A theoretical approach to predict the structural parameters of ABO_3 type perovskite oxides

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Abstract

In the present research work two aspects of ABO_3 type perovskite has to be studied namely structural and mechanical. We have started our work by making an extensive survey of the literature regarding structral properties of ABO_3 type perovskite. There has been found a number of approachces in order to understand structural properties of ABO_3 type perovskite such as Experimental approaches, Computer based Approaches, Physical Method approaches and Statistical Method approaches to investigate structural properties of ABO3 type perovskite oxides. It is observed that a theoretical unified approach may resolve the variation in the results obtained by different approaches and can predict the actual existing values of structural properties of the materials under investigation. Therefore we have employed a theoretical approach to understand the trends and values regarding structural properties of the above said compounds.

Keywords: Elastic constant, Crystallographic Ratio. Refractive Index, Specific Heat, Conductivity, Polarizability. Electronegativity.

Introduction

In modern high-speed computer techniques, they allow researchers to investigate many structural and physical properties of materials only by computation or simulation instead of by traditional experiments. In the theoretical approach, the empirical methods are basically used to predict the structural parameters of solids. Empirical relations have become widely recognized as the method of choice for computational solid-state studies. In many cases empirical relations do not give highly accurate results for each specific material, but they still can be very useful. In particular, the simplicity of empirical relations allows a broader class of researchers to calculate useful properties, and often trends become more evident. Empirical concepts such as valence, empirical radii, electro negativity, ionicity and plasmon energy are very useful. These concepts are directly associated with the character of the chemical bond and thus provide means for explaining and classifying many basic properties of molecules and solids.

With the help of databases of known structures or models which have physical meaning, certain regularities, such as laws, rules, principles, factors, tendencies or patterns, might be found to help predict unknown structures. The prediction based on correlations is a powerful tool for measuring the association between two variables and for expressing the dependence of one variable on the other, it measures only linear

association. Some correlations have a simple theoretical basis while others can be found by empirical methods by an appropriate search routine. These correlations can be classified as three different types: purely empirical, partly empirical but based on some theoretical concept, and purely theoretical. Within these, the first is often unreliable and may not be worthy; the third is seldom adequately developed. The most widely used correlations are of a form suggested in part by theory, with empirical constants based on experimental data. Both of above two examples belong to the second kind of correlations.

Perovskite compounds comprise a very large and immensely important family of ferroelectric materials. Crystals are classified into seven systems according to the different axes used to describe them. In order, they are: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic. These seven systems can be further divided into 32 crystal classes, or point groups. Of these, 11 are centro-symmetric and therefore do not possess polar properties. The remaining 21 groups do not have a center of symmetry and therefore can have one or more polar axes. 20 of the 21 are in fact polar crystals and they form the piezoelectric class. The pyroelectrics form a subclass of the piezoelectrics, comprising 10 of the 20. The ferroelectrics are members of the pyroelectric subclass. Out of all the polar crystals, the most widely studied and technologically important are the perovskite oxides.

Complex oxides and halides are typical representatives of perovskite compounds, although the perovskite-type structure can also be formed by various classes of inorganic compounds, namely sulphides, hydrides, cyanides, oxyfluorides, oxynitrides, inter-metallic, and metal organic compounds. The diversity of chemical elements, which form perovskite structures, their ability to create cation- or anion-deficient structures, and a rich variety of distorted perovskite structures lead to an extremely broad range of physical properties. Because of this, the perovskite structure is often called the ‘inorganic chameleon’. A large number of perovskite-type oxides have been studied because of their interesting properties, including superconductivity, insulator–metal transition, ionic conduction characteristics, dielectric properties and ferroelasticity etc. Additionally, they have received great attention as high temperature proton conductors with the possibility of applications in fuel cells or hydrogen sensors and these solids are currently gaining considerable importance in the field of electrical ceramics, refractories, geophysics, astrophysics, particle accelerators, fission, fusion reactors, heterogeneous catalysis etc.

The Structural Stability and Formability of Perovskite Solids

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. Lattice parameter is one of the most critical parameters of the solids in materials design, especially for interface applicants. In this regard, a fast and reliable solution to predict lattice constant for a large number of unknown compounds becomes the winning edge in high technology development. Often, there are two broad methods to determine the crystal structure of unknown compounds. The first method is Traditional method of determining lattice constants (LC) is usually based on X-ray,

neutron or electron diffraction techniques, and the other is by theoretical or empirical models.

The first method is usually a complicated, difficult and time-consuming. Specifically, for large number of unknown compounds, these are very slow processes. These techniques form a powerful approach and are very popular among crystallographers, and widely used for structure determination. However, it is very difficult if not impossible to prepare the form of single crystals of sufficient size and quality for conventional single-crystal X-ray diffraction studies for many important crystalline materials.

We have work out on various meachnical perameters of ABO_3 type perovskite. The bulk modulus is an important mechanical property of a material and defines its resistance to volume change when compressed. Therefore, we have presented and studied the various models and theories describing the bulk modulus (B) of these materials. The bulk modulus, elastic moduli, which are of importance in assessing the competition between the ductile and brittle failures, have been extensively investigated in relation to various microscopic characteristics of different sorts of materials, such as metals and covalently bonded crystals. Recently, the bulk modulus, elastic modulus evaluations are carried out using ab-initio method; first-principles calculations for understanding the nature of the chemical bonding and its attributes in various solid systems. But due to the long process, as well as complicated computational methods involving a series of approximations, such a method has always been complicate. Therefore it seems an urgent need to evolve some sort of correlation by simulation of ionic charge and bulk modulus of perovskite materials. We have made efforts in this regards and succeed to establish an empirical relation between these two parameters.

Results and Conclusion

In the present research work two aspects of ABO_3 type perovskite has to be studied namely structural and mechanical. We have started our work by making an extensive survey of the literature regarding structral properties of ABO_3 type perovskite. There has been found a number of approachces in order to understand structural properties of ABO_3 type perovskite such as :-

1. Experimental Approach

The Experimental approach is traditional method of determining the crystal structures of materials. Experimental determination work began in 1911 by von Laue and his colleague; and Bragg using X-ray, neutron or electron diffraction techniques. These techniques form a powerful approach and are very popular among crystallographers, and widely used for structure determination of the materials.

2. Computer-Based Approach

Computer-based numerical modeling and simulations play an increasingly significant role in the conceptual design, synthesis, manipulation, optimization and testing of structured materials. There are two highly productive approaches used to find the structural and electronic properties of solids. Hartree-Fock theory is the simplest

method, involving optimization of a single determinant; however, its usefulness is limited because of complete neglect of electron correlation.

3. Physical Method

This method has been characterized by multi-scale; linking the simulation models and techniques across the micro-to-macro length and time scales with the goal of analyzing and controlling the outcome of critical materials processes. By combining different modelling methods, such as quantum mechanical calculations, Monte Carlo simulations, finite element analysis (FEA), the complex problems can be dealt with in a much more comprehensive manner than when the methods are used individually. These kinds of method are based on recognizing the relationships between a structure and its properties: if a structure can be calculated and optimized from given stoichiometry and connectivities, its properties can be calculated as well.

4. Statistical Method

When dealing with difficult problems where the physical models are not available or tedious to apply, it is helpful to correlate the results with chosen parameters by applying regression analysis, in which the data are best-fitted to a specified relationship that is usually linear. The result of linear regression is an equation, in which each of input x_i is multiplied by a parameter $a_{i;}$ and the sum of all such products and a constant C then gives an estimate of the output y.

Acknowledgement

One of the authors (Anoop Singh Yadav) thanks to Dr. Wasim Zaved for valuable support in understanding structural properties of some compounds. The theoretical works in this paper are supported by the Department of Physics, NIMS University and possible cooperation of Department of Physics, Govt. Polytechnic, Manesar, Haryana.