

Binary perovskite solid solutions and trends in their phase transitions temperatures variation

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Received 19 April 2021; Revised 28 June 2021; Accepted 16 July 2021; Published 8 September 2021

Some of the known binary ABO_3 perovskites with ferro- (FE) or antiferroelectric (AFE) at T_C and different magnetic phase transitions (PT): ferro- and antiferromagnetic at T_N and also some of their solid solutions are considered. Some correlations between their FE or AFE and/or magnetic PTs temperatures, on the one hand, and their interatomic bond $A-O$ strains, on the other hand, have been constructed. It is shown that in the plotted diagrams these temperatures change with a change in δ_{AO} values as follows: classical FEs are followed by multiferroics, starting with $BiFeO_3$ and ending with YVO_3 , followed by classical AFEs. At the same time, the temperatures T_C and T_N experience maxima at the corresponding points for $BiFeO_3$, then quickly decrease, and the difference between them, $T_C - T_N$, basically also decreases, slightly increasing along the way to the point $EuTiO_3$, which made it possible to systematize these T_C and T_N .

Keywords: Perovskite structure; binary oxides; solid solutions; ferroelectric phase transition; magnetic phase transition; phase transition temperature.

1. Introduction

Some of the known^{1–5} binary $A^I B^V O_3$, $A^{II} B^{IV} O_3$ and $A^{III} B^{III} O_3$ perovskites with ferro- (FE) or antiferroelectric (AFE) and sometimes also with magnetic phase transitions: ferro- (FM) and antiferromagnetic (AFM) are considered here. They have FE or AFE properties below their phase transition (PT) temperatures, T_C , together with (or without) magnetic properties — below their magnetic PT temperature T_N . These compounds in the pure state rarely are used in electronic technique, in particular, as ferro piezoelectric functional materials in some devices. They are used in a form of more complex in composition their solid solution (SS) of two-, three-, four-component or more complex systems. Perovskite-type oxides are very important materials, exhibiting unique properties such as ferroelectric, ferromagnetic, piezoelectric, and some others.

The main currently known functional materials for the manufacture of piezoelectric elements^{6,7} are the compositions of lead-containing multicomponent SS based on the PZT system: $(1-x) PbTiO_3 - x PbZrO_3$ where $PbTiO_3$ is a ferroelectric and $PbZrO_3$ is antiferroelectric. The development of functional materials based on SS located near the morphotropic region of this system made it possible to obtain compositions

with high values of piezomodulus and electromechanical coupling coefficients in a wide temperature range. Further development of other necessary properties in such materials is associated with their modifications, and then with the creation of multicomponent SS systems based on them. These are such Russian materials^{6,7}: PZT-21; PZT-45; PZT-B; PZT-12P; PZT-19; PZT-19M; PZT-26; PZT-36 and PCR-1; PCR-7M and many others. Important characteristic of these materials is their Curie temperatures, upon which their working temperatures depend. Nevertheless, these and other multicomponent SS systems contain in their “arsenal” interesting properties combinations of binary SS, that make up their compositions.

Recently, there has been a search for other systems of SSs, for example, high-temperature Bi-containing materials based on binary SS systems such as $BiB^{III}O_3 - PbTiO_3$, where B^{III} - Fe, Sc or In, which can have rather high piezoelectric properties and $T_C \geq 670$ K to 780 K.⁷ It should be borne in mind that not only such SS systems are in demand for this, but also based on or with other compounds such as $A^{II} B^{IV} O_3$, or $A^I B^V O_3$ or $A^{III} B^{III} O_3$, especially with magnetic PTs and consequently magnetic properties.^{8–31}

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The creation and research of different crystalline family's ferroelectrics in the world has been going on for over 100 years. The discovery of the ferroelectric properties of BaTiO₃ in 1945 marked a long epoch in the production and study of about 1000 binary and ternary representatives of the perovskite family and a much larger number of SSs between them, including above all binary SSs. Based on the electronic structure of *A* and/or *B* atoms, compositions of new ferroelectrics, ferroics, multiferroics and functional materials based on them are proposed.

Expectations of special electrical and/or magnetic properties in a particular atomic composition are not always justified in an experiment, both because of the internal atom interactions features, and because of the synthesis technology peculiarities of compound or SS. As a result, since the middle of the last century, a group of binary oxides with a perovskite-type structure has been formed, which are recognized as multiferroics,^{8–31} since below the T_C they exhibit FE or AFE properties, and below the FM or AFM properties. Some of them are the objects of our research also, including some their SS.

Now it becomes necessary to try to establish the relationships between the physical properties of such compounds and SSs of various crystal families with their atomic structure peculiarities. The most studied in this sense family of complex oxides and their SSs with a perovskite-type structure, the compositions of which are described by formulas of the ABO_3 type or more complex, is very rich in both FE or AFE, and magnetic PT, due to their sufficiently studied model structure, still attracts increased attention, including ours.

The different existence forms of such research objects, especially of multiferroics, are diverse.^{8–30} These are mainly polycrystalline materials (ceramics or powders), except for thin films, composites or superlattices. In isolated cases, single crystals are used. In most works, such a wide range of real existence states is not accompanied by appropriate reliable studies of the structural details. Nevertheless, some correlations between their structural parameters or their change from various factors, on the one hand, and electrical and/or magnetic properties, on the other hand, can be established if for this we try to use their common characteristic, for example, the characteristic of their structure, despite this difference in the existence form sometimes. There is, of course, no reason to deny the influence of the existence form or the compound preparation technology on the final result of the constructing correlations or establishing regularities. Exceptions from the established general patterns are also possible for this or other numerous natural or man-made reasons. Exceptions can lead to discoveries. Thus, some general correlations between their some structural parameters and their observed physical properties, in particular, T_C and T_N values can be revealed in principle.

2. Problem Formulation

Ferroelectrics and their SSs (Fig. 1) are basic of the functional materials for electronics,^{6,7} and their PTs temperature values play an important role. In this connection, understanding why a compound is ferro- or antiferroelectric, or multiferroic and

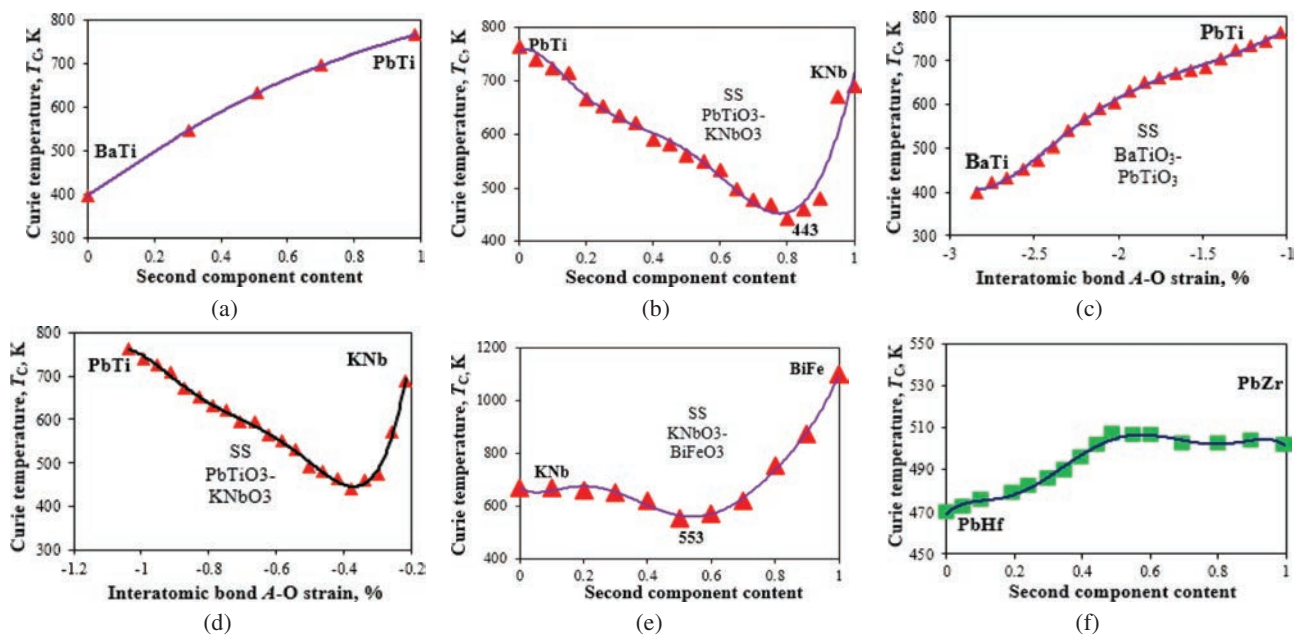


Fig. 1. Experimental FE (*triangles*) and AFE (*squares*) PT temperatures T_C dependences on the interatomic bond A–O strains for SS systems: (a and c) BaTiO₃–PbTiO₃; (b and d) PbTiO₃–KNbO₃; (e and g) KNbO₃–BiFeO₃; (f and h) PbHfO₃–PbZrO₃; (i and k) PbTiO₃–PbZrO₃; (j) a common dependence for three systems: PbSnO₃–PbHfO₃; PbHfO₃–PbZrO₃ and PbZrO₃–PbTiO₃; (l) KNbO₃–KTaO₃. For each considered SS system, there are dependences of T_C both on the calculated δ_{AO} and on the second component content x .

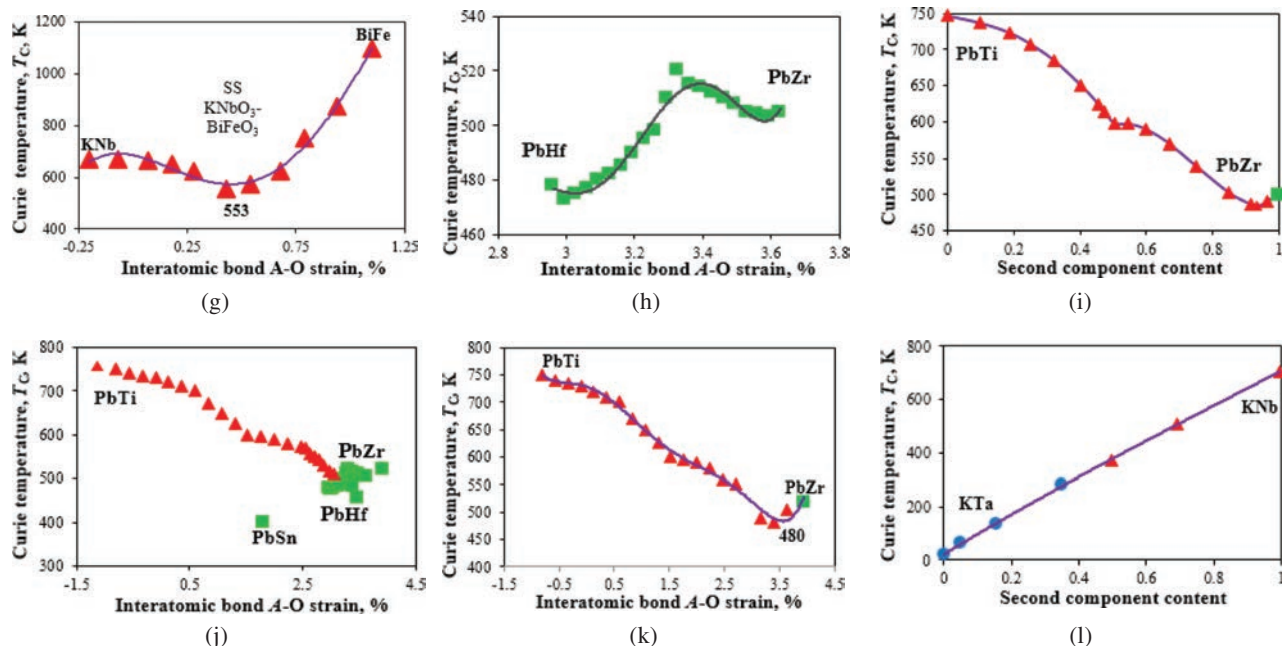


Fig. 1. (Continued)

what its PT temperature can depend on is of great theoretical interest as well as has practical implications, in particular, for directed research into new compounds and materials with the certain structure and properties.

First, some correlations between the interatomic bonds A–O strains and the PT temperatures of binary and ternary perovskites with FE and AFE properties already were considered.^{31–33} They turned out to be quite complex and not always unambiguous. In the case of binary FE perovskites, a T_C maximum was observed at the PbTiO_3 point, and for the AFE perovskites, at the CdTiO_3 point. For ternary perovskites, any T_C pronounced maxima are not observed and their T_C temperatures are on average lower than the characteristic temperatures for binary ones. Some correlations³² between their FE - or AFE T_C and magnetic PT T_N temperatures, on the one hand, and their interatomic bond A–O strains, on the other hand, have been constructed.

From these facts, it can be concluded that a composition complication leads to a decreasing in T_C , including, apparently, their solid solutions, for which such studies have not yet been carried out systematically.

Second, we considered³³ what tendencies (trends) in the variation of T_C and Néel temperature T_N and also their difference are observed in the same theme in binary and ternary multiferroics with a perovskite structure in aggregate and in comparison, with each other. The results there were new generalized diagrams of relationships between the interatomic A–O bond strain, on the one hand, and the temperatures of FE and AFE PT together with the corresponding magnetic ones. Third, and most importantly, the “power” of the applied

structure parameter, namely, the weakest in perovskite (and not only in the perovskite) structure interatomic A–O bond strains, has been demonstrated³⁴ in the study of general relationships “composition — structure — properties” for similar compounds, including compounds with other perovskite-like structures.

And now, when we “got close” to solid solutions between various perovskites, in particular, between binary perovskites, we can also try to construct some correlations (tendencies, trends) of these PT temperatures, on one hand, and the calculated or experimental values of the interatomic bond strains δ_{AO} in the compounds and their SSs cells to which this paper particularly is devoted. Knowing some tendencies in the change in the temperatures of different nature PTs, it is possible to assume the trends in T_C change of the yet unstudied SS systems, using their calculated *a priori* δ_{AO} only. Nevertheless, to do this it was necessary to systematize the PTs temperatures of potential components of possible SSs between magnetics and find out what structural parameters they can depend on. The various T_C and T_N on δ_{AO} values systematization is our goal.

3. Correlation’s Construction

The most acceptable and accessible characteristics of such interatomic interactions in the perovskite oxides structure may be the lengths of interatomic bonds that can be determined theoretically with the help of the quasi-elastic model^{34,35} of the perovskite structure. Its main feature is the assumption that the interatomic bonds A–O lengths L_{AO} in

real oxides with perovskite structure can significantly differ (by our estimates, up to ~25%) from the corresponding unstrained (free) interatomic bond lengths L_{AO}^0 . When atoms A and B enter a complex compound lattice, these lengths of the free interatomic bonds change, that is, as it is customary to say in the model under consideration, are forced to strain somehow (stress or compress as compared to unstrained L_{AO}^0), so that the corresponding atom, be it atom A or B , could enter the crystal lattice of a complex compound or SS provided that the minimum energy of its lattice is preserved. The A - O interatomic bond strains are defined as their relative deformation: $\delta_{AO} = (L_{AO} - L_{AO}^0)/L_{AO}^0$, and L_{AO}^0 values were tabulated.^{34–36} Of course, if these atoms with their L_{AO}^0 may not enter the lattice of a complex compound or SS, and then the structure, in this case of perovskite, may not be formed. The conditions for their entry into the lattice of a compound of a certain structural type, that is the conditions of the structure formation and its existence areas were partially discussed in our previous paper,³² but it is definitely necessary to talk about them separately for each structural type and composition type.

We tried to construct some correlations between their FE T_C and magnetic T_N PT temperatures, on the one hand, and their interatomic bond A - O strain δ_{AO} , calculating with use of perovskite structure quasi-elastic model proposed, on the other hand. In this case, we consider several well-known binary systems of SS based on the most studied binary oxides with a perovskite structure — ferroelectrics: $BaTiO_3$, $PbTiO_3$, $BiFeO_3$ and $KNbO_3$, and also antiferroelectrics: $PbSnO_3$, $PbHfO_3$ and $PbZrO_3$. Apart from $BiFeO_3$, they do not have any magnetic PT.

3.1. Ferroelectrics and antiferroelectrics with perovskite structure and their solid solutions

In the considered real SS systems (see Fig. 1) with FE or AFE PTs, the dependences of PT temperatures on the second component concentration have been constructed with use of the well-known experimental data where these temperatures are changed in various ways. Corresponding of known rules, reminiscent of the well-known Vegard rule about the conditions for the formation of a continuous series of SSs between components that have or not for this a number of listed below advantages, these dependences can be linear when SS components have similar structure type, some common atom A^i or B^j , the same valences of each from these atoms and/or the same PT nature. In the considered figures (Fig. 1) such systems are



for which these dependences are straightforward ones.

They are differed from such ones in other systems:

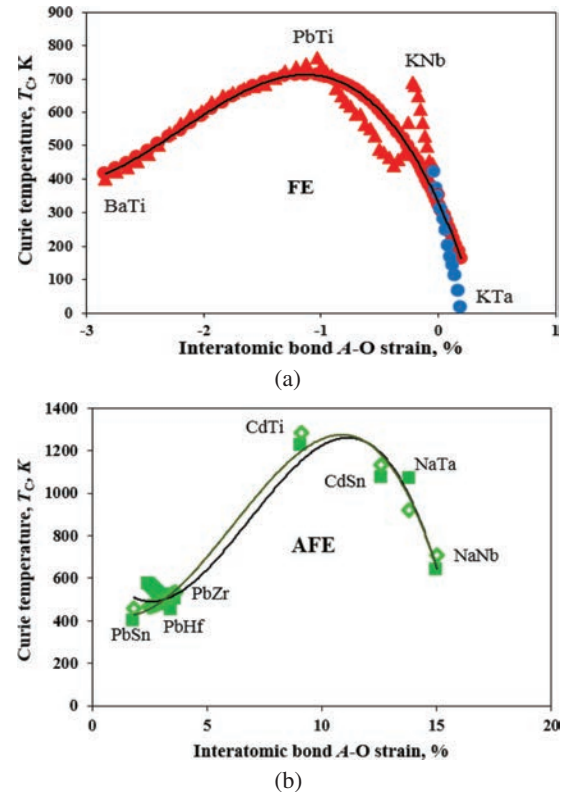
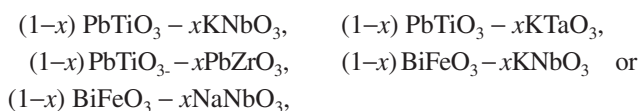


Fig. 2. Common diagrams of the binary perovskites (a) FE (triangles) and (b) AFE (squares) PT temperature with T_C dependences on their δ_{AO} . The calculation by LSM values are designed by empty rhombus. Polynomial trends of degree 3 were carried out which describe all points in the best way. They are built using a special program sewn into Excel program.

where the components have or different A^i and/or B^j atoms valences, or the different PT nature, and, accordingly, their T_C dependence differs from the rectilinear one, and moreover, it can break off, as in the case of the $(1-x) PbZrO_3 - xPbSnO_3$ system, where “ $PbSnO_3$ ” is poorly formed in the perovskite structure, except at a sufficiently high pressure.

These dependences are located in Fig. 1 so that the T_C dependence on the interatomic bond strain is under the corresponding experimental dependence on the second component content the SSs. The general diagrams, are constructed separately for the FE (see Fig. 2(a)) and AFE (see Fig. 2(b)) SSs show the T_C dependences on δ_{AO} with envelope curves obtained as a result of trial approximation by the least squares method. The result of such an approximation shows that the dependences for individual SSs, satisfactorily coincide with the general trends of T_C change — polynomials of the third degree both for FE and AFE. The same circumstance is demonstrated in Fig. 3, where these dependences are combined into a general trend of the sixth degree polynomial, which satisfactorily bends around the combined dependences.

Until now, we have been talking about the trends in the Curie temperatures variation for the PT of FE and AFE oxides

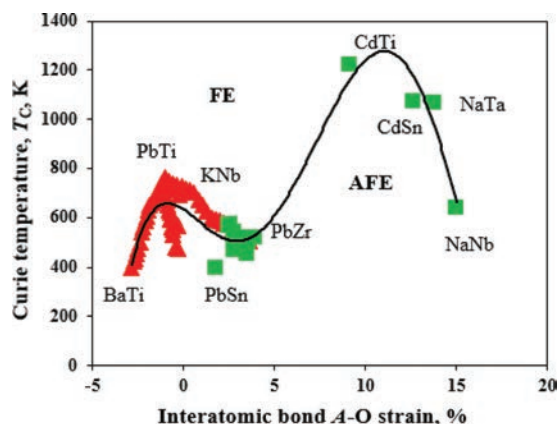


Fig. 3. Common diagrams, in which are carried trends of different PT temperatures for the binary perovskites: T_C for FE (triangles) and AFE (squares) on their interatomic bond A–O strains. Polynomial trend of sixth degree is carried out which describe all points in the best way. It is built using a special program sewn into Excel program.

and their SSs, and it was interesting for us to determine how this general dependence will be continued by considering multiferroics that also have FE PT and will it be possible to combine the T_C dependence for FE with the T_C dependence for multiferroics? It was revealed that binary multiferroics with FE PTs, according to their δ_{AO} values, fall into the field of binary antiferroelectrics³² and overlap this field, however, being located somewhat lower in temperature T_C , excluding T_C of BiFeO_3 , which can be a kind of the corresponding trends maximum. For binary AFEs, the δ_{AO} variation interval is $\delta_{AO} = 2\text{--}15\%$, and for the considered multiferroics of the $A^{\text{III}}B^{\text{III}}\text{O}_3$ type, with $\delta_{AO} = 1.1\%$ for BiFeO_3 , does not exceed $\delta_{AO} = 5\%$.

In order not to clutter up the further diagrams' construction with unnecessary details, we have excluded for the time being the plotting of the points of the general dependence for the AFE PT and then we will try to construct a general diagram (δ_{AO} , T_C) only for binary ferroelectrics and multiferroics, which have the FE PT as their first PT. If it is possible to combine these two different hypostases of physical properties into a general trend and then connect the tendency of their T_N changes, then it will be expected that these trends are close to reality, and the trends obtained can be used both to search for new multiferroics based on the calculated δ_{AO} and new SSs between them or between them and ferroelectrics that do not have magnetic PTs.

3.2. Multiferroics with perovskite structure

Multiferroic BiFeO_3 possesses the highest T_C among multiferroics with a perovskite-type structure, which have the first FE PT, and Bi-based compounds with the general formula BiMO_3 , where M — a magnetic transition metal, have received a lot of attention as multiferroics. Calculation of

electronic structure of one of them, namely, BiCoO_3 ⁸ has showed the importance of Bi–O bonds for the non-center symmetric deformation and also O–O bonds for stability of BiCoO_3 multiferroic phase. Pure and bulk BiFeO_3 has shown poor performance in various technological applications because of low saturation magnetization, high current leakage, and poor magnetoelectric response at room temperature. The substitution of atoms in its A or B sites by others has proved to be another successful approach which have a great influence on magnetic, electrical and other properties of the multiferroic SSs.

It has already been noted in the literature that a sufficiently high temperatures (not lower than room one) of the FE and magnetic PTs are required for the successful functioning of a multiferroic. But not only these temperature values, but their difference $T_C - T_N$ plays a significant role to construct multiferroics for their using. For a multiferroics functioning, this difference should be minimized and the temperature themselves should be raised to at least room temperature. This task is difficult if at all solvable. Nevertheless, on the base of perovskite structure compounds there are in the literature a large number of descriptions of various SS systems whose compositions also have magnetic properties when the components-multiferroics are present in them, in particular, the same BiFeO_3 . Then it was necessary to determine where these temperatures come closest to each other on the correlations constructed here (Fig. 4) between the arguments of their structure — the A–O interatomic bond strains δ_{AO} , on the one hand, and the temperatures of their different PTs and their differences, on the other hand. The constructed diagrams (see Fig. 4) and trends of T_C and T_N variations on the interatomic bond A–O strains indicate that for binary perovskites with structural FE PTs, as and AFE ones, their temperatures in some way depend on their interatomic bond A–O strains δ_{AO} .

Moreover, for SSs between FE or between FE and AFE perovskites between every point pair the same dependence form which is observed in Fig. 1. Nevertheless, the dependence of the PT temperature is not always rectilinear, that fact corresponds to the empirical rules that were set out above. General dependences of these temperatures for all considered compounds (see Fig. 2), including the general trend in the temperatures of FE and AFE PTs together (see Fig. 3) repeat the same “bends” as in the individual diagrams (δ_{AO} , T_C) in Fig. 1. The experimental points SSs T_C fit satisfactorily. Nevertheless, the most general polynomial trend of the T_C dependence for FE and AFE PT (see Fig. 3) has a degree of 6, and not 3, as trends in Fig. 2.

Figure 4 shows the dependences (trends) of T_C and T_N changes on δ_{AO} for binary FE perovskites with magnetic PT and without them. For FE BaTiO_3 , PbTiO_3 , KNbO_3 and BiFeO_3 are shown T_C changes in their SSs by smaller icons: at first, the BaTiO_3 – PbTiO_3 system joins with the PbTiO_3 – KNbO_3 system and the process goes through the KNbO_3 – BiFeO_3 system, throwing a bridge between the ferroelectrics

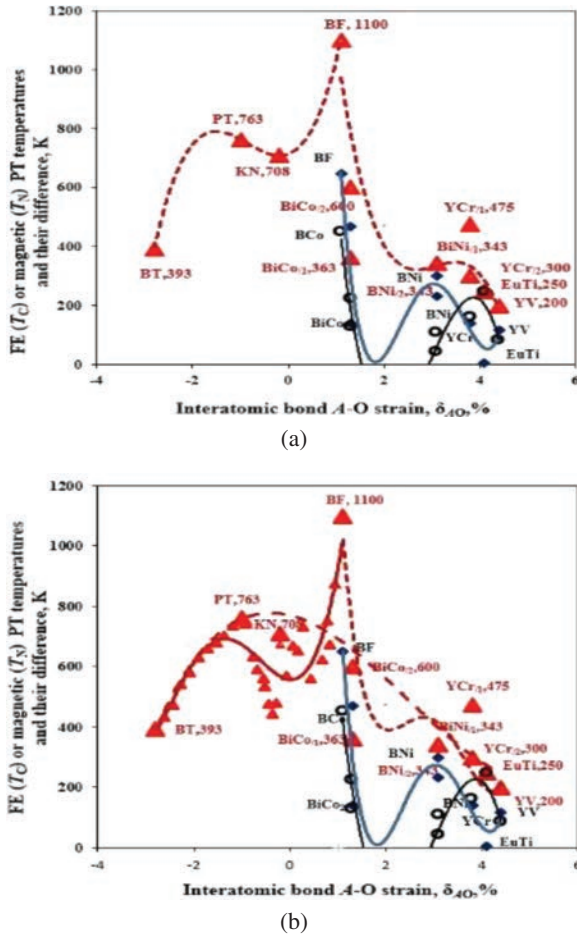


Fig. 4. The dependences (trends) of T_C and T_N changes on δ_{AO} for binary FE perovskites with magnetic PT and without them: (a) without taking into account the temperatures T_C and T_N change in their SS (only large icons) and (b) taking into account T_C changes in real SS systems (small icons along with large ones for oxides).

only without magnetic PTs and ferroelectrics with magnetic properties. The dependences depicted here are the main results of our research. This result confirms the main idea or hope that the interatomic bond, in particular, A–O strains in perovskite cell, determined both or in experiment, or calculated with the help of the perovskite structure quasi-elastic model cannot but influence in a certain way such important characteristics of ferro-, antiferroelectrics and multiferroics with a perovskite structure as their PT temperatures: T_C and T_N and their difference for multiferroics.

The dependences of the difference between the temperatures T_C of the FE and the corresponding magnetic PT temperatures T_N , on the one hand, and the values of the interatomic bonds A–O and B-strains, on the other hand, are shown in Fig. 5. It is notable that the minima of these values are presented, which correspond to such FE compounds as BiCo₃, BiNiO₃, or YVO₃, and among the AFE binary compounds, is presented only BiGaO₃. The dependences of the FE and magnetic PT temperatures and their T_C - T_N differences

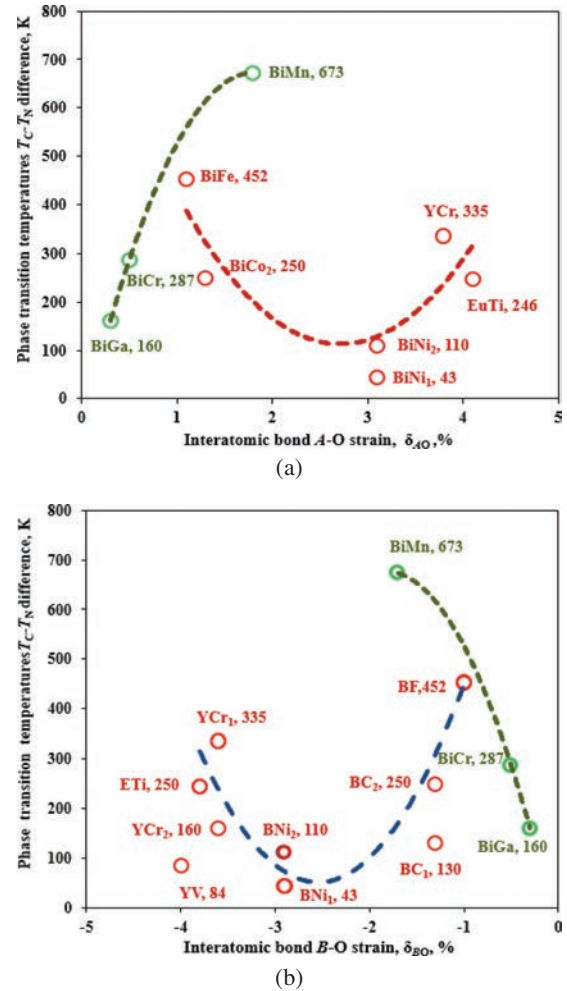


Fig. 5. Dependences of the FE and magnetic PT temperatures T_C - T_N difference for binary perovskites with FE and magnetic properties. Polynomial trends of degree 3 were carried out which were built using a special program sewn into Excel program.

for binary perovskites together with manganites $A^{III}MnO_3$ with FE and magnetic PT are shown in Fig. 6. Having very high Curie temperatures of FE PTs, slightly below the T_C of the famous BiFeO₃, they have extremely low temperatures of magnetic PTs – below 100 K.

4. Conclusions

We systematize the temperatures of various PTs of some binary perovskites by arranging them on the general field of their δ_{AO} values. It was done in order to show the intervals δ_{AO} where these PTs temperatures are located, and how far the intervals for different PTs are separated from each other in this field δ_{AO} , and how they can change when various SSs are created between them. At the same time, we assumed that the form of the dependence T_C or T_N on δ_{AO} for binary perovskites in their general dependence should correspond (see

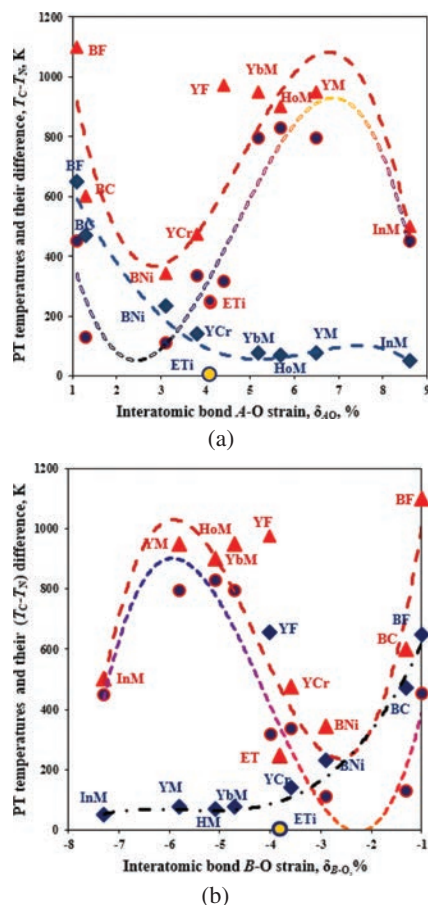


Fig. 6. Dependences of the FE (triangles) and magnetic PT (rhombus) temperatures T_C-T_N differences (circles) for binary perovskites and manganites $A^{III}MnO_3$. Polynomial trends of degree 3 were carried out which describe all points of every curve in the best way. They are built using a special program sewn into Excel program.

Fig. 4) to the form of same dependence that actually exists in every individual SS system (see Fig. 1) and is repeated, as it was, in the general picture of the all considered PTs. A kind of “bridge” between the FE and magnetic PTs is formed by the compositions of the system $(1-x)KNbO_3-xBiFeO_3$ (see Figs. 1(e) and 1(g)), although some it details were built earlier without any help of this SS system and were seen in previous author’s works.^{32,33}

The authors are yet to understand the observed trends in PTs temperatures variation on the strains of A–O interatomic bonds, and to what extent these trends are related to the reality of physical processes occurring in the observed compounds and their SSs. The point is that FE and AFE PTs are structural ones, that is, they abruptly change the symmetry of the compound structure,^{37–43} in contrast to magnetic PTs, the nature of which is different, and they are not purely structural ones. Nevertheless, the observed pattern of joint trends in the change in FE and magnetic PTs temperatures for the

considered compounds and their SSs does not allow us to discount their elastic structural characteristics influence.

Nevertheless, the magnetic properties of the compounds and their SSs under consideration clearly depend on their compositions, and it will not be entirely correct if for such compounds in the general relationships “composition-structure-properties” the middle link — “structure” with all its features, will be completely canceled. Such an elastic structural characteristic as the strain of interatomic A–O bond the degree of deformation of which explicitly depends on the composition, cannot but affect the magnetic PTs parameters. Therefore, we used them to systematize temperatures and also magnetic PTs.

Of course, the authors do not insist that this δ_{AO} value is the reason for the appearance of magnetic PTs and the corresponding properties of considered compounds and their SSs. But if they have arisen already, then their PTs temperatures of somehow changes, as we see from the constructed correlations, with an increase or decrease in their δ_{AO} . Thus, using their values δ_{AO} it is possible to suppose not only the FE PT Curie temperatures, but also the Neel temperature of the corresponding magnetic PT, if their SS contains a component with magnetic properties. It should be noted that a lot of binary or more complex SS systems with $BiFeO_3$ or on its basis and with binary and/or ternary components with FE, AFE, magnetic properties or without ones, are known.^{8–31,37–53}

Here we tried only to throw a thin bridge between FE and magnetic PTs with using SS system $(1-x)KNbO_3-xBiFeO_3$. The point is that, whether we like it or not, the SSs properties depend to some extent on the initial properties of their final components. It has long been noted that, as a rule, up to 40% to 50% of the second component the SS properties are dictated by the first component to a certain extent, if a continuous and complete series of SSs is formed, and then after that they can be dictated by the second component as well. But in a certain morphotropic region of their greatest mixing, the extreme SSs properties are always expected and often observed. In the presented figures, similar maximums and minimums are also visible.

We previously established³² that the T_C of FE and/or AFE PTs depend on their interatomic bond A–O strains δ_{AO} . Nevertheless, it was not yet clear whether the magnetic PTs T_N temperatures depend on the interatomic bond A–O elastic characteristics, for example, and if so, how? It was established here, first, that the differences between temperatures of ferroelectric FE and magnetic PTs, T_C-T_N , depend on δ_{AO} values to some extent. Of course, these temperatures and their difference depend not only on δ_{AO} . In the works^{8–31} to which we have referred already, and in numerous other works^{44–53} devoted to various studies of the same multiferroics are presented a lot of features of their compositions, and atoms in its, and various methods of their preparation in various existence forms. In this way, the presented dependencies (trends) of the PTs temperatures only, and on δ_{AO} only,

could not be so smooth and monotonic, although not without exceptions, if they could not take place in reality, despite many other factors that can influence similar PT temperature dependences.

Thus, it is possible to find out such SS systems on constructed correlations that are characterized negative or positive δ_{A0} values, but enough high temperatures T_C and T_N and to bring their T_C and T_N for them closer to each other, using such dependences and calculating *a priori* their interatomic bond strains in their perovskite cells. Systems, that could be recommended in this sense are the following (see Fig. 5): $(1-x) \text{BiNiO}_3 - x\text{BiFeO}_3$, $(1-x) \text{BiCoO}_3 - x\text{BiFeO}_3$, $(1-x) \text{YVO}_3 - x\text{BiFeO}_3$, in which can be the lowest differences $T_C - T_N$, or other SS systems based on BiFeO_3 with hexagonal manganites (see Fig. 6), as the solid solutions with the highest $T_C - T_N$ differences, which have the high Curie temperatures of FE PTs, slightly below the T_C of the famous BiFeO_3 , have extremely low temperatures of magnetic PTs below 100 K.

Acknowledgments

The study was financially supported by the Ministry of Science and Higher Education of the Russian Federation [State task in the field of scientific activity, scientific project No. 0852-2020-0032 (BAS0110/20-3-08IF)].

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