Influence of the Ionic Radii on the Transition Temperature of Tilted Perovskites*

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It is shown that the temperature of the transition to the cubic phase in the perovskites with tilted octahedra, considering compounds with the same central ion, is a decreasing function of the tolerance factor. An explanation is given in terms of empty spaces of the crystal structure and the rms thermal motion necessary to fill them.

Mostra-se que a temperatura da transição para a fase cubica nas perovskitas com octaedros inclinados, considerando compostos com o mesmo íon central, é uma função decrescente do fator de tolerância. É dada uma explicação em termos dos espaços vasios da estrutura cristalina e do movimento térmico quadrático médio necessário para preenche-los.

The perovskite family has since long ago deserved a great amount of attention due to the interesting structural phase transitions presented by many of its members. The compounds whichadopt the perovskite structure have the general formula ABX_3, where A is a metal of large ionic radius, B is a metal of small ionic radius and X is oxigen or an halogen. The structure is found only for compounds in which the tolerance factor[1] t defined by

$$R_A + R_X = \sqrt{2}\ t\ (R_B + R_X)$$

it between 0.80 and 1.0; however, not all the ABX_3 compounds with the tolerance factor between 0.8 and 1.0 adopt the perovskite structure.

One readily sees-thatwhent is small (let us say $t < 0.90$) each anion X has some available space to move along the two crystallographic

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axes perpendicular to the axis containing B an X. Then, the octahedra formed by the anions is liable to rotate around one of the directions <100> or <111>, resulting in a deviation from the ideal cubic perovskite structure. A classification of the possible anion rearrangements was done by Glazer[2]. If, on the other hand, t is large, the anions octahedra are well clamped, but the small cations may have some freedom to move along the <111> directions and the crystal may show a ferroelectric transition associated to cations displacement.

Recently the perovskites presenting tilted octahedra have been extensively investigated, specially those which have a phase transition from the cubic to a lower symmetry. A few papers were dedicated to the reviewing of the results and the classification of tilted perovskites[2-5]. Rousseau *et al.*[6], discussing the phase transition in the fluoperovskites, introduced a parameter ΔR_{AF} defined by

$$\Delta R_{AF} = \frac{1}{2} a - (R_A + R_F) \ ,$$

where a is the cubic lattice parameter and R_F is the radius of the fluorine ion, and pointed out that a phase transition occurs when ΔR_{AF} is positive, whereas the crystal stays cubic at low temperature if ΔR_{AF} is negative. Tello *et al.*[5] investigated the $ABCl_3$ compounds and found tolerance factors between 0.81 and 0.90 for' the compounds with the perovskite structure.

In this paper we try to relate the temperature of the transition from the cubic symmetry in the tilted perovskites to the tolerance factor, basing on trivial common sense ideas about the motion of the ions in their potential. When t is small the anions are loosely bounded to their symmetric sites. The potential for their motion, when the rms deviations of the cations is small (ie., at low temperatures), is a shallow single well or a feature with four minima along <100> directions. For t very small the four-minima kind of potential is expected to occur, so that the square of the harmonic frequency ω_0 of one or more lattice modes associated with the rotation of the octahedra is negative for at least one wavevector at the boundary of Brillouin Zone[7]. Above a temperature T_0 the mode is stabilized by the anharmonic mode interaction and the crystal stays cubic. If the zero-point fluctuations of the lattice are not suf-

ficient to stabilize the rotation of the octahedra, T_0 is a positive temperature and a phase transition should occur at a temperature T_{tr} somewhat below T_0 *. The smaller the tolerance factor, the more negative the value ω_0^2 is expected to be and consequently the higher will be the temperatures T_0 and T_{tr}. Obviously the ionic radii are not the sole variable in the idefinition of the transition temperature. The short range restoring forcas are affected by the whole electronic configurations of the ions, the long range forces are mainly sensitive to the ionic charges, and the effect of the anharmonic interactions in the renormalization of the phonon frequencies depends on the inertial properties of the lattice, specially at low temperatures. However, the exam of the available data shows that colecting together the series of perovskite crystals with the same cation B (and consequently also with the same ionic charges of the three elements), the tolerance factor is a dominant parameter in the definition of T_{tr}. In the figure we show the variation of T_{tr} with t for six series of tilted perovskite compounds. The different series, containing differant cations B, behave differently. The most relevant parameter in the cation B, apart from its valence, was assumed to be its ionic radius; consequently, since Ca^{++} and Cd^{++} have almost the same size, the compounds $ACaX_3$ and $ACdX_3$ where put in the same series.

The series of the rare earth aluminates has three compounds which are kiiown to present a phase transition; $SmAlO_3$ melts a little below its phase transformation but the transition temperature and the O_h' symmetry of the higher phase were inferred from the soft modebehaviour[9]. Five other rare earth aluminates are known to cristalize in the perovskite structure: $YAlO_5$ [12] ($t = 0.855$), $DyAlO_3$ [13] ($t = 0.861$), $GdAlO_4$ [14] ($t = 0.872$), $EuAlO_3$ [14] ($t = 0.877$) and $CeAlO_3$ [15] $t = 0.910$). The four first ones stay tilted until their menting point, as one should expected from the graph. $CeAlO_3$ is tilted at $R.T.$, but the graph suggests that this compound goes to the O_h' symmetry below 600 K. The compound $PmAlO_3$ ($t=0.888$), if existing in the perovskite form, is expected to have its phase transition around 1900 K. The sole variable affecting the tolerance factor in the rare earth Aluminates is the radius of the rare earth cation. Scott[16] noticed the continuous decrease in the transition temperature of these compounds for increasing size of the rare earth cation and presented an explanation basically on the same lines of the present one. The factthat

the radii of the rare earth cations are known with good precision makes the study of this series specially attractive.

The series of the titanium has three known tilted compounds, $CaTiO_3$ and $SrTiO_3$, shown in the figure, and $CdTiO_3$[19]$(t=0.810)$ which stays tilted until the melting point. The other known titanium perovskites, $PbTiO_3$[20]$(t = 0.891)$ and $BaTiO_3$[21] $(t = 0.940)$ are never tilted; due to their large tolerance factor the Ti^{+4} ion, instead of the oxigen ions, is loosely bounded and they have a ferroelectric transition associated to the motion of that ion. $SrTiO_3$ is a very interesting case, for it has a tilting transition at a low temperature and almost has aferroelectric transition near 0 K.

The series of lead has the two known compounds $CsPbBr$ and $CsPbCl_3$ shown in the figure.

The series of magnesium has the two compounds shown in the figure and $KMgF_3$[26]$(t = 0.945)$, which stays cubic down to 0 K, as demanded by its large t.

The series containing calcium and cadmium presents five compounds with known phase transitions, shown in the figure. However there are four more compounds that cristalize in the perovskite structure: $KCaCl_3$[31] $(t = 0.793)$ and $RbCaCl_3$[31]$(t = 0.829)$, which are known to be tilted by R.T., $CsCaCl_3$[32]$(t = 0.879)$ which is known to becubicat $R.T.$, and $CsCdF_3$[6] $(t = 0.922)$ and $CsCaF_3$[33]$(t = 0.914)$, which are allways cubic.

The serie of the manganese has three compounds with have a transition, shown in the figure, and $RbMnF_3$[37]$(t=0.930)$, which is allways cubic.

The series of niobium and tantalum has four known perovskites: $NaNbO_3$[38]$(t = 0.806)$, $NaTaO_3$[39] $(t = 0.809)$, $KNbO_3$[40] $(t = 0.932)$ and $KTaO_3$[8] $(t = 0.937)$. The two first compounds have tilting transitions at 916K and 903K, respectively. $KNbO_3$ becomes ferroelectric and $KTaO_3$ has a ferroelectric soft mode which extrapolatès to zero at -10K. The structure and behaviour of the compounds $AgNbO_3$[41] $(t = 0.908)$ and $AgTaO_3$[41]$(t = 0.912)$ are still not satisfactorily known.
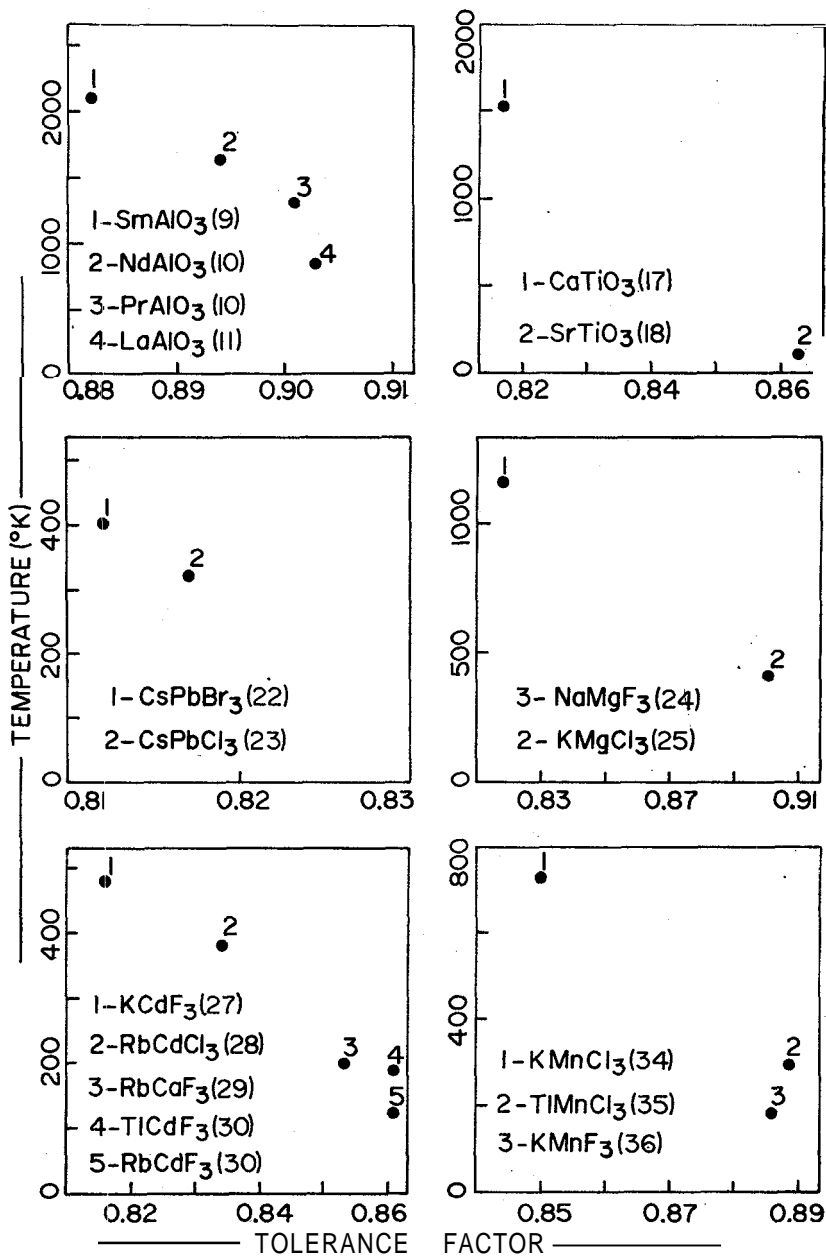
Variation of the temperature of transition to the cubic phase with the toleraiice factor for several series of tilted perovskites.

A reference number is given inside brackets in front of each cmpound. The ionic radii were taken frm Handbook of Chemistry and Physics. 57th edition, CRC Press Inc. (1976).

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We conclude that for each serie of perovskite compounds the tilting temperature is a decreasing function of the tolerance factor t; for t larger than a certain t_{max} typical of the serie, the compounds do not become tilted. It is also interesting to note when the charge of the small cation B is large and $t > t_{max}$ the crystal becomes ferroelectric soft mode; examples of this rule are $BaTiO_3$, $KNbO_3$, $KTaO_3$ and $PbTiO_3$. However when the charge of B is small, the crystal never becomes ferroelectric, even for t much larger than t_{max}; examples of this rule are $KMgF_3$ and $RbMnF_3$. We adventure the following explanation to this fact. For $t > t_{max}$ the ion B is loosely bounded to its site. The long range forces which tend to displace this ion from its symmetric site in a ferroelectric transition are expected to increase with the square of its electric charge, and becomes important when the atom is four or five times ionized.

There is some relation between the tolerance factor and the parameter ΔR_{AF} introduced by Rousseau et $al.$[6]: A partial exam of the available data showed to the autor that ΔR_{AF} increases when t decreases; consequently T_{tr} increases with ΔR_{AF}. However, it is more convenient to relate T_{tr} with t because this last parameter contains only atomic variables and consequently can be known even before the chemical synthesis of the compound.

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