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Chapter

Synthesis Techniques and Applications of Perovskite Materials

Dinesh Kumar, Ram Sagar Yadav, Monika, Akhilesh Kumar Singh and Shyam Bahadur Rai

Abstract

Perovskite material is a material with chemical formula ABX_3-type, which exhibits a similar crystal structure of $CaTiO_3$. In this material, A and B are metal cations with ionic valences combined to +6, e.g., Li^+:Nb^{5+}; Ba^{2+}:Ti^{4+}; Sr^{2+}:Mn^{4+}; La^{3+}:Fe^{3+}, and X is an electronegative anion with ionic valence (−2), such as O^{2-}, S^{2-}, etc. The properties of a perovskite material strongly depend on the synthesis route of materials. The perovskite materials may be oxides (ABO_3:$CaMnO_3$), halides (ABX_3: X = Cl, Br, I), nitrides (ABN_3:$CaMoN_3$), sulfides (ABS_3:$LaYS_3$), etc., and they may exist in different forms, such as powders, thin films, etc. There are various routes for the synthesis of several perovskites, such as solid-state synthesis, liquid-state synthesis, gas-state synthesis, etc. In this chapter, we discuss various techniques for the synthesis of oxide perovskites in powder form using solid-, liquid-, and gas-state synthesis methods, and we also present an overview on the other type of perovskite materials. The X-ray diffraction, scanning electron microscopy, and optical techniques are used to study the purity of crystallographic phase, morphology, and photoluminescence properties of the perovskite materials. Some applications of different perovskite materials are also discussed.

Keywords: XRD, perovskite, Rietveld refinement, FullProf Suite, lanthanide phosphor

1. Introduction

The general chemical formula of a perovskite material is ABX_3, which contains a crystal structure similar to $CaTiO_3$. It was initially discovered by German geologist Gustav Rose in 1839 in Ural Mountains, and named after Russian mineralogist Lev Perovski [1, 2]. In ABX_3 perovskite, A and B are termed as metal cations having ionic valences combined to +6, e.g., (Li^+:Nb^{5+}; Ba^{2+}:Ti^{4+}; Sr^{2+}:Mn^{4+}; La^{3+}:Fe^{3+}) and X is an electronegative anion with ionic valence −2 such as O^{2-}, S^{2-} etc. [3–6]. The perovskite materials may be oxides, halides, nitrides, sulfides, etc., and they may exist in different forms, such as powders, thin films, etc. [7–10]. The perovskite material has attracted our attention as it can house up a variety of cations at A- and B-sites individually and/or simultaneously along with anions at X-site [11, 12]. The perovskite materials can be classified in ideal and distorted perovskite materials.

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An ideal perovskite material crystallizes into a simple cubic structure with $Pm\bar{3}m$ space group. In the $Pm\bar{3}m$ space group with perovskite structure, A atoms occupy *1(a)* site at (0, 0, 0) and B atoms occupy *1(b)* site at (1/2, 1/2, 1/2) whereas X atoms occupy *3*(*c*) site at (1/2, 1/2, 0). However, equivalently A, B, and X atoms can also occupy 1(*a*) site at (1/2, 1/2, 1/2), 1(*b*) site at (0, 0, 0) and *3(c)* site at (0, 0, 1/2), respectively, as shown in **Figure 1**. In this figure, A, B, and X are presented in terms of ionic radii [13, 14]. In the unit cell of a perovskite, the cation "B" forms octahedral arrangement with X-anions, i.e., BX_6 and the cation "A" occupies cuboctahedral site with X-anions, i.e., AX_{12}.

The family of perovskite material includes numerous types of oxide forms, such as transition metal oxides with the general formula of ABO_3. The oxide perovskite materials are widely synthesized and are studied for wide applications in various technological fields. In light of these properties, we describe oxide perovskites in more detail.

Victor Moritz Goldschmidt presented an empirical relationship among the ionic radii of A, B, and O, known as tolerance factor (t) to estimate the stability of a perovskite structure. This relation is valid for the relevant ionic radii at room temperature [15]. The numerical value of the tolerance factor can be found by Eq. (1):

$$t = \frac{r_A + r_o}{\sqrt{2}\left(r_B + r_o\right)} \tag{1}$$

where, the term r_A is the ionic radius of cation A and that of r_B is ionic radius of B cation whereas r_O is the ionic radius of oxygen anion (O^{2-}). The ionic radius of A cation is always larger than that of the B cation. The tolerance factor provides an idea about the selection of combination of A and B cations in order to prepare an ideal perovskite material. Eq. (1) can also be expressed in other form, which may be valid for any temperature as given by Eq. (2):

$$t = \frac{d_{A\text{-}o}}{\sqrt{2}\, d_{B\text{-}o}} \tag{2}$$

where d_A-O and d_B-O are average bond-lengths between A-O and B-O, respectively [16].

The distorted perovskite materials are those materials, which crystallize into other than the cubic structures. As far as we know that the perovskite material can accommodate different ions at the A- and B-sites. The variation in the A- and/or B-sites cations causes a variation in the tolerance factor. The variation in tolerance factor leads to a change in the perovskite structure from cubic to non-cubic distorted perovskite structure. For a stable perovskite, the value of tolerance factor should lie in the range of 0.88–1.09 [17]. An ideal perovskite crystal exhibits tolerance factor equal to unity (i.e., t = 1). For t < 1, the perovskite materials show the rhombohedral or monoclinic structure while in the case of t > 1; it reveals tetragonal or orthorhombic structure [18]. Due to distortion in the perovskite system, the BO_6 octahedral led tilted from an ideal situation and causes a change/enhancement in unit cell volume. Thus, the tolerance factor is a measure of the extent of distortion in the perovskite structure. **Figure 2** shows unit cells for some distorted perovskite structures.

There are two general requirements for the formation of a perovskite material, which are given as:

1. **Ionic radii:** the average ionic radii of A- and B-sites cations should be greater than 0.90 Å and 0.51 Å, respectively, and the value of tolerance factor should lie in the range of 0.88–1.09 [19, 20].