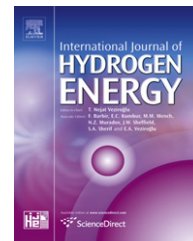


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## Dependence of critical radius of the cubic perovskite $ABO_3$ oxides on the radius of A- and B-site cations

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### ABSTRACT

Critical radius ( $r_c$ ) for cubic perovskite structure is an important factor affecting the migration energy of oxygen ions. The monotonic dependence of the critical radius on the ionic radii of A- and B-site cations in cubic perovskite  $ABO_3$  structure was systematically investigated by strict mathematical derivation. When the tolerance factor ( $t$ ) < 1, the critical radius is a decreasing function but an increasing function with respect to the radius of A-site cation ( $r_A$ ) and B-site cation ( $r_B$ ), respectively. For the case of  $t > 1$ , there is a reverse dependence of  $r_c$  on  $r_A$  and  $r_B$ . With respect to the case of  $t = 1$ ,  $r_c$  displays a decreasing function with respect to both  $r_A$  and  $r_B$ .

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## 1. Introduction

The mixed oxygen ionic and electronic conductors with perovskite or related structure had received much attention owing to their controllable electrical and catalytic properties, thus they can be used as membrane reactors for partial oxidation of methane to syngas ( $CO + H_2$ ) [1–4], electrodes of solid oxide fuel cells [5–9], oxygen separator [10], and so on [1,11]. Among them, the materials with cubic perovskite structure ( $ABO_3$ ), whose  $BO_6$  octahedra are connected via vertices, were considered to be one of the most promising candidates owing to that they can tolerate high concentration of dopant elements and have relatively open paths for oxygen migration [12]. The oxygen ionic conductivity is one of the most important properties for mixed conductors, and is

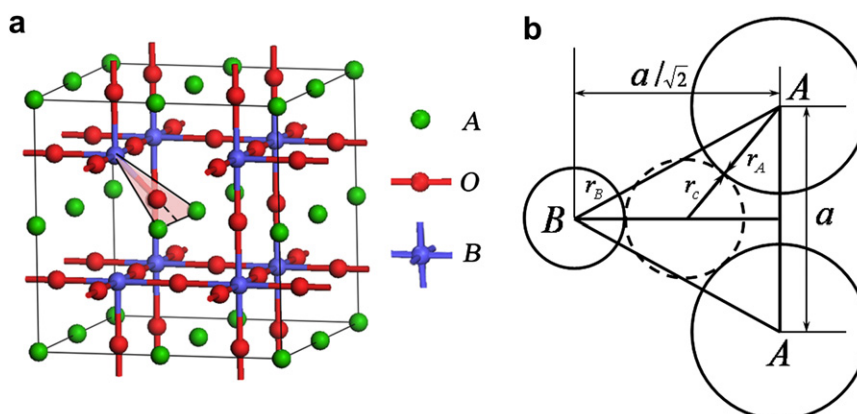
mainly governed by the charge carrier concentration and the migration activation energy for oxygen ion [13]. For perovskite-type oxides ( $ABO_3$ ), the charge carrier concentration, usually oxygen vacancy, relates to the concentration of aliovalent dopant and the prepared atmosphere [13]. While for the activation energy of oxygen ions, according to Cook and Sammells [14,15], it is influenced by: (1) the critical radius,  $r_c$ ; (2) the average metal-oxygen bond energy; (3) the lattice free volumes; and (4) the lattice polarizability. Here, the critical radius ( $r_c$ ) for cubic perovskite structure is the effective radius of the triangular cavity formed by two A-site cations and one B-site cation, as shown in Fig. 1, which is the narrowest pass for the oxygen ion migration. Generally, the critical radius does not exceed 1.05 Å [16] while the ionic radius of oxygen is 1.4 Å [17], i.e. it is a crucial factor controlling the oxygen ion

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**Fig. 1 – Geometry structure of the critical radius. (a) the crystal structure with a oxygen ion pass through the saddle point; (b) the geometry of the critical radius.**

transport. Greater the critical radius is, smaller the migration activation energy should be. The critical radius can be calculated from the geometrical structure and expressed by the lattice parameter ( $a$ ), the average radii of the A-site cations ( $r_A$ ) and B-site cations ( $r_B$ ), as shown in Eq. (1) [18].

$$r_c = \frac{-r_A^2 + \frac{3}{4}(a^2) - \sqrt{2}(a)(r_B) + r_B^2}{2(r_A) + \sqrt{2}(a) - 2(r_B)} \quad (1)$$

Because the lattice parameter  $a$  is dependent on the size of  $r_A$  and  $r_B$  (will be discussed later), the critical radius  $r_c$  is a complicated function of both  $r_A$  and  $r_B$ . In material design, it is always need to know how the cation size influences the value of the critical radius, which can provide guideline for the doping ion selection. In other words, it is desired to get the monotonicity of  $r_c$  with respect to  $r_A$  and  $r_B$ . To the best of our knowledge, no systematic analysis was reported on the correlation of  $r_c$  with  $r_A$  or  $r_B$ .

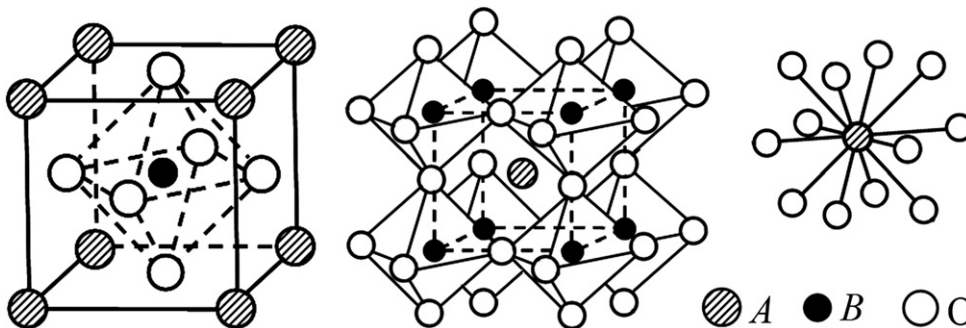
In this work, the relationships between the lattice parameter ( $a$ ) and the ionic radii of A-site and B-site cations ( $r_A$  and  $r_B$ ) under different tolerance factors ( $t = (r_A + r_O)/[\sqrt{2}(r_B + r_O)]$ ) for cubic perovskites [19] were established based on the crystal geometry structure, and then the monotonic dependence of the critical radius on the ionic radii of A-site and B-site cations was systematically investigated by strict mathematical derivation. Although the rotation and tilt of  $BO_6$  octahedra and the deviation of ions are frequently observed in perovskites, which usually leads to other types of structure

such as orthogonal, tetragonal and hexagonal, the discussion in this work is carried out only for cubic perovskite because cubic structure usually displays high oxygen conductivity and hence being the desirable structure for mixed conductors due to the equi-position of oxygen vacancy [20,21].

## 2. Theory

Fig. 2 shows the crystal structure of cubic  $ABO_3$  perovskite oxides with space group  $Pm\bar{3}m$ . For the ideal  $ABO_3$  cubic perovskite structure, the crystal was composed of a three-dimensional framework of corner-sharing  $BO_6$  octahedron, and the A-site cation occupied the 12 coordinate cavities formed by the  $BO_3$  network and was surrounded by 12 equidistant oxygen ions [22]. If the ions can be regarded as rigid balls, all the ions in  $ABO_3$  should be in a mutually tangent state and as a result, the lattice parameter  $a = \sqrt{2}(r_A + r_O) = 2(r_B + r_O)$ . Usually, in the real materials the value of  $\sqrt{2}(r_A + r_O)$  do not equal to that of  $2(r_B + r_O)$ , but they can still form cubic perovskite structure. Early in the 1920s, Goldschmidt [19] proposed a “tolerance factor”, given by Eq. (2), to evaluate the stability of the perovskites, and indicated that the cubic perovskite structure could be maintained for  $0.95 \leq t \leq 1.04$ .

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (2)$$



**Fig. 2 – Crystal structure of cubic perovskite oxides  $ABO_3$ .**

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