International Journal of Research in Science And Technology http://www.ijrst.com
(IJRST) 2014, Vol. No. 3, Issue No. V, October-December ISSN: 2249-0604

STUDY THE PEROVSKITE-TYPE MIXED METAL OXIDES WITH THE GENERAL FORMULA ABO_3

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ABSTRACT

Perovskite materials exhibit many interesting and intriguing properties from both the theoretical and the application point of view. Colossal magnetoresistance, ferroelectricity, superconductivity, charge ordering, spin dependent transport, high thermo power and the interplay of structural, magnetic and transport properties are commonly observed features in this family. These compounds are used as sensors and catalyst electrodes in certain types of fuel cells and are candidates for memory devices and spintronics applications. Perovskite-type mixed metal oxides with the general formula ABO_3 (in which A is a rare earth or alkali earth ion and B is 3d, 4d or 5d transition metal ion), have been recently attracting attention as oxidation catalysts.

Key Words properties of Perovskite materials, ferroelectricity, superconductivity, charge ordering, high thermo power.

INTRODUCTION

The perovskite structure class is one of the most commonly occurring and important in all of materials science. Perovskites are ceramics (or rather, electro-ceramics), which constitute the Earth's most abundant mineral group and hold clues to the planet's history. A number of synthetic perovskites are of major technological importance. Barium titanate ($BaTiO_3$) and lead zirconate-titanate (PZT) ceramics form the basis of a sizable industry in ferroelectric and piezoelectric materials crucial to transducers, capacitors, and electronics. The perovskite structure occupies a prominent place under all the known ternary systems of composition ABX_3. This is due not only to its wide occurrence, but also to a series of interesting and useful properties associated with this structural type. Colossal magnetoresistance, ferroelectricity, superconductivity, charge ordering, spin dependent transport, high thermo power and the interplay of structural, magnetic and transport properties are commonly observed features in this family. These compounds are used as sensors and catalyst electrodes in certain types of fuel cells and are candidates for memory devices and spintronics applications.

Many superconducting ceramic materials (the high temperature superconductors) have perovskite-like structures, often with 3 or more metals including copper, and some oxygen positions left vacant. One prime example is yttrium barium copper oxide which can be insulating or superconducting depending on the oxygen content. Chemical engineers are considering this material as a replacement for platinum in catalytic converts in diesel vehicles Important properties of perovskites for their catalytic applications include the stability of mixed and unusual valence states of the transition metal ions in their structure, the presence of defect sites, and the high mobility of oxygen ions. Substitution in both the A and B sites changes the composition and symmetry of the perovskite and can affect the stability of different valence states of the metal cations. Furthermore, substitution with ions of a different valence can create cation or anion vacancies, which have a major influence on the catalytic behavior of these materials. Finally, when compared to noble metal-based catalysts, perovskites have better thermal stability, are less sensitive towards poisoning by sulfur, phosphorus and halogens, and are less expensive.

REVIEW 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 ($LaCrO_3$) 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

The ideal ABO_3 perovskite structure is cubic (space group Pm_33m) and is composed of a three-dimensional network of vertex-sharing BX6 octahedra. The A-site cation fills the 12-coordinated cavities (cuboctahedra) of the three-dimensional network. This structure is very flexible and it can accommodate most of the metallic elements of the periodic table. Depending on the ionic radii of A and B, octahedral are tilted, thus reducing the volume of the cuboctahedron until it fits the size of the A cation. Tilting of octahedra reduces the symmetry of structure. Analysis of perovskite-related structures has shown that in many cases the BX6 octahedra aredistorted, which may be a cause for the reduction of symmetry by itself. There are many ways in which the octahedra can tilt and distort, each leading to a different symmetry .The highly versatile ABX_3 perovskite crystal structure is formed by the B cations filling 25% of the octahedral holes in the cubic close-packed AX_3 array. In the ideal cubic structure, each a cation is coordinated to twelve X anions and each B cation is coordinated to six X anions. An example of the ideal cubic structure is shown in Figure 1. The substitution of different atoms into the A and B positions is possible if they are of similar size to A and B respectively, and total equivalent oxidation state.

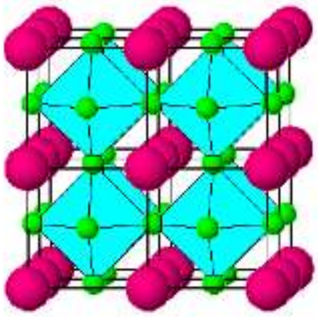

Figure 1: An ideal cubic perovskite $SrTiO_3$ with Pm-3m symmetry.

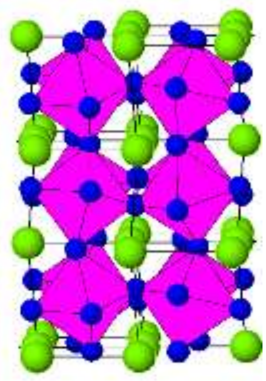

Figure 2: A distorted perovskite $SmNiO_3$ with orthorhombic symmetry.

Most perovskite structures are distorted and do not have cubic symmetry. Common distortions such as cation displacements within the octahedra and tilting of the octahedra are related to the properties of the A and B substituted atoms. Factors that contribute to distortion in the structure include radius size effects and the Jahn-teller effect. The $SmNiO_3$ structure shown in Figure 2 is a distorted perovskite with orthorhombic symmetry. The distortions exhibited by perovskites as a consequence of cation substitution can be used to fine tune and adjust properties of interest. A few of the physical properties of interest in various perovskite systems include conductivity, dielectrics, and colossal magnetoresistance. The following subsections contain examples of perovskite type structures and explanations of their properties and relations to the ideal perovskite structure.

RESULT AND DISCUSSION

A minor accessory mineral, formula $CaTiO_3$ occurring in basic rocks. Perovskite has given its name to a large family of materials, synthetic and natural, crystallizing in similar structures. The crystal structure is ideally cubic, with a framework of corner-sharing octahedra, containing titanium (Ti) or other relatively small cations surrounded by six oxygen (O) or fluorine (F) anions. Within this framework are placed calcium (Ca) or other large cations, surrounded by twelve anions. Tilting of the octahedra and other distortions often lower the symmetry from cubic, giving the materials important ferroelectric properties and decreasing the coordination of the central cation. This flexibility gives the structure the ability to incorporate ions of different sizes and charges. Substitution of niobium (Nb), cerium (Ce), and other rare-earth elements in natural calcium titanate ($CaTiO_3$) is common and can make perovskite an ore for these elements.

The atomic arrangement for ABO_3 perovskite structure was first found for the mineral perovskite $CaTiO_3$. It was earlier thought that the $CaTiO_3$ unit cell could be represented by Ca (A) ions at the corners of a cube with Ti (B) ions at the body center and oxygen ions at the center of the faces. This simple cubic structure is called perovskite, even though; $CaTiO_3$ was later determined to be of orthorhombic symmetry at room temperature. The perovskite structure is viable to wide departures in compositions from the ideal formula ABO_3. Many perovskite materials have symmetry different from cubic at room temperature, but transform to cubic symmetry at high temperatures .The low temperature (low symmetry) structure is called hettotype and the high temperature cubic structure is called aristotype ABO_3 form an important class since they are useful in several device applications, some examples of which follow. These materials are used in special ceramic capacitors. The resulting materials can be insulators (as most perovskites have high electrical resistivity), semiconductors, superconductors and ionic conductors. Perovskites find technical application in ceramics, refractories, and electronics, as well as possible hosts for nuclear waste.

The perovskite structure is one of the most frequently encountered structure types in solid-state inorganic chemistry. It accommodates cations of most of the metallic elements in the periodic table and a significant number of anions .Although most of the compounds that adopt the perovskite structure are oxides and fluorides, some hydrides, oxyfluorides and oxynitrides are also found to crystallize in this structure.

Table1. Lists the properties and applications of some commonly investigated perovskites

property	application	compound
optical property	Electrooptical modulator, laser host, switch, second harmonic generator	(Pb, La)(Zr, Ti)O_3, $YAlO_3$, $LiNbO_3$, $KNbO_3$
ferroelctric/piozoelectric	Piezoelectric transducer, P.T.C. thermistor, electrostrictive actuator	$BaTiO_3$, Pb(Zr,Ti)O_3, Pb(Mg,Nb)O_3
Magnetic property	Magnetic bubble memory, ferromagnet	$GdFeO_3$, $LaMnO_3$
electrical property		
dielectric	Multilayer capacitor,	$BaTiO_3$, $BaZrO_3$

	dielectric resonator, thin film resistor	
ionic conducting	Solid electrolyte	$(La,Sr)(Ga,Mg)O_3\text{-}\delta$
proton conducting	SOFC electrolyte, hydrogen sensor	$BaCeO_3$, $SrCeO_3$, $SrZrO_3$, $(La,Sr)MnO_3\text{-}\delta$
mixed conducting	SOFC electrode	$BaPrO_3$, $LaCoO_3$
Super conducting	superconductor	$Ba(Pb,Bi)O_3$
catalytic property	catalyst	$LaFeO_3$, $La(Ce,Co)O_3$

CONCLUSION

The perovskite structure is one of the most frequently encountered structure types in solid-state inorganic chemistry. It accommodates cations of most of the metallic elements in the periodic table and a significant number of anions .Although most of the compounds that adopt the perovskite structure are oxides and fluorides, some hydrides, oxyfluorides and oxynitrides are also found to crystallize in this structure. Structurally, the ideal perovskite oxide has a stoichiometry formula of ABO_3 and belongs to the cubic space group Pm3m (No. 221), with the A cation in a 12-fold coordination site and the B cation in a sixfold coordination site. As shown in Fig. 1, the A cation is located at the body center of the cube, the B cation is at each of the eight corners and the O anion is at each of the centers of the 12 edges. The most common description of a perovskite structure is a three dimensional framework of corner-sharing BO_6 octahedra, with the A cation filling the 12-coordinate cavities.

Owing to the non-Stoichiometric of the cation or anion, the distortion of the cation configuration and the electronic structure arising from mixed-valence, perovskite and perovskite- related materials exhibit versatile physical and chemical properties, which have attracted considerable research interest in materials chemistry. For instance, perovskite ceramics with ferroelectric and piezoelectric properties, such as $BaTiO_3$, $PbTiO_3$, $Bi_2\,ZnTiO_6$ and $Bi\ (Mg1/2Ti1/2)O_3$ play a dominant role in the electro ceramics industry. Other industrial applications of perovskites are: catalysis, ion conduction linear and nonlinear optical switching ($LiNbO_3$;) , super conduction ($YBa\ _2Cu\ _3O_7$;) , colossal magnetoresistance etc. Therefore, it is desirable to search for the regularities governing whether perovskite compounds can be formed and the factors governing their structural stability, with the aim of providing useful clues for the discovery of novel materials.

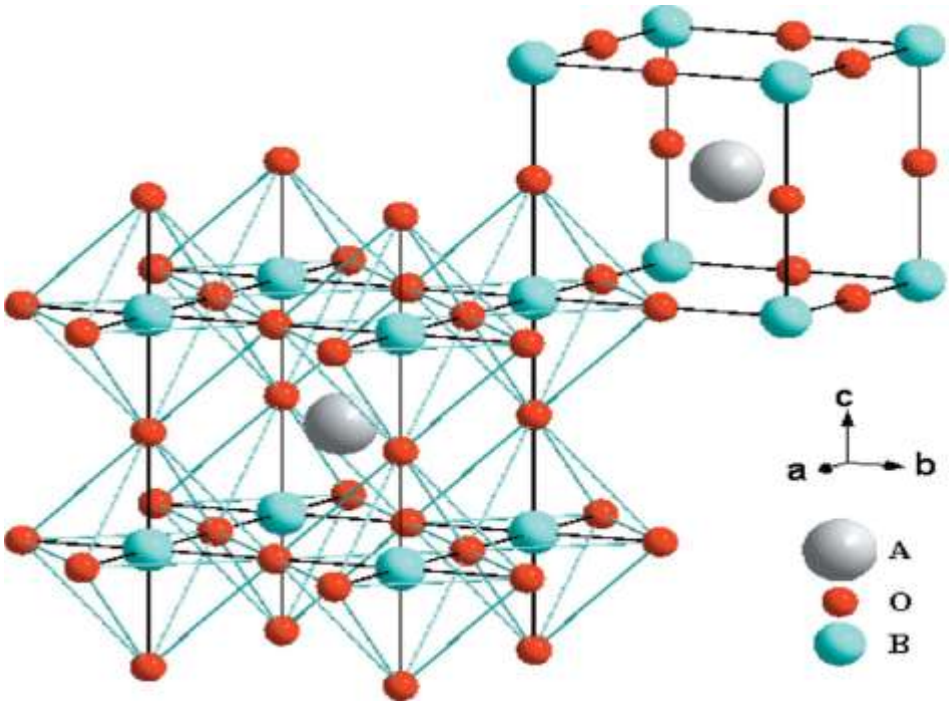

Figure 3 Fragment of the crystal structure of an ideal cubic perovskite. Note the corner-sharing BO_6 octahedra, extending in three dimensions to form the network.

REFERENCES

[1] F.S.Galasso, Structure, Properties and Preparation of Perovskite- Type Compounds, Pergamon Press, Oxford, 1969.

[2] R.S.Roth, J.Res.Natl. Bur.Stand. 58 (1957) 75.

[3] J. B. Goodenough and J. M. Longo.Crystallographic and Magnetic Properties of Perovskite and Perovskite Related Compounds. Landolt-Bornstein New Series group III, Springer Verlag, New York (1970) Vol. 4a, p. 126.

[4] N.Ramdass, Mater.Sci.Eng. 36 (1978) 231.

[5] O.Fukunaga and T.Fujita, J.Solid State Chem. 8 (1973) 331.

[6] M. Viret; S. von Molnaacuter "Mixed-valence manganites". Advances in Physics 48: 167–293, (1999).

[7] Alexandra Witze "Building a cheaper catalyst". Science News Web Edition. (2010).

[8] T. Nitadori, T. Ichiki, M. Misono, Bull. Chem. Soc. Jpn. 61 (1988) 621.

[9] R. Schneider, D. Kiessling, P. Kraak, M. Haftendorn, G. Wendt, Chemische Technik 47 (1995) 4.

[10] K. Song, H.X. Cui, S.D. Kim, S. Kang, Catal. Today 47 (1999) 155.

[11] R. Tamazyana and Sandervan Smaalen. Acta Cryst. (2007). B63, 190–200

[12] Woodward, P.M., Acta. Cryst. 1997, B53, 32-43.

[13] Crystallography and Chemistry of Perovskites, M. Johnsson and P. Lemmens, in “Handbook of Magnetism and Advanced Magnetic Media”,Ed. H. Kronmüller, John Wiley & Sons, New York, (2006), cond-mat/0506606.

[14] A.F.Wells, Structural Inorganic Chemistry, 5th.Edit., Clarendon Press, Oxford, 1984.

[15] O..MUller and R.Roy, The Major Ternary Structural Families, Springer, Berlin-Heidelberg-New York, 1974.

[16] H.Krebs, Grundziige der Anorganischen Kristallchemie, F.Enke, Stuttgart, 1968.

[17]. A. Navrotsky and D. J. Weidner. Perovskite: A Structure of Great Interest to Geophysics and Materials Science. A. Navrotsky and D. J. Weidener (Eds), American Geophysics Union, Washington, DC (1989) Vol. 45, p. xi