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PEROVSKITES: METHODS FOR OBTAINING AND STRUCTURES (REVIEW)

BY

DANIEL IOAN DUPALĂU* and DANIEL SUTIMAN

“Gheorghe Asachi” Technical University of Iași,
Faculty of Chemical Engineering and Environmental Protection

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Abstract. Perovskite structure is one of the simplest chemical formulas existing in nature, ABX_3 , where A and B are metal cation and anion X, usually oxygen. The perovskite formula is ABX_3 and it belongs to the ternary family of crystalline structures. Thanks to this remarkable structures are plenty of possible combinations and partial or total replacements, which gives us a very large number of compounds.

In this work we review a series of perovskites presenting their general synthetic methods and structure.

Keywords: Perovskite; structure; synthesis.

1. Introduction

Perovskite mineral was discovered by German chemist and mineralogist Gustav Rose in 1839 in the Ural Mountains in Russia. This mineral was named after dignitary, mineralogist, Russian military officer Lev Alexeivitch Perovsky (Moure and Pena, 2015).

*Corresponding author; *e-mail*: dupalau_daniel@yahoo.ro

Among the most studied materials in solid state chemistry and physics are compounds that crystallize in structure perovskite (Bhalla *et al.*, 2000).

ABX_3 structure is distributed as follows: each cation A is surrounded by twelve coordinating anion X in a cube - octahedral, and each cation B is surrounded by six anions X, in octahedral coordination type. Each anion X is surrounded by two positions and four positions cation B cation (Fig. 1) (Moure and Pena, 2015).

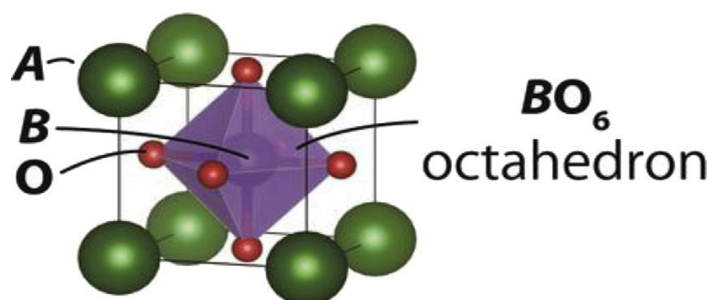


Fig. 1 – Ideal perovskite structure (cube). B cation anion is surrounded by six oxygen octahedral configuration. A it is surrounded by 12 oxygen anions ([http://commons.wikimedia.org/wiki/File:BaTiO₃_oxygen_coordination.png](http://commons.wikimedia.org/wiki/File:BaTiO3_oxygen_coordination.png)).

Thanks to this remarkable structures are lots of possible combinations and partial or total replacements, which gives us a very large number of compounds. Stability of the perovskite phase for a group of cations and anions is related to the so-called factor “tolerance t ”. This parameter defines the symmetry of the system and significantly affect its dielectric properties. Tolerance is a factor on the variable size limits for cations and allow formation of a perovskite phase When the tolerance factor is less than 1, the symmetry of the system is decreased; t greater than 1 corresponds cations cations B and lower A, so B cations have more space to move. When t is less than 1, cations B are enlarged (Moure and Pena, 2015).

Perovskites can crystallize all possible symmetries of the cube (high symmetry) to triclinic (very low symmetry).

For preparing perovskite compounds are used various methods including: solid oxide synthesis, sol-gel synthesis, hydrothermal synthesis, high-pressure synthesis, synthesis mechanically activated. It is important to note that different procedures can lead to compounds with the same chemical formula but different crystal symmetry and even different structures. Most of the compounds are multi-phase perovskite as a function of temperature, in particular the oxygen content may be based on the heat treatment. For these reasons, wellcontrolled processing techniques are essential not only to get well crystallized and pure materials, but also to stabilize the metastable phase. Needless to say with the recent progress of nanotechnology and a

microstructure control is fundamental to develop reproducible materials at lower cost and lower working temperatures (Moure and Pena, 2015).

2. General Synthetic Methods

2.1. Solid State Synthesis of Oxides and Carbonates

The first technique developed for the synthesis of these oxides is the so called ceramic route: a mixture of oxides and/or carbonates subjected to heat treatments at high temperatures. The compound is then processed with the conventional techniques and converted to powder (Moure and Pena, 2015).

2.2. Mechanical Synthesis

One of the most recent procedures to obtain compounds of the fine particles is High Energy Milling, also known as mechanical synthesis. This technique not only allows the preparation of very fine powder in the form of nanoparticles, and the ability to synthesize at room temperature, the compounds that have been obtained only by high temperatures and/or high-pressure methods (Moure and Pena, 2015).

2.3. Coprecipitation

Co-precipitation method requires oversaturated conditions of soluble metal cation solutions where it is mixed with another solution called precipitating agent (Duran *et al.*, 1988).

2.4. Synthesis Sol-Gel Precursor

A variety of sol-gel techniques are used to prepare the perovskite. In preparing perovskite, Pechini method has become the most used due to its versatility in preparing perovskite membranes. The most important advantages of this method are high purity and homogeneity of perovskite structures, coupled with precise control of material composition final (Del Toro *et al.*, 2013).

3. Types of Perovskites

3.1. Ideal Perovskite with Cubic Structure

Ideal structure (cubic) perovskite corresponds to $t = 1$. When t varies from 1 perovskites are obtained with low symmetry.

Ideal cube structure is obtained, for example, in CaRbF_3 and SrTiO_3 (Fig. 2).

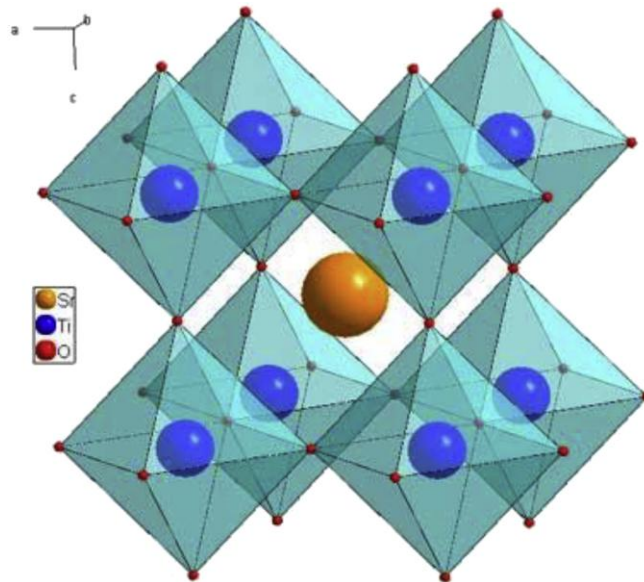


Fig. 2 – SrTiO_3 is an example of the ideal cubic perovskite structure (<http://www.princeton.edu/~cavalab/tutorials/public/structures/perovskites.html>).

3.2. Tetragonal Perovskite-Type Structures

When A it is higher, $t > 1$, then the connection is distorted octahedral BaO and growth occurs along the c axis. The typical compound of this class is BaTiO_3 (Fig.3).

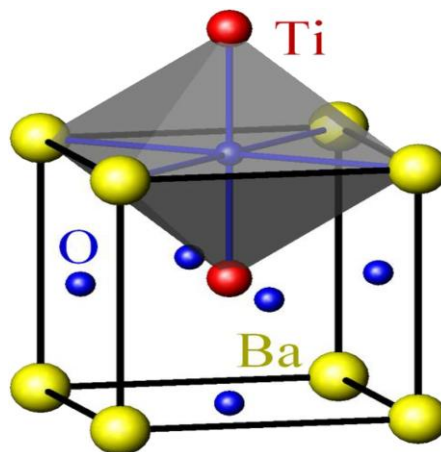


Fig. 3 – BaTiO_3 , perovskite structure (http://commons.wikimedia.org/wiki/File:BaTiO3_oxygen_coordination.png).

3.3. Tetragonal Perovskite-Type Structures

There are several compounds that exhibit a rhombohedral distortion, one of the most common being LaAlO_3 compound (Fig.4).

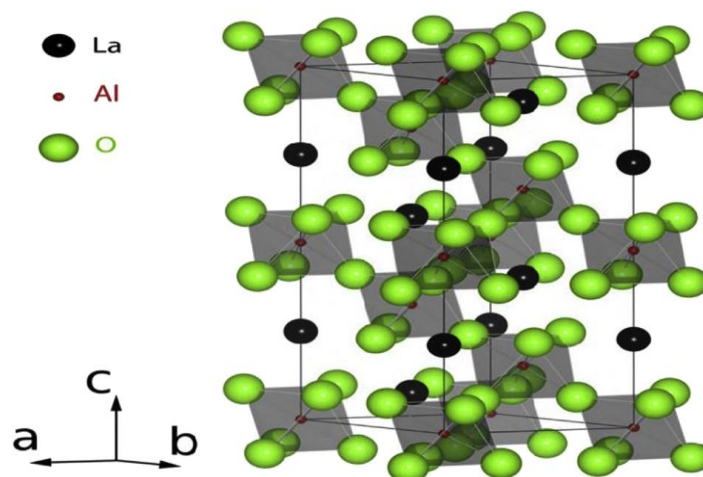


Fig. 4 – LaAlO_3 , distorted rhombohedral perovskite structure (Sanz-Ortiz *et al.*, 1988).

3.4. Orthorhombic Perovskite Structure Compounds

Of all distorted orthorhombic perovskites, GdFeO_3 is probably the most common (Moure and Pena, 2015).

3.5. Monoclinic Symmetry

CaTiO_3 presents a distorted monoclinic structure. There is controversy about the type of orthorhombic or monoclinic structure of the perovskite, however its crystal structure seems to be rather pseudocubic (Corredor *et al.*, 2011).

3.6. Perovskite Compounds with Triclinic Structure

The highest degree of distortion is found in compounds such as BiMnO_3 (Belik *et al.*, 2007).

4. Conclusions

Perovskite compounds have shown great potential in a wide range of applications. Because their capabilities change in the terms of the crystal

structure and capacities to accumulate cation changes, lead to a series of new properties: ability to model composition, properties and shaping.

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PEROVSKIȚI: METODE GENERALE DE OBȚINERE ȘI STRUCTURI (RECENZIE)

(Rezumat)

Structura perovskit este una dintre cele mai simple formule chimice existente în natură, ABX₃, unde A și B sunt cationi metalici și anionul X, de obicei oxigen. Formula generală a perovskitelor este ABX₃, fiind o clasă de oxizi micști, cu structură cristalină și multiple aplicații. Mulțumită acestei structuri remarcabile sunt o mulțime de combinații posibile și înlocuiri parțiale sau totale, ceea ce ne oferă un număr foarte mare de compuși. În această lucrare vom examina o serie de perovskiti, metodele generale de sinteză și structura.