text{Coul}/\text{cm}^2$). Thus these crystals are also one-layer ferroelectrics with $T_c \approx 30^\circ\text{C}$ and 10°C .

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