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# STUDY OF THE FORMABILITY IN CUBIC PEROVSKITES OXIDES

**Amar Singh**
**Assistant Professor, Deptt. Of Physics,**
**SMSD Govt. College Nangal Chaudhary, Haryana.**

**ABSTRACT:-**
*Perovskite is one of the most frequently encountered structures in solid-state physics, and it accommodates most of the metallic ions in the periodic table with a significant number of different anions. During the last few years, many experimental and theoretical investigations were devoted to the study of perovskite solids. Many researchers try to design and*
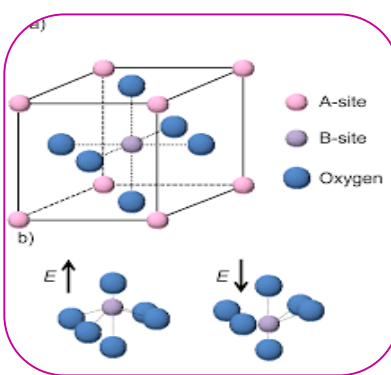


*synthesize new cubic perovskites used as substrate materials. Obviously, if new cubic perovskites compounds and their lattice constants can be predicted, it will be helpful to design new substrate or buffer materials with cubic perovskite structure. The physical and chemical properties of perovskite and perovskite-related materials are diverse and can be applied in a variety of fields so it is useful to discover the regularities that govern the formation of perovskite-type compounds in order to guide the exploration of new materials in the huge compositional spaces available. In this chapter we have studied some structural properties such as lattice constants, formability of a large no of ABO₃-type perovskites solids.*

**KEY WORDS** *cubic perovskites, ABO₃-type perovskites solids, perovskite-type compounds.*

**INTRODUCTION:-**

The study of $ABO_3$ compounds has a long history. Megaw accurately determined the structure of a number of doubled perovskites by examining high angle lines on X-ray powder photographs. Salinas-Sanchez introduced a parameter called the global instability index (GII), which can be used to determine the overall structural stability of perovskites. Giaquinta and Loye later predicted the perovskite structure for a number of compounds based on the combination of ionic radii and bond ionicities, predicting the structure of $ABO_3$ (A = In, B = Mn, Fe) with this method. Lufaso and Woodward used a bond-valence model to tolerance factor ($t_{BV}$) which they proposed as a new criterion of the structural stability of $ABO_3$-type perovskite compounds. Ye *et al.* applied a pattern recognition method and found some regularity in the formation and the lattice distortion of perovskites. Li *et al.* used $r_A - r_B$ structure maps to study the perovskite formability of 197 $ABO_3$ compounds by octahedral factor ($r_B/r_O$) and tolerance factor ($t$). Another structure map was constructed to predict the perovskite formability. In 2007, Ubic used a different approach based solely on ionic size and derived a simpler and more accurate empirical relationship between ionic size and lattice constant. Zhang *et al.* based on the bond-valence model (BVM) and structure-map technology, investigated the structural stability and formability of $ABO_3$-type perovskite compounds, established new criteria for the structural stability of such compounds. In 2008, Feng *et al.* used a method similar to that of Li *et al.* to predict the formability of $ABO_3$ cubic perovskite using the octahedral factor and tolerance factor. Regularities governing perovskite formability were recently investigated using an empirical structure-map method for a limited

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number of $ABO_3$-type compounds.however, the physical meaning of some parameters was not clear enough and more compounds should be further studied in this case.

## REVIER OF LITERATURE;-

In the literature of physics, the Perovskite properties constitute an important area of research. Due to the increasing technical importance of several perovskite-type materials, a number of books, monographs and review articles on different aspects of their structural characteristics and properties have been published in recent years and the pertinent sections. So it becomes very difficult to summarize the available information in a reduced space such as that available here. At present, environment-friendly and efficient technologies are doing put into practice at an ever increasing rate and for their adequate implementation; new, advanced materials are needed. Lanthanum chromate (LaCrO3) and related materials find applications in fuel cells and high-temperature electric heaters. Perovskite materials exhibit many interesting and intriguing properties from both the theoretical and the application point of view.

## MATERIAL AND METHOD:-

A new modified structure map method for determinations the formability of $ABO_3$-type perovskite compounds. In these maps the perovskite formation regions are shown clearly, which may help us design novel materials with a perovskite or perovskite-related structure.

In 1926, Goldschmidt had used ''tolerance factor'' to study the stability of perovskites. Goldschmidt found that, t values of cubic perovskites are in the range of 0.8–0.9. Goldschmidt's tolerance factor t has been widely accepted as a criterion for the formation of the perovskite structure, and therefore, it is an important factor for the stability of cubic perovskites, so tolerance factor t constructs one axe of the structure map . However, up to now, it seems that t is not a sufficient condition for the formation of the cubic perovskite structure, for example, in many systems whose t are even within the range (0.8–0.9), no cubic perovskite structure is stable, such as, $LaVO_3$, $DyMnO_3$, and $CaMoO_3$. So, another important factor governing formability of cubic perovskites should be introduced. Prediction criterions for the formabilities of perovskite-type oxides are obtained by using the empirical structure map methods constructed by two parameters octahedral factor ($r_B/r_O$) and tolerance factor, on this structure map, simple point representing systems of forming and non forming are distributed in distinctively different regions. In this chapter we found that the octahedral factor ($r_B/r_O$) is as important as the tolerance factor with regards to the formability of perovskite-type oxides. We have applied the proposed model to 173 $ABO_3$ perovskites and it can be used to search for new perovskite-type oxides by screening all possible elemental combinations.

First, Mooser and Pearson applied a two-dimension graphic to study the stability of different compounds, the two factors they used were the difference of electronegativity between the cation and the anion and the average principle quantum number. They succeeded to discriminate the crystal structures of AB-type compounds, of $AX_2$-type halides, and the metallic or non-metallic ternary fluorides ABX. Similar methods were called the structural map technology, and more parameters were used to draw the graphic. Muller and Roy proposed to plot ''structural map'', which took the ionic radius of A and B as coordinates to study the distribution of different structures for many ternary structural families. Furthermore, the schematic distribution map of different crystal structure for $A^{+1}B^{+5}X_3$, $A^{+2}B^{+4}X_3$ and $A^{+3}B^{+3}X_3$ systems separately, were given by the same method . However, the criterion for perovskite formability was not discussed, possibly due to the lack of accurate data of crystal structure of some $ABX_3$ compounds at that time. The ionic radius is the most important ionic parameter that dominates the crystal structure of ionic compound. In this study, the same method will be used to find the regularities governing cubic perovskites formability.

The ideal cubic structure form may be seen as a network of $BX_6$ octahedra, where all the octahedra are corner sharing. The $A$ ions occupy the cubo-octahedral holes in between the octahedra. Many derivatives of the ideal structure are found and the distortion of the structure from cubic is often considered to be determined by the relative sizes of the different ions of the compound. The basic requirements of the formation of the 'ideal' perovskite structure are the following characteristics: (I) the formation of $BX_6$ octahedra; (II) these $BX_6$ octahedra are connected with each other by corner-sharing; (III) the arrangement of $BX_6$ octahedra to make their 12 $X^-$ ions to be a cubo-octahedron around $A^+$ ion such that the A–X bond length is nearly equal to the sum of their ionic radii. Since Goldschmidt's t factor corresponds to the requirement

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(III) only, it is necessary to find some complementary criteria related the basic requirements (I) and (II) for the formability of perovskite structure.

The much used Goldschmidt's tolerance factor (t) is defined as

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \qquad (1)$$

Where $r_A$, $r_B$ and $r_X$ are the ionic radii of A, B and $X_3$ respectively.

$t=1$ corresponds to an ideal perovskite, while a $t<1$ indicates tilting or rotation of the $BX_6$ octahedra. A $t>1$ indicates preference for hexagonal perovskite structures, where the octahedra at least to some extent share faces. The face-sharing octahedra then form chains along the hexagonal $c$ axis, bound to each other by $A$-X bonds. The face sharing octahedra give relatively short $B$-$B$ distances, thus increasing the electrostatic repulsion between the $B$-site cations. Hexagonal stacking and face sharing is therefore introduced in stages with increasing size of the $A$ cation. Alkaline-earth-metal manganese oxides show this importance of size well [14]. $CaMnO_3$ forms an orthorhombic derivative of the cubic structure with slightly tilted octahedra [15]. At high temperatures $SrMnO_3$ takes a cubic perovskite structure with corner-sharing octahedra only .

At low temperatures, on the other hand, $SrMnO_3$ forms a four-layer hexagonal structure (Fig. 4.1b) with both face-sharing and corner-sharing octahedra corresponding to hexagonal and cubic stacking, respectively. $BaMnO_3$ forms a hexagonal structure with face sharing of octahedra only. The stabilization of the hexagonal structures at low temperatures has long been ascribed to the formation of metal-metal interactions across the shared face . However, the Mn-Mn $d$-orbital overlap has recently been shown to be minimal instead covalent interactions between manganese and oxygen atoms are indicated. Both the relative sizes of the cations and the covalency of the Mn-O bonds appear to be important for stabilizing the hexagonal structures of $SrMnO_3$ and $BaMnO_3$ at low temperatures .

Tolerance factor (t) has been widely accepted as a criterion for the formation of the perovskite structure, many researchers have used it to discuss the cubic perovskites stability, and therefore, it is an important factor for the stability of cubic perovskites, so tolerance factor (t) constructs one axe of the structure map. Another important octahedron factor ($r_B/r_O$)  is as important as the tolerance factor to form cubic perovskites, so octahedron factor constructs another axe of the two-dimension structure map. As shown in figure 1, all cubic perovskites and non- perovskites are located in two different regions, and clear border between two kinds of compounds is identified.
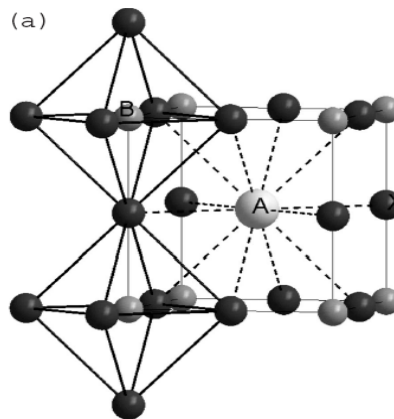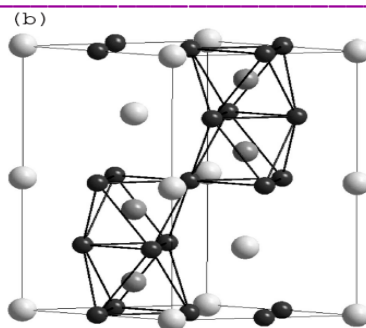


**Figure 1 (a) Ideal cubic perovskite structure,**

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**Figure 1 (b) four layer hexagonal perovskite structure**

## CONCULSION

The tolerance factor is a widely used parameter in perovskites study, which takes all the ionic radii into consideration. And it is known that almost all perovskites have a t value ranging from 0.75 to 1.00. According to Goldschmidt's point, t values of cubic perovskites are in the range of 0.8–0.9. it is indicated that t values of cubic perovskites, except $BaMoO_3$, are in the range of 0.857–1.032, which is wider than Goldschmidt's range. However, t = 0.857–1.032 is a necessary but not a sufficient condition for the formation of the cubic perovskite structure. The 85 systems, the t values of which are in the range (0.857–1.032), cannot form cubic perovskite structure. The evaluated results are good agreement with Medarde and may imply other criterion for cubic perovskites formability. it can be seen that some systems of all 173 ''non-cubic perovskites'', including $SrPbO_3$, $SrTbO_3$, $SrTcO_3$, $AgBiO_3$, $AgNbO_3$ and $BaUO_3$ are wrongly classified in ''cubic perovskites'' region by the criterion mentioned above. However some points near the boundary between ''cubic perovskites'' and ''non-cubic perovskites'' few points, representing like as $AgNbO_3$ (at 610°C) and $AgBiO_3$ just inside the boundary, which has distorted perovskite structure can transfer to cubic perovskite structure at 610°C.

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