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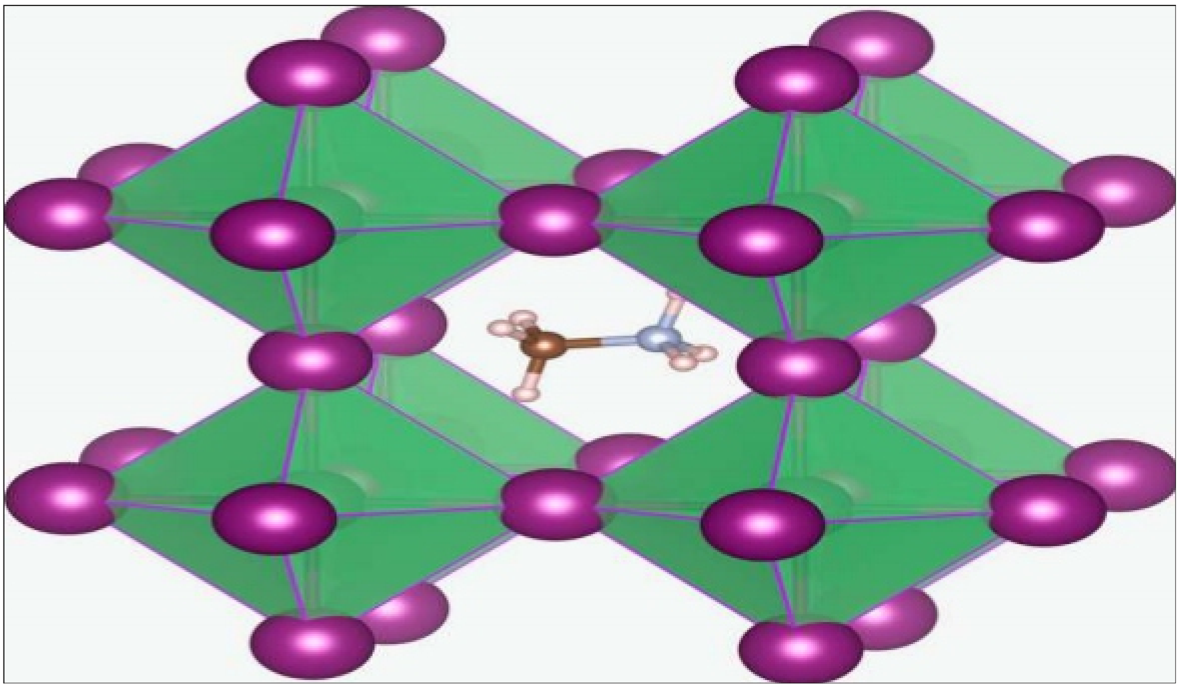
STUDY CRYSTAL CHEMISTRY OF THE PEROVSKITE STRUCTURE



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Abstract

The earliest description of the common atomic arrangement having the general formula ABX3 and a simple cubic structure was for the mineral known as perovskite, CaTiO3. The structure of CaTiO3 was later found to adopt a distorted perovskite lattice and thus an orthorhombic unit cell. However the term perovskite has been universally adopted to describe the structure of ABX3 compounds. Indeed, most structures described as perovskite are essentially orthorhombic yet still assume the ideal simple cubic unit cell at elevated temperatures.

KEY WORDS - cubic structure, perovskite lattice orthorhombic unit cell, etc.

INTRODUCTION=

The ideal cubic perovskite structure (shown in Figure 1 and Figure 2) comprises the body centre occupied by the A cation with the B cations situated on the corners of the unit cell and the X anions located halfway along each edge of the unit cell. The A cation tends to be larger than the B cation, as the A cation is coordinated with 12 anions whilst the B cation is coordinated with 6. The larger A cations tend to be either alkaline earth or lanthanide cations, whilst the smaller B cations are generally transition metal cations. Commonly the X anion is oxide, but halide and nitride anions are also readily accommodated.

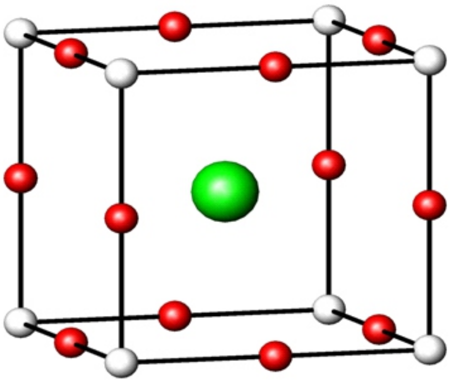

Figure1 The perovskite unit cell ABX3 where the larger A cation is depicted in green, the B cations are shown in white and the X anions are shown in red.

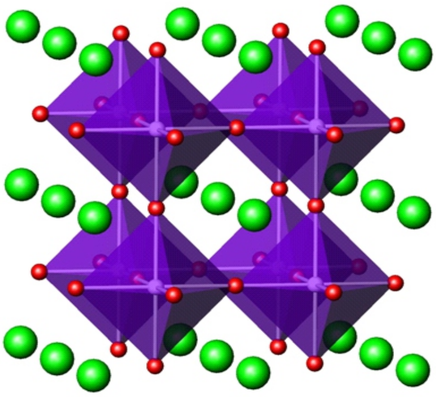

Figure 2 An expanded view of the perovskite structure, with white lines showing the B-X bonds and the BX6 octahedral highlighted in purple.

Review Of Literature=

Perovskite materials exhibit many interesting and intriguing properties from both the theoretical and the application point of view. 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=

Within the ABX3 perovskite structure, there is contact between A, B and X only if the ionic radii of its constituent atoms satisfy the condition expressed in Equation 1.1 (where R = ionic radii of A, X, and B ions, respectively).

$$RA+RX=\sqrt{2}\ RB+RX \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

For a proposed composition, the perovskite structure is usually feasible if the Goldschmidt tolerance factor, t, is in the range $0.8 < t \leq 1.0$. Equation 1.2 expresses the Goldschmidt tolerance factor as a function of the ionic radii of A, B, and X ions.

$$t = (RA+RX)/\sqrt{2}\ (RB+RX\ ) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

A tolerance factor t = 1 would ordinarily result in an ideal simple cubic perovskite structure consisting of spherical ions of sufficient ionic radii to make slight contact with their nearest neighbors. Any deviation from the model result of t = 1 leads to a distortion of the cubic structure to orthorhombic, tetragonal or rhombohedra symmetry.

Result and Disscusion=

The structure of an ideal cubic ABX3-perovskite is usually depicted schematically as shown in Fig.l, A being the larger cation, B the smaller one and X the anion. This anion may be oxide, fluoride and, in a few cases, chloride, bromide, iodide, sulphide or hydride. In this article we will concentrate mainly on oxidic systems. The structure can be related also, in a direct way, to that of Re03. For an ideal perovskite, t is unity; however, the perovskite structure is also found for lower t-values (0.75 < t S 1). In such cases, the structure distorts to tetragonal, rhombohedral or other lower symmetries. Indeed, many perovskitic oxides are polymorphs. Moreover, the above given geometric relations are not a sufficient condition for the stabilization of the perovskite lattice, since the A and B cations must, in themselves, be stable in twelvefold (12 or (8+4) or (6+6)) and sixfold coordination respectively. This latter condition sets lower limits for the cationic radii.In oxide systems these limits are rA > 0.90 i and rB > 0.51 I . A typical and well known example of the ideal cubic structure at room temperature is SrTi03 with a = 3.905 i and space group Pm3m in which the Ti06- octahedra are undistorted with 90" angles and six equal Ti-0 bonds at 1.952 i. Each strontium ion is surrounded by twelve equidistant oxygen atoms at 2.761 i. Some other materials that adopt this ideal structure are KU03, KMgF3, SrLiH3, CaI03, SrZr03, SrHf03, BaSn03, TlMn03, NH4CoF3, BaCe03, ZnNiF3, LaMn03, etc. [10, 11]. It is interesting to remark that many compounds present the ideal cubic structure only at high temperatures, and generally this high-temperature form cannot be quenched.

CONCLUSION=

For perovskites with t < 1, the ionic radii of the B cations are too large relative to the ionic radii of the A cations, thus compressing the B-X bonds and putting the A-X bonds under tension. In this scenario, it is often the case that some degree of tilting of the BX6 octahedral will arise in order to relieve these stresses by optimizing the cation coordination environments.

For perovskites with t > 1, the ionic radii of the B cations are too small relative to the ionic radii of the A cations. In this case, the B cations have been observed to be displaced from the centre of the BX6 octahedra such that the B-X bonding may be slightly improved. Displacement of the B cation towards an apex of the octahedra is known as a tetragonal displacement, whilst displacement towards an equatorial edge of the octahedral is an orthorhombic displacement and displacement towards a face of the octahedra is known as a rhombohedral displacement. Much empirical research has been carried out quantifying the correlation between ionic radii and stability of the perovskite-type structure and charting the variation of the perovskite structure with changes in ionic radii and charge . Aside from incompatible cationic radii, deviation from simple cubic symmetry in Perovskites can also be caused by anion non-stoichiometry and John-Teller distortions.

REFERENCES:

(1) P. K. Lam, M. L. Cohen and G. Martinez, Phys. Rev. B, 35, 9190, (1987).
[2] J. C. Phillips, Bonds and Bands in Semiconductors, (Academic Press, New York, 1973).
[3] V. Kumar, G. M. Prasad, A. R. Chetal and D. Chandra, J. Phys. Chem. Solids, 57, 503, (1996).
[4] V. Kumar, and B. S. R. Sastry, J. Phys. Chem. Solids, 66, 99, (2005).
[5] Y. Al-Douri, H. Abid, A. Aourag, Materials Letters, 59, 2032, (2005).
[6] A. S. Verma and S. R. Bhardwaj, J. Phys: Condensed Matter, 18, 8603, (2006).
[7] A. S. Verma and S. R. Bhardwaj, J. Phys: Condensed Matter, 19, 026213, (2007).