

Correlations "interatomic bond strain – Curie temperature" for complex oxides on the perovskite structure quasielastic model base

G.A. Geguzina

*Southern Federal University, Research Institute of Physics, 344090, Rostov-on-Don, Russia
geguzina@sfnu.ru*

The known perovskite structure binary and ternary oxides (PSO) [1], which undergo ferroelectric (FE) or antiferroelectric (AFE) phase transitions (PT) at the corresponding Curie temperatures, T_C are considered. The purpose of the article: to establish qualitative and/or quantitative correlations between the values of the interatomic bond strains $A - O$, δ_{A-O} , or $B - O$, δ_{B-O} , in their structure, on the one hand, the nature and the values T_C , at which their FE or AFE PT occur, on the other hand.

Values of δ_{A-O} or δ_{B-O} can be determined from the proposed by Sakhnenko V.P. and co-authors of the quasi-elastic model of the perovskite structure [1-4], which makes it possible to calculate the theoretical average parameter of the perovskite cell with an accuracy no worse than 1%. The values of the interatomic bond strains can be determined from both the calculated and experimental average parameter, $\bar{a} = \sqrt[3]{V_{per.cell}}$, of the perovskite cell, containing one formula unit. For binary and ternary PSO $\delta_{A-O} = (L_{AO} - L_{AO}^0) / L_{AO}^0$ where L_{AO}^0 is the length of the unstrained (free) interatomic bond $A - O$, and L_{AO} is the length of the strained bond in the complex oxide structure. The L_{AO} values can be determined either from the experimental \bar{a}_{exp} or calculated \bar{a}_{calc} average cell parameter: $L_{AO} = \bar{a} / \sqrt{2}$. The values L_{AO}^0 were calculated [4] by the author from an array of experimental parameters of a reduced perovskite cell of ~1000 known binary and ternary PSO.

The values δ_{A-O} in binary PSO can be both negative, for example, in the structures of ferroelectrics $BaTiO_3$, $PbTiO_3$ and $KNbO_3$, demonstrating the tightness of the bonds $A - O$ in them, as well as can be equal 0, for example, in the structures of some ternary ferroelectrics, showing zero interatomic bond $A - O$ strain. For ternary PSO possessing an FE PT, almost zero or small positive ones are characteristic, and for ternary PSO with an AFE PT, they are much larger. These values indicate that for all FE PSO δ_{A-O} exceed a certain value, above which δ_{A-O} of the AFE PSO are located. Thus, it was possible to separate the FE PSO from the AFE PSO by their δ_{A-O} values. At the same time, the "virtual" FE PSO, for example, $SrTiO_3$ and $KTaO_3$, are located between the FE and the AFE PSO in terms of their δ_{A-O} values.

The correlations between the δ_{A-O} , on the one hand, and FE and AFE PT T_C values, on the other hand, built on diagram (Fig. 1a) for binary PSO, show that the PT temperatures for them among other their composition and structure factors is determined by the interatomic bond strains $A - O$, δ_{A-O} . If for a binary PSO it is $\delta_{A-O} > 0$, the ferroelectric properties are not observed at all, and starting with $\delta_{A-O} > 2\%$ for binary PSO already AFE PT is observed, for example, for AFE PSO $PbSnO_3$ with $\delta_{A-O} = 2$, $PbHfO_3$ with $\delta_{A-O} = 3$ or $PbZrO_3$ with $\delta_{A-O} = 3.6\%$. The $A-O$ bond of AFE PSO $CdTiO_3$ is even more strained – $\delta_{A-O} = 9.1\%$, and $T_C = 1223$ K – maximum T_C for AFE PSO. Then for the binary PSO T_C drops to 630 K for AFE PSO $NaNbO_3$ with $\delta_{A-O} = 15\%$ (Fig. 1c). The ternary PSO in the diagrams c and d with their δ_{A-O} and T_C values are somewhat shifted in the direction of δ_{A-O} increasing and have lower T_C values compared with the FE PT. For ternary AFE PSO, as well as for binary PSO, with the δ_{A-O} growth T_C also grows, but does not reach a pronounced maximum.

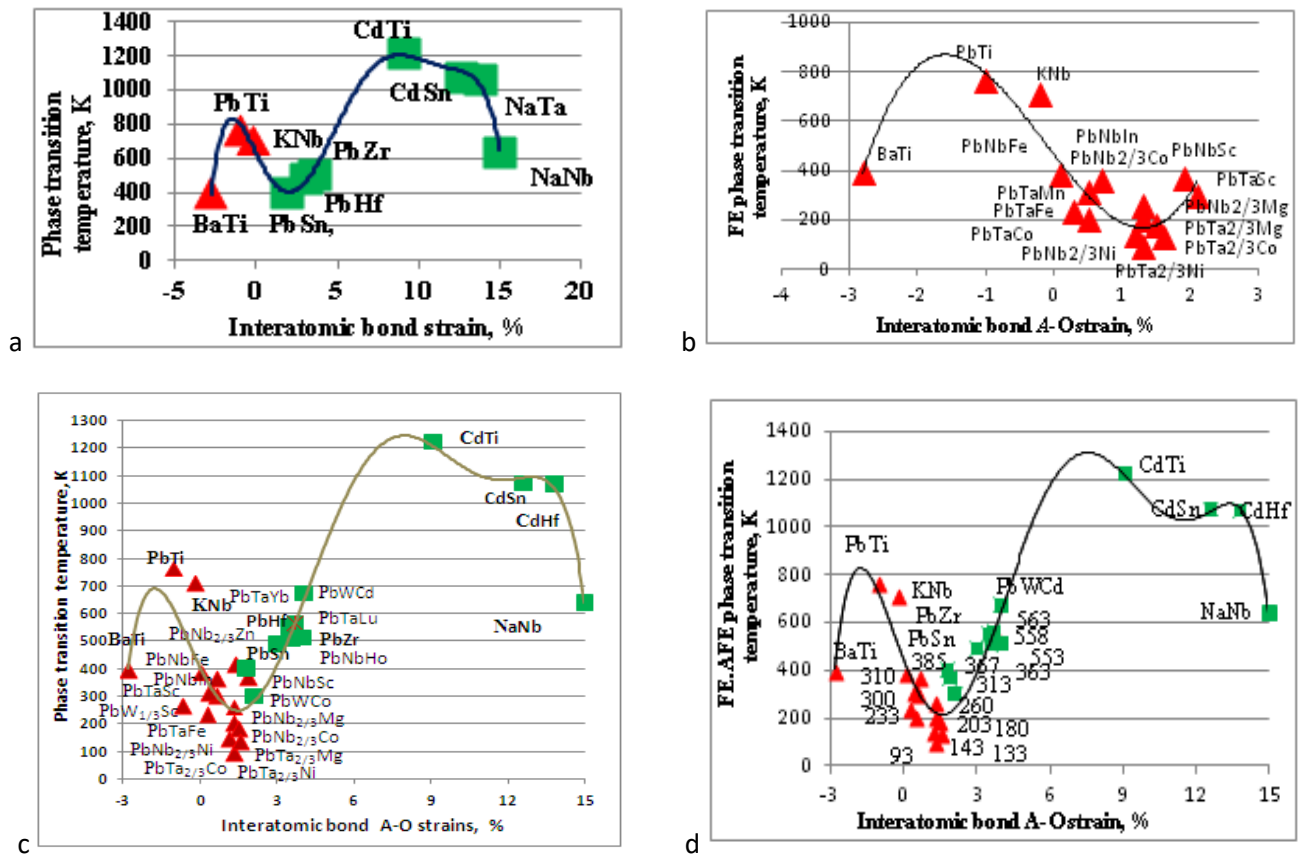


Figure 1. Dependences of the T_C on δ_{A-O} for: (a) FE (triangles) and AFE (squares) binary PSO; (b) binary and ternary FE PSO together; (c) binary and ternary FE and AFE PSO together and (d) the same, but with the corresponding T_C values. Composition formulae are written briefly: there is always no "O3" in them; if the ternary oxide has $\beta_1 = \beta_2 = 1/2$, then these fractions are not indicated; if one of the Bj atoms in the ternary oxide formulae contain the fraction $\beta_1 = 2/3$, then second fraction $\beta_2 = 1/3$ is not indicated, to save space.

For each PT nature there is a certain interval of δ_{A-O} values change and a certain T_C maximum: for the FE PT – 763 K (for PbTiO_3), and for the AFE PT – 1223 K (for CdTiO_3). Ternary PSO have lower PT temperatures than binary PSO. Neither for the FE, nor for the AFE ternary PSO there are no pronounced T_C maxima. For ternary PSO with the following increasing δ_{A-O} after KNbO_3 , T_C drop and quite steeply from 385 K for $\text{PbNb}_{1/2}\text{Fe}_{1/2}\text{O}_3$ to 93 K for $\text{PbTa}_{2/3}\text{Ni}_{1/3}\text{O}_3$, which is minimal for ternary PSO at $\delta_{A-O} = 2\%$. With a further δ_{A-O} increasing in the diagrams c and d (Fig. 1) for ternary AFE PSO values T_C increase as grows along with T_C of binary AFE PSO, and this process continues until $\text{PbW}_{1/2}\text{Cd}_{1/2}\text{O}_3$ with $T_C = 673$ K and $\delta_{A-O} = 4\%$. Thus, in diagrams c and d (Fig. 1) T_C of both binary and ternary PSO has a general tendency to change its values with a change of the δ_{A-O} in their structures regardless of their composition features. Constructed correlations can be taken into account in the directed search for new solid solution compositions between different PSO with special properties.

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3. V.P. Sakhnenko, N.V. Ter-Oganessian, *Acta Crystallogr. B.* **74**, 264 (2018).
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