

DEPENDENCES OF PHASE TRANSITIONS TEMPERATURES OF PEROVSKITES ABX_3 ($X = O$ or F) UPON THE INTERATOMIC A-X BOND STRAINS

ЗАВИСИМОСТИ ТЕМПЕРАТУР ФАЗОВЫХ ПЕРЕХОДОВ ПЕРОВСКИТОВ ABX_3 ($X = O$ или F) ОТ НАПРЯЖЁННОСТЕЙ МЕЖАТОМНЫХ СВЯЗЕЙ А-Х

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Abstract. The ferro-, antiferroelectric and rotational phase transitions of known binary perovskite structure oxides (ABO_3) and fluorites (ABF_3) have been considered. Some correlations between their phase transition temperature values, on the one hand, and the interatomic bond A-X ($X = O$ or F) strain values, on the other hand, have been constructed. It has been established that the known perovskite structure binary oxides and fluorites with different phase transition nature, caused of a lot of their composition and structure factors, are conditioned, among another, by the interatomic bond A-X strains in their structure.

KEYWORDS: OXIDES, FLUORITES, PEROVSKITE STRUCTURE, BOND STRAINS, PHASE TRANSITION TEMPERATURE, FERROELECTRICS, ANTIFERROELECTRICS, POTENTIAL TRANSITION

1. Introduction

Solid state binary perovskite structure oxides (PSO) and fluorites (PSF) which compositions are described by the general ABX_3 formula, where $X = O$ or F , have been intensively synthesized and studied and study for more than 60 years [1-5], because some of them undergo structural phase transitions (PT) of different nature at appointed temperatures. Those are ferroelectric (FE) phase transitions, at which polar phases appear in the substance; antiferroelectric (AFE) PT, at which antipolar phases appear as well as ϕ - and ψ -type rotational, R, nonferroelectric ones at which different transformations of the octahedral frame of crystal lattice have place. As effect of the structural PT symmetry O_h^1 of preceding phase reduces abruptly into a lower symmetry and, as rule, transforms to any of its subgroups. Ferroelectrics and their solid solutions are basic of the active functional materials for electronics, and their PTs temperature values play an important role. In this connection, understanding why a compound is ferro- or antiferroelectric or undergoes rotational phase transitions and what its temperatures can depend on is of great theoretical interest as well as has practical implications for directed search of new compounds and materials on its basis with the certain structure and properties.

Is there a common feature of the binary PSO and PSF structure that can determine their PT nature and their temperature values? What a feature is necessary to classify their PTs? The theory of ferroelectricity tries different concepts, values or parameters for this role. They are used to construct some qualitative and quantitative correlations between the PT nature and temperature values, on the one hand, and these parameters, on the other hand. Some of them can be determined only experimentally, others - both experimentally and calculated *a priori*. Why are there no ferroelectric or antiferroelectric phase transitions in fluorites, while there are no symmetric constraints for them? Can polar or antipolar phases appear in those compounds in principle? Why do take place similar rotational phase transitions in both the PSO and the PSF? The aim of this work is to answer the above and other questions using the proposed the interatomic bonds A-O strains, δ_{AO} , or A-F, δ_{AF} , calculated using the perovskite structure quasi-elastic model proposed by Sakhnenko VP in 1972 [6] and to construct some correlations between these quantities, on the one hand, and corresponding PT temperatures, on the other hand.

2. Model and the interatomic bond A-X strain determination

Review briefly the unstrained cation-anion bonds elastic model or quasi-elastic perovskite cell model [1, 6-10]. In its creation, analysis and use participated author too. The internal energy of a crystal is modeled as the elastic energy of deformable cation-anion bonds in perovskite structure. The main assumption of the model is that for any cation-anion bond one can introduce an equilibrium bond length – the length of an unstrained bond A-X or B-X, and their stiffness coefficients. These parameters are assumed to be constants for such cation-anion pairs in every compound ABX_3 belonging to the same structural type.

In the case of a binary perovskite with chemical formula ABX_3 , taking into account 12 A-X and six B-X bonds in the reduced cubic perovskite cell one can write the elastic energy as

$$(1) \quad U = 6k_{AX} \left(\frac{a}{\sqrt{2}} - L_{AX}^0 \right)^2 + 3k_{BX} \left(\frac{a}{2} - L_{BX}^0 \right)^2,$$

where a is the reduced cubic cell parameter corresponding to one ABX_3 formula unit of a usual slightly distorted perovskite cell, L_{AO}^0 and L_{BO}^0 are unstrained bond lengths of the A-X and B-X pairs, and k_{AX} and k_{BX} are their respective stiffness coefficients. In the perovskite compounds the interatomic distances can differ substantially from the respective lengths of the unstrained bonds. According to our estimates, their difference for A-X bond can be up to 25%. Therefore, it is assumed that the equilibrium state corresponds to the minimum of the elastic energy (1).

The stiffness coefficients k_{AX} and k_{BX} can be estimated from the generalization of empirical relations found by Gordy [11] in 1946 from the analysis of molecules, which for the case of perovskites can be simplified to

$$(2) \quad k_{AX} = \frac{n_A}{4} \gamma; \quad k_{BX} = n_B \gamma,$$

where n_A and n_B are valences of the ions A and B, respectively, and γ is a constant. By minimization of the energy U given by equation (1), we obtain the following relation for the reduced lattice constant of the cubic ABO_3 perovskite unit cell:

$$(3) \quad a = \frac{4\sqrt{2}k_{AX}L_{AX}^0 + 2k_{BX}L_{BX}^0}{4k_{AX} + k_{BX}}.$$

Unstrained elastic bond lengths for many chemical elements frequently encountered in perovskite compounds were calculated and are given in the supporting information to this work.

Despite the seeming simplicity of the reviewed model, it allows the prediction of the reduced cubic lattice constants of perovskites with an accuracy of better than 1 %. Another striking conclusion that can be drawn from the model is the equation

$$(4) a_1 + a_4 = a_2 + a_3$$

between the reduced cubic lattice constants a_1 , a_2 , a_3 and a_4 of the perovskite-like compounds with the chemical formulae ABX_3 , $A'BX_3$, $AB'X_3$ and $A'B'X_3$, respectively, where A , A' and B , B' are pairs of cations with equal valences, and X is oxygen or a halogen. As shown in papers [7, 10] the relation (4) holds for more than 50 analyzed sets of perovskites to accuracy better than 1%. This striking relation, who holds for the lattice parameters of completely different perovskites, justifies assumption used in the model.

Substituting in (3) the values k_{AX} and k_{BX} (2) through the valences of the atoms A and B n_A and n_B , we obtain a formula for determining the average parameter $\alpha_{exp} = \sqrt[3]{V_{cell}}$ of the reduced perovskite cell, which can be slightly distorted, that is, differ from the ideal cubic one:

$$(4) \alpha_{calc} = \frac{\sqrt{2n_A L_{AX}^0 + 2n_B L_{BX}^0}}{n_A + n_B}$$

Expression (4) will be used later to calculate the interatomic bond $A-X$ strains.

Table 1. Phase transition nature and temperatures and the calculated interatomic bonds $A-X$ strains in oxides and fluorites

PT type, composition, bond $A-X$ and $B-X$ strains ($\delta_{A-X}/\delta_{B-X}$), % and T_{PT} , K			R PT: T_{PT} and final phase	
FE ¹⁾ and *FE ²⁾	AFE ¹⁾ and *AFE	rotational PT, R PT	T_1 , K	G_1
KNbO₃ (-0.2/0.0) $T_{PT}=708$	NaNbO₃ (15/-2.5) $T_{PT}=630$	NaNbO₃ (15/-2.5)	914	00 ψ
*KTaO ₃ (0.2/-0) $T_{PT}=13$	CdTio₃ (9.1/-4.0) $T_{PT}=1223$	NaTaO₃ (15.4/-2.6)	903	00 ψ
*SrTiO ₃ (1.4/-0.7) $T_{PT}=10$	*CdSnO ₃ (12.6/-5.3) $T_{PT}=1073$	CaTiO₃ (6.2/-2.8)	1533	$\phi\phi\psi$
PbTiO₃ (-1.0/0.5) $T_{PT}=763$	*CdHfO ₃ (13.8/-5.7) $T_{PT}=1050$	SrZrO₃ (6.2/-2.8)	1440	00 ϕ
BaTiO₃ (-2.8/1.5) $T_{PT}=403$	*PbSnO ₃ (2.0/-1.0) $T_{PT}=400$	SmAlO₃ (-0.3/0.3)	2100	$\phi\phi\phi$
-	*PbHfO ₃ (3.0/-1.4) $T_{PT}=490$	PrAlO₃ (-0.8/0.9)	1320	$\phi\phi\phi$
-	PbZrO₃ (3.6/-1.6) $T_{PT}=505$	LaAlO₃ (-1.4/1.4)	770	$\phi\phi\phi$
-	-	NaMgF₃ (13.1/-5.4)	1170	$\phi\psi\phi$
-	-	KMnF₃ (7.0/-3.3)	185	00 ϕ
-	-	KCdF₃ (11.6/-4.8)	488	00 ψ
-	-	KCaF₃ (13.1/-5.6)	560	0 $\phi\psi$
-	-	TlCdF₃ (7.7/-3.5)	191	00 ϕ
-	-	RbCdF₃ (7.7/-3.5)	124	00 ϕ
-	-	RbCaF₃ (9.4/-4.1)	198	00 ϕ

The length of the strained interatomic bonds $A-X$ or $B-X$ differs, sometimes considerably, from their unstrained equilibrium length, and their relative strains can be determined by the formula:

$$(5) \delta_{AX} = \frac{L_{AX} - L_{AX}^0}{L_{AX}^0}, \delta_{BX} = \frac{L_{BX} - L_{BX}^0}{L_{BX}^0},$$

where

$$(6) L_{AX} = \alpha_{calc} / \sqrt{2} \text{ and } L_{BX} = \alpha_{calc} / 2.$$

Expression (5) and (6) will be used to calculate (Table 1) the interatomic bonds $A-X$ strains.

3. Separation of phase transitions of different nature from the interatomic bond $A-X$ strain values

The considered binary oxides and fluorides having phase transitions of various natures together with the calculated interatomic bond strains are shown in Table 1. In its ¹⁾ - in boldface, the formulas of binary oxides and fluorites are identified, the strains of the interatomic bonds in them, the abbreviated names of the established nature of their phase transitions and the bonds $A-X$ strains in binary oxides and fluorites values of their temperatures, while ²⁾ - in the usual font formulas – are written, the value of the interatomic bond strains in them, the abbreviated names of the assumed phase transitions nature and the values of their temperatures, which is also noted by the sign "*".

Таблица 2 - The intervals of calculated values (δ_{AX})_{calc} and (δ_{BX})_{calc} for binary PSO and PSF testing: ferro- (FE), anti-ferroelectric (AFE) and rotational (R) ϕ - and ψ -types PT and intervals of their experimental temperatures (T_{PT})_{exp}

PT nature	Intervals (δ_{AX}) _{calc} , % and PT temperatures (T_{PT}) _{exp} , K		Intervals (δ_{BX}) _p , % and PT temperatures (T_{PT}) _{exp} , K	
	from	up to	from	up to
Ferro- and antiferroelectric PT of PSO				
FE	$\delta_{AO} = -2.8$; $T_{PT} = 393$	$\delta_{AO} = -0.2$; $T_{PT} = 763$	$\delta_{BO} = 0.0$; $T_{PT} = 763$	$\delta_{BO} = 1.5$; $T_{PT} = 393$
AFE	$\delta_{AO} = 1.8$; $T_{PT} = 400$	$\delta_{AO} = 15.0$; $T_{PT} = 638$	$\delta_{BO} = -5.7$; $T_{PT} = 1070$	$\delta_{BO} = -1.0$; $T_{PT} = 400$
Rotational PT of ϕ- и ψ-types of PSO				
R PT	$\delta_{AO} = -1.6$; $T_{PT} = 700$	$\delta_{AO} = 6.2$; $T_{PT} = 1440$	$\delta_{BO} = -2.8$; $T_{PT} = 1440$	$\delta_{BO} = 1.4$; $T_{PT} = 700$
ϕ -type	$\delta_{AO} = 6.2$; $T_{PT} = 1533$	$\delta_{AO} = 15.4$; $T_{PT} = 914$	$\delta_{BO} = -2.8$; $T_{PT} = 914$	$\delta_{BO} = -2.5$; $T_{PT} = 1533$
RPT	$\delta_{AO} = 6.2$; $T_{PT} = 1533$	$\delta_{AO} = 15.4$; $T_{PT} = 914$	$\delta_{BO} = -2.8$; $T_{PT} = 914$	$\delta_{BO} = -2.5$; $T_{PT} = 1533$
ψ -type	$\delta_{AO} = 6.2$; $T_{PT} = 1533$	$\delta_{AO} = 15.4$; $T_{PT} = 914$	$\delta_{BO} = -2.8$; $T_{PT} = 914$	$\delta_{BO} = -2.5$; $T_{PT} = 1533$
Rotational PT of ϕ- и ψ-types of PSF				
R PT	$\delta_{AF} = 7.7$; $T_{PT} = 124$	$\delta_{AF} = 9.4$; $T_{PT} = 198$	$\delta_{BF} = -4.1$; $T_{PT} = 198$	$\delta_{BF} = -3.3$; $T_{PT} = 124$
ϕ -type	$\delta_{AF} = 7.7$; $T_{PT} = 124$	$\delta_{AF} = 9.4$; $T_{PT} = 198$	$\delta_{BF} = -4.1$; $T_{PT} = 198$	$\delta_{BF} = -3.3$; $T_{PT} = 124$
R PT	$\delta_{AF} = 11.6$; $T_{PT} = 488$	$\delta_{AF} = 13.1$; $T_{PT} = 560$	$\delta_{BF} = -5.6$; $T_{PT} = 560$	$\delta_{BF} = -4.8$; $T_{PT} = 488$
ψ -type	$\delta_{AF} = 11.6$; $T_{PT} = 488$	$\delta_{AF} = 13.1$; $T_{PT} = 560$	$\delta_{BF} = -5.6$; $T_{PT} = 560$	$\delta_{BF} = -4.8$; $T_{PT} = 488$

In the structures of the majority of binary PSO, as in the structures of the binary PSF, bonds $A-O$ or $A-F$ are stretched ($\delta_{AO} > 0$ or $\delta_{AF} > 0$), and $B-O$ or $B-F$ bonds are compressed ($\delta_{BO} < 0$ or $\delta_{BF} < 0$), in comparison with the tightest packing of atoms. Nevertheless, several PSO, among which there are famous ferroelectrics $KNbO_3$, $PbTiO_3$ and $BaTiO_3$ (See Table 1), have compressed interatomic $A-O$ bonds and, on the contrary, though slightly but stretched $B-O$ bonds.

The calculated values are the intervals of variation of the computed δ_{AO} or δ_{AF} (Table 2) and the intervals of the experimental temperatures of the corresponding PTs of various nature for the PSO and the PSF, which are quite clearly separated from each other in the values δ_{AO} or δ_{AF} in the case of FE and AFE PT (Fig. 1), and on the generalized diagram the line of the polynomial trend of degree 6 most accurately describes this dependence. Nevertheless, it can be seen that the trend of degree 6 more accurately describes this dependence for AFE PT.

4. Correlations between the phase transition temperatures and the interatomic bond A-X strains

Several correlations on the diagrams (δ_{AO} , T_{PT}) or (δ_{AF} , T_{PT}) are constructed to determine how the nature of the observed PT of these compounds can be connected with their interatomic bond strain values. Taking into account the fairly clear separation of phase transitions in terms of δ_{AO} or δ_{AF} values it is established that, firstly, in the binary ferroelectric PSO structures (Fig.1) the interatomic A-O bonds are compressed i.e. $\delta_{AO} < 0$, in contrast to the always stretched interatomic bonds A-O in the structure of every PSF, i.e. $\delta_{AO} > 0$ [11]. Secondly, in the PSF the interatomic A-F bonds are stretched always and much stronger, and the B-F bonds are more compressed than in ferroelectric PSO, which possibly interfere with the appearance of ferroelectric properties in it. Is this not the answer to one of the posed in the introduction questions, in particular, about the reason for the absence of ferro- and antiferroelectric phase transitions in PSO? However, the sum of the dipole polarizabilities of atoms in each PSF composition are noticeably lower [12] than for any PSO, and, of course, lower, than for ferroelectric PSO, which can also be one more reason of the ferroelectric properties absence for PSF.

Third, in comparison with ferroelectric PSO, in virtual ferroelectrics KTaO_3 and SrTiO_3 the interatomic A-O bonds are already slightly stretched, i.e. $\delta_{AO} > 0$. Nevertheless, the introduction of other A or B atoms into the corresponding sublattices, for example, in the solid solutions of the systems $\text{KTaO}_3\text{-LiNbO}_3$ or $\text{KTaO}_3\text{-KNbO}_3$ [13-15], together with the inevitable decreasing of the average interatomic bond A-O strains led to the appearance of any ferroelectric properties. By values of its interatomic bond A-O strains its closer to AFE PSO section, which starts from PbSnO_3 (See Fig 1) and ends on NaNbO_3 , which has the most stretched interatomic bonds A-O ($\delta_{\text{NaO}} = 15\%$) among antiferroelectric PSO.

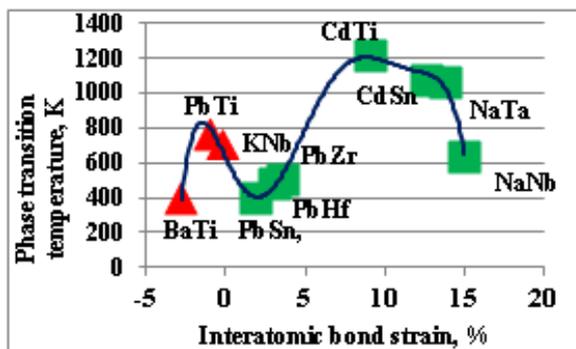


Fig.1. Correlation between the interatomic bond A-O strains in the PSO and the temperature of their FE and AFE phase transitions: FE - red triangles; AFE - green squares

Fourthly, for each δ_{AO} or δ_{AF} values individual interval of certain PT nature there is a maximum T_{PT} : in the ferroelectric PSO δ_{AO} interval - at the point PbTiO_3 equal to 763 K; in the antiferroelectric PSO δ_{AO} interval (See Fig. 1) - at the point CdTiO_3 equal to 1223 K. Fifthly, a situation with the dependences T_{PT} of different rotational phase transitions are more complicated (Fig. 2). With increasing δ_{AO} and/or δ_{AF} , the ϕ -type rotational PT temperatures increase almost precipitously and after a certain δ_{AO} real representatives on the narrow interval ends, as if forming a kind of automatically built-in by the program "virtual" (without representatives) dome in the temperature range, certainly above the melting points for such solid state substances. The maximum of this trend can shift to high temperatures up to ~9000 K. Temperature T_{PT} dependence for PSO with the rotational ϕ -type PT starts from the temperature LaAlO_3 $T_{PT} = 770$ K, closed to the maximum temperature for ferroelectrics PbTiO_3 with $T_{PT} = 763$ K, and ends on SmAlO_3 with the maximum among real such PSO $T_{PT} = 2100$ K. That above virtual dome is by its greatest middle part locates between the ferroelectric and antiferroelectric

intervals δ_{AO} (see Fig. 2) starting from $\delta_{AO} = -0.3\%$ for SmAlO_3 and ending on $\delta_{AO} = 6.0\%$ for SrZrO_3 on the decline of this dependence.

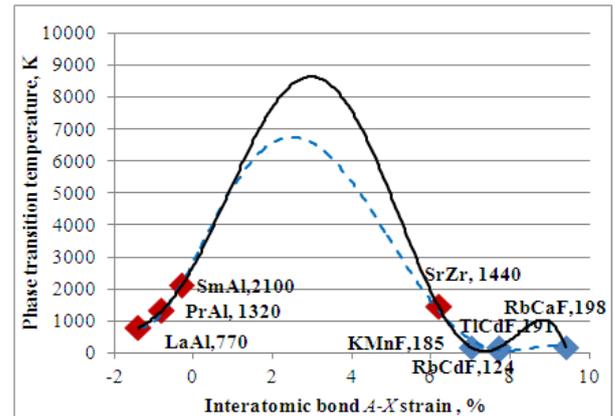


Fig. 2. Correlation between the PSO interatomic bond A-O and PSF A-F strains and the temperatures of their rotational phase transitions ϕ -type: T_{PT} of the PSO - dark red rhombuses; PT of the PSF - blue rhombuses; approximation by a polynomial trends of degree 5 - blue curve; of degree 6 - black one

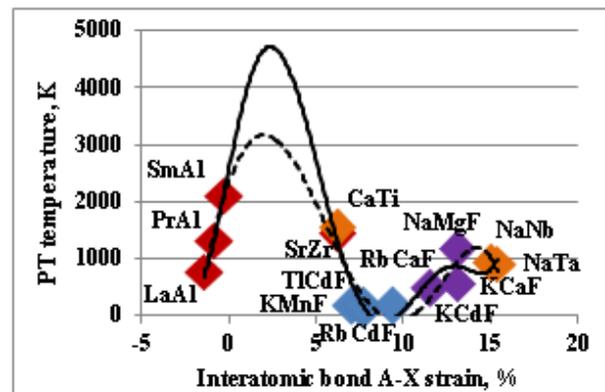


Fig. 3. Generalized correlation between the PSO interatomic bond A-O and PSF interatomic bond A-F strains, on the one hand, and the temperatures of their rotational phase transitions ϕ - and ψ -type PT: ϕ -type of the PSO - dark red and PT of the PSF - blue rhombuses; PT ψ -type of the PSF - purple rhombuses and PT ψ -type of the PSO - orange rhombuses

In principle, in order to describe well the dependence of the T_{PT} of PSO rotational ϕ -type PTs as a δ_{AO} function, a polynomial trend of degree 2 is suitable. Constructed general dependences for PSO and PSF (See Fig. 2) are well approximated by polynomial trends of the fifth or sixth degree, where the author dared to combine the dependencies for PSO and PSF on two different intervals in general dependence. Sixthly, after the previous interval, no longer overlapping with its, but into the antiferroelectric PSO interval, the PSF rotational ϕ -type PT interval starts from $\delta_{AO} = 7.0\%$ for KMnF_3 and ends on $\delta_{AO} = 9.4\%$ for RbCaF_3 , which T_{PT} is very low in comparison with T_{PT} for antiferroelectric PSO: less than 200 K.

However, if in this diagram (See Fig. 2), devoted to the rotational ϕ -type PT, we add the T_{PT} temperatures of the rotational PTs of the ψ -type, both for the PSO and the PSF (Fig. 3) that above the virtual maximum will greatly decrease. Such construction with the combination of different FPs and different objects is completely justified because the R PTs of ψ -type are observed quite rarely both among the PSO and the PSF, although they are fairly well separated by the values of δ_{AX} . It turns out that these dependencies and the temperatures of their PTs are somehow interrelated, since they can be described by one common curve.

5. Conclusions

Thus, all binary PSO and PSF that undergo phase transitions of different nature can be separated by the values of their interatomic bond $A-X$ strains. Phase transitions of every nature under consideration: the ferroelectric, antiferroelectric, and rotational φ - and ψ -types, are located on separate intervals of their interatomic bonds $A-X$ strain values. At the same time, ferroelectrics are quite clearly separated from antiferroelectrics. The δ_{AX} intervals of ferroelectric PTs overlapped with rotational φ -type PTs for PSO are partially, as well as AF PTs for PSO with rotational φ - and ψ -types PT. Thus, the answer to the most important question posed in the Introduction was found: the structure general argument δ_{AO} was found and tested for all the considered binary PSO and PSF: interatomic bond $A-X$ strains, which can be calculated *a priori* from a quasi-elastic perovskite type structure model. The same parameter can be proposed for other perovskite-like structures. Moreover, here it is clearly demonstrated not only that the temperatures of PTs, which are experimentally determined in various laboratories of the world and fixed in recognized monographs and reference books [1 - 5], depend on these values of interatomic bond strains, but also rather difficult. Nevertheless, one can assume their appearance.

It seems that the temperatures of PTs of different nature in the respective interval of δ_{AX} vary in one scenario: with increasing of the interatomic bond $A-O$ or $A-F$ strain values, to some extent, the of each nature PT temperature, T_{PT} , increases to a certain maximum, after which it decreases. When the $A-O$ bond is strongly compressed, as, for example, in $BaTiO_3$ ($\delta_{AO} = -2.8\%$), the $B-O$ bond is relatively small, but stretched, which, generally speaking, is not typical for this connection in the structures of the PSO. That is why, when the ferroelectrics $BaTiO_3$ was discovered, the "stretching" of the $Ti-O$ bond in it was considered [2] as the cause of its FE state, which distinguished it not only from non-ferroelectric PSO, but also from other ferroelectrics with the perovskite structure. They talked [1 - 3] about some "freedom" for the Ti atom, which determines the nature of $BaTiO_3$ PT as FE PT. Nevertheless, as the stretching of $B-O$ bonds from $BaTiO_3$ to $PbTiO_3$ decreases (see Fig. 1) and moreover, with decreasing contraction of the $A-O$ bond, the temperature of its FE PT and even the value of the spontaneous polarization, P_s , that is one of the main ferroelectric state characteristics, is higher than their values for $BaTiO_3$.

It seems that the cause of the FE state is just the contraction of the $A-O$ bond, as in $PbTiO_3$ or $KNbO_3$ with higher temperatures of the FE PT, than for $BaTiO_3$, rather than the stretching of the $B-O$ bond, as was thought about $BaTiO_3$. Moreover, the increasing of the interatomic bond $A-O$ stretching in the future leads to the absence of ferroelectricity already in $SrTiO_3$ and $KTaO_3$ with the interatomic bonds $A-O$ comparatively small strains and then the strain starting already from 2%, leads to the AFE PT in $PbSnO_3$, $PbHfO_3$, $PbZrO_3$, et al. At some the $A-O$ bond strain, its elasticity goes over a certain limit, after which the temperature of the AFE PT drops sharply. The shown separation of different nature phase transitions into separate intervals for binary perovskites of ABX_3 can be carried out for ternary and more complex perovskites, as well as representatives of other structural families.

Author want to finish the message with the prophetic words of Professor Fesenko EG, stated by him in the monograph [1] in a free translation of the author: "The study of regularities and connections is greatly facilitated by the simplicity of the structural type of perovskite, so we can expect that they will be successful and will form an important stage in the near future in the development of solid-state physics and crystal chemistry. This will make it possible not only to explain the physical properties of the PSO and to solve the problem of computational design and creation of new highly effective materials on the basis of PSO, but also to make important generalizations that go far beyond the family limits to the boundless "sea" of ion-covalent crystals. "

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