



Rapid Communication

Geometric parameterization of the $YBaCo_4O_7$ structure type: Implications for stability of the hexagonal form and oxygen uptakeM. Avdeev^{a,*}, V.V. Kharton^b, E.V. Tsipis^c^a Bragg Institute, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee, NSW 2232, Australia^b Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal^c Chemistry Department, Instituto Tecnológico e Nuclear, CFMC-UL, EN10, 2686-953 Sacavém, Portugal

ARTICLE INFO

Article history:

Received 22 July 2010

Received in revised form

10 August 2010

Accepted 12 August 2010

Available online 18 August 2010

Keywords:

A. $YBaCo_4O_7$

C. "114" Structure type

C. Structural phase transition

D. Oxygen storage

ABSTRACT

We explore the stability of the hexagonal form of $MBaCo_4O_7$ cobaltites in terms of geometric characteristics of the crystal structure and Global Instability Index (GII) based on the bond-valence considerations. Mismatch between an $M^{3+/2+}$ and the three-dimensional network of CoO_4 tetrahedra, whether expressed using an M ionic radii or GII, is shown to essentially determine both the temperature of structural transition to an orthorhombic modification and oxygen storage properties. A number of M cations not reported in the literature are identified to be suitable for the octahedral sites in an $MBaCo_4O_7$ structure.

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1. Introduction

Recent discovery of the new family of cobaltites $MBaCo_4O_7$ ($M=Y$, rare-earth) [1,2] generated considerable interest due to demonstrated frustrated magnetism ([3,4] and references therein) and unusual large and reversible oxygen uptake [5]. The high oxygen-storage capacity, in combination with the substantially large concentration of cobalt cations with respect to perovskite-type phases and significant electronic conductivity, may open prospects for numerous applications. In addition to the oxygen storage materials and chemical sorbents, these properties have critical importance for oxide precursors of highly active catalysts for partial oxidation of hydrocarbons, electrode materials for various fuel cells and electrolyzers, and sensors [6–8] and references therein.

Although a number of isostructural oxides and nitrides was reported chronologically earlier, i.e. swedenborgite $NaSbBe_4O_7$ [9], $LnBa(Al, Zn)_4O_{7-d}$ [10–12], $YbBaSi_4N_7$ [13], the cobaltites are now commonly referred to in the literature as belonging to the " $YBaCo_4O_7$ " or "114" structure type, following the work of Valldor [2]. The structure (Fig. 1) features a three-dimensional network of corner sharing tetrahedra CoO_4 with Ba and Ln occupying antioctahedral and octahedral sites, respectively. The framework was shown to accommodate cations M^{3+} of an ionic radii [14] ranging from 1.00 Å ($M=Lu$) [15] to 1.06 Å ($M=Tb$) [16] with an intermediate $M=Yb$ [17,18], Tm [15], Er [19], Ho [1], Y [2],

Dy [19]. Below some critical temperature (ranging from 170 K for Lu [20] to 300–310 K for Y [21]) the structure undergoes a displacive structural transition to an orthorhombic modification. It has been argued that the transition is driven by severe deviation from bond valence sum requirements [18,22] rather than by magnetostriction [23] or Co^{2+}/Co^{3+} charge ordering [15]. It is therefore of interest to investigate geometry of the $YBaCo_4O_7$ structure type in more details.

In this communication, we explore geometric characteristics of the $YBaCo_4O_7$ structure type and quantify the mismatch between the size or bond valence sum requirements of Ba^{2+} , M^{3+} and the framework consisting of CoO_4 tetrahedra that dictates the stability of the hexagonal modification against either a structural phase transition on cooling (under pressure) or against oxygen uptake and formation of oxygen-rich phases $LnBaCo_4O_{7+\delta}$ ($\delta=1-1.5$) [5,19,24].

2. Calculations

There is some debate whether the correct space group of the high symmetry modification of $MBaCo_4O_7$ is $P6_3mc$ (No. 186) or $P31c$ (No. 159). However, in the context of our analysis both space groups lead to the same result and therefore, we will consider the $P6_3mc$ as a higher symmetry group. In the $P6_3mc$ model, M , Ba , Co , and O atoms occupy $2b$, $2b$, $(2a+6c)$, and $(6c+6c+2a)$ Wyckoff sites, respectively. All the occupied positions have at least one variable coordinate and the unit cell origin is usually defined by fixing a z -value of either $2a(0,0,z)$ or $2b(1/3,2/3,z)$ position. Here, we follow the original report of Valldor [2] and place the Ba atoms

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to the position at $z=0$, i.e. at $2b(1/3,2/3,0)$, or equivalently at $(2/3,1/3,1/2)$.

Examination of the experimentally determined atomic coordinates reveals that the completely undistorted $MBaCo_4O_7$ structure type with an ideal CoO_4 tetrahedra, MO_6 octahedra, and BaO_{12} anti-cuboctahedra will have atoms located at the positions listed in Table 1.

Considering CoO_4 tetrahedra as the primary structural blocks, it is trivial to show that in the undistorted structure the dimensions of the unit cell and MO_6 and BaO_{12} polyhedra may be expressed in terms of a CoO_4 tetrahedron size or Co–O distance (d_{Co-O}) as

$$a_{hex}^{ideal} = \frac{4\sqrt{6}}{3}d_{Co-O}, \quad c_{hex}^{ideal} = \frac{16}{3}d_{Co-O}, \quad d_{M-O}^{ideal} = \frac{2}{\sqrt{3}}d_{Co-O},$$

$$d_{Ba-O}^{ideal} = \frac{4}{\sqrt{6}}d_{Co-O}$$

That suggests that a simple parameter

$$\tau = \frac{\sqrt{3}R_M + R_O}{2R_{Co} + R_O} \quad (1)$$

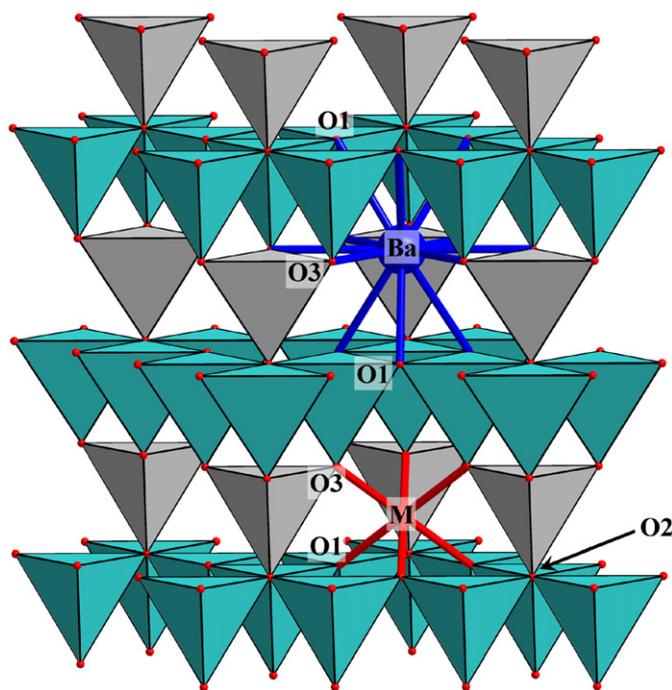


Fig. 1. General view of the $MBaCo_4O_7$ structure type. Polyhedra of two colours represent the inequivalent Co1 and Co2 sites, blue and red spheres show the positions of Ba and M in anti-cuboctahedral and octahedral coordination, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Ideal atomic coordinates in undistorted $MBaCo_4O_7$ structure type.

Atom	Wyckoff site	x	y	z
M	2b (2/3,1/3,z)	2/3	1/3	7/8
Ba	2b (2/3,1/3,z)	2/3	1/3	1/2
Co1	2a (0,0,z)	0	0	7/16
Co2	6c (x, -x, z)	1/6	5/6	11/16
O1	6c (x, -x, z)	1/2	1/2	3/4
O2	2a (0,0,z)	0	0	1/4
O3	6c (x, -x, z)	1/6	5/6	1/2

where R_M , R_{Co} , and R_O are ionic radii, may serve as an indicator of suitability of an M^{3+} cation to the octahedral site in $MBaCo_4O_7$, analogously to the “tolerance factors” widely used for other structural types, e.g. perovskites [25]. The more τ deviates from unity, the more tensile or compressive strain M will exert on six tetrahedra connected to the MO_6 octahedron.

However, since the structure contains two inequivalent cobalt sites, and therefore has more degrees of freedom than the perovskite structure type, it may be useful to investigate additional stability indicators. The overall mismatch of radii and oxidation states of ions in a crystal structure may be expressed in terms of the Global Instability Index [26]

$$GII = \sqrt{\sum_{i=1}^N \left\{ \left(\sum_{j=1}^N s_{ij} - V_i \right)^2 \right\}} / N \quad (2)$$

where $(\sum_{j=1}^N s_{ij} - V_i)$ is the difference between the bond valence sum (BVS) for the i^{th} ion and its formal oxidation state and N is the number of atoms in the formula unit. The bond valences are calculated following [27] as

$$s_{ij} = \exp((R^* - d_{ij})/0.37) \quad (3)$$

where R^* is an empirical parameter for a given metal–oxygen pair and d_{ij} is an interatomic distance. (Note that we use “ R^* ” instead of the original “ R_0 ” in order to better distinguish it from the ionic radius of oxygen “ R_O ”.)

According to the recent Mössbauer data [28], there is no evidence of charge ordering in the hexagonal form of $MBaCo_4O_7$, and therefore $BVS(Co1) = BVS(Co2)$ and $R^*(Co1) = R^*(Co2)$. Also the topology of the crystal structure provides the identical coordinations of O1 and O3 by cations, and therefore $BVS(O1) = BVS(O3)$. Taking into account these conditions, the analytical form of the GII for the undistorted $MBaCo_4O_7$ may be written as

$$GII = \left(\left(6e^{\left(\frac{R^*(M) - \frac{2}{\sqrt{3}}d_{Co-O}}{0.37} \right)} - 3 \right)^2 + \left(12e^{\left(\frac{R^*(Ba) - \frac{2\sqrt{6}}{3}d_{Co-O}}{0.37} \right)} - 2 \right)^2 \right. \\ \left. + 4 \left(4e^{\left(\frac{R^*(Co) - d_{Co-O}}{0.37} \right)} - \frac{9}{4} \right)^2 \right. \\ \left. + 6 \left(2e^{\left(\frac{R^*(Co) - d_{Co-O}}{0.37} \right)} + 2e^{\left(\frac{R^*(Ba) - \frac{2\sqrt{6}}{3}d_{Co-O}}{0.37} \right)} + e^{\left(\frac{R^*(M) - \frac{2}{\sqrt{3}}d_{Co-O}}{0.37} \right)} - 2 \right)^2 \right. \\ \left. + \left(4e^{\left(\frac{R^*(Co) - d_{Co-O}}{0.37} \right)} - 2 \right)^2 / 13 \right)^{1/2} \quad (4)$$

The bond valence parameter for cobalt, $R^*(Co^{2.25+})$, was calculated by averaging the parameters for Co^{2+} and Co^{3+} ions with respect to their fractions in $MBaCo_4O_7$, i.e. $R^*(Co^{2.25+}) = 0.75R^*(Co^{2+}) + 0.25R^*(Co^{3+}) = 1.694 \text{ \AA}$, with R^* of Co^{2+} and Co^{3+} being 1.692 and 1.700 \AA , respectively [29]. Then, the same parameter $R^*(Co^{2.25+})$ was used to derive the unstrained $Co^{2.25+}$ –O distance by reversing Eq. (3), i.e. $d_{Co-O} = R^*(Co^{2.25+}) - 0.37 \ln(2.25/4) = 1.907 \text{ \AA}$. The R^* values for Ba^{2+} (2.285 \AA) and M^{3+} were also taken from [29].

3. Results and discussion

The GII as a function of $R^*(M)$ calculated, using Eq. (4) is presented in Fig. 2(a). Examination of Fig. 2(a) suggests the following.

1. Even in the case of Lu^{3+} providing the lowest GII, the structure is severely strained as GII values for stable structures are typically less than 0.1 ([30] and references therein). It is not surprising

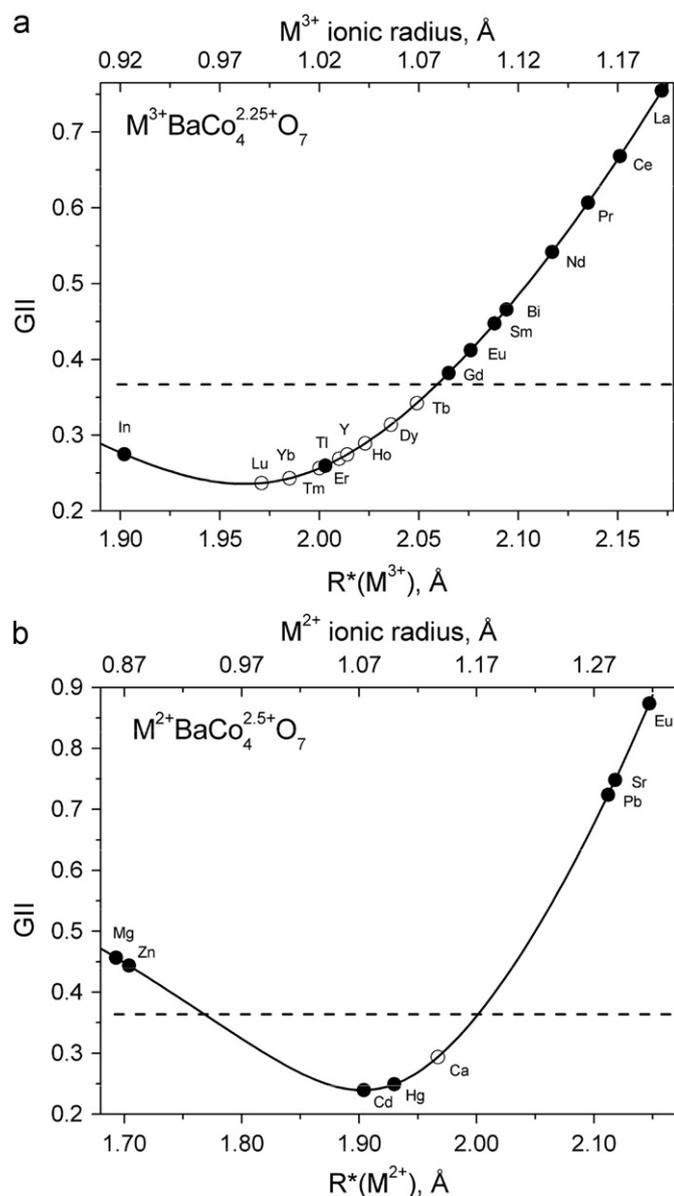


Fig. 2. Global Instability Index, GII , as a function of the bond valence parameter R^* [29] for $M^{3+}BaCo_4^{2.25+}O_7$ (a) and $M^{2+}BaCo_4^{2.5+}O_7$ (b). Open and solid symbols indicate materials, which were and were not reported in literature, respectively. Solid line was calculated, using Eq. (4) with $R^*(Ba)=2.285 \text{ \AA}$ [29], $R^*(Co^{2.25+})=1.673 \text{ \AA}$ and $d_{Co^{2.25+}-O}=1.907 \text{ \AA}$ (a), $R^*(Co^{2.5+})=1.696 \text{ \AA}$ and $d_{Co^{2.5+}-O}=1.870 \text{ \AA}$ (b); see text for the details. Top X-axis was calculated by reversing Eq. (3) as $(R^*(M^{n+})-0.37 \ln(n/6)-R(O))$, where n is the oxidation state equal to 3 (a) or 2 (b), $R(O)$ is the oxygen ionic radius (1.24 \AA [14]). Dashed line is drawn arbitrarily to indicate what appears to be a stability limit for $MBaCo_4O_7$.

then that, as was noted before, the $MBaCo_4O_7$ materials are kinetically stabilized and annealing at temperatures below $\sim 900\text{--}950 \text{ }^\circ\text{C}$ results in phase decomposition [5,19,28].

2. GII dependence on $R^*(M^{3+})$ well reproduces the reported increase of the hexagonal–orthorhombic phase transition temperature with increasing $R^*(M^{3+})$ (or ionic radius) from Lu^{3+} to Ho^{3+} (Fig. 3).
3. GII also appears to be directly related to the reversible oxygen uptake properties. It was found that oxidation temperature decreases and amount of absorbed oxygen increases in the series $Lu \rightarrow Dy$ (Fig. 4). Fig. 2(a) suggests that materials with higher $R^*(M^{3+})$, i.e. $Gd \rightarrow La$, might be expected to demonstrate even further improvement in oxygen storage properties, essentially becoming less and less stable. However, it may be progressively

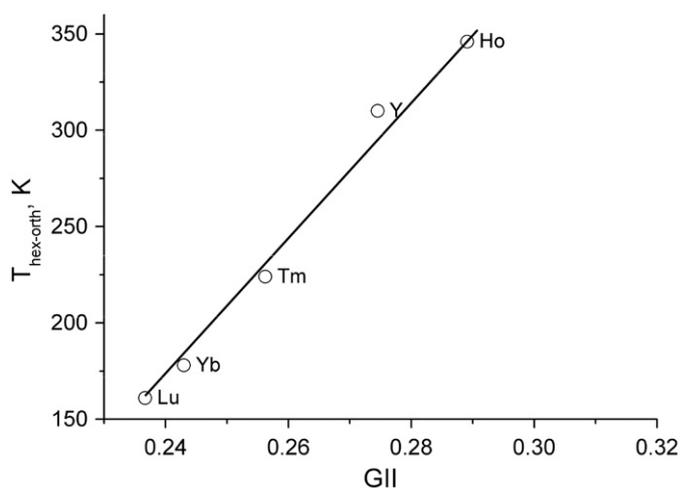


Fig. 3. Temperature of phase transition between hexagonal and orthorhombic modifications for $M^{3+}BaCo_4^{2.25+}O_7$ as a function of GII . Data are compiled from [15,32,33]. The line is a guide for the eye.

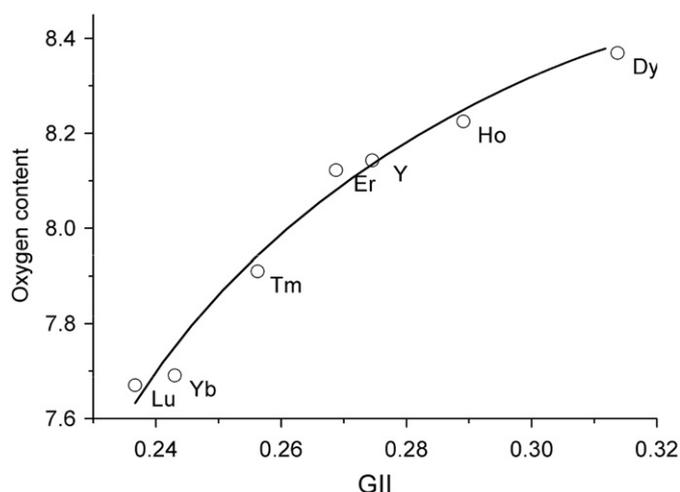


Fig. 4. Oxygen content recorded for $M^{3+}BaCo_4^{2.25+}O_7$ heated in O_2 gas flow at $300\text{--}350 \text{ }^\circ\text{C}$. Data are adapted from [19]. The line is a guide for the eye.

more and more difficult, if not impossible, to prepare single $MBaCo_4O_7$ phases with $M=Gd \rightarrow La$. Only In^{3+} and Tl^{3+} appear to lie within the explored structure type stability domain.

Following the same chain of calculations, we can also investigate the stability of $M^{2+}BaCo_4^{2.5+}O_7$. As Fig. 2(b) suggests there may be other suitable M^{2+} candidates in addition to the only reported example, $CaBaCo_4O_7$ [31], although crystal chemical factors other than bond-valence considerations, e.g. oxidation state stability or tendency to form highly distorted coordination, may prevent incorporation of certain ions into the structure.

4. Conclusions

The $YBaCo_4O_7$, or “114,” hexagonal crystal structure type has been parameterized in terms of its specific tolerance factor τ , based on ionic radii, and the Global Instability Index. For the $M^{3+}BaCo_4O_7$ family, the structure is severely strained even in the case of $M^{3+}=Lu$ having the most optimal size. Cations M^{3+} with larger ionic radii further destabilize the structure that result in the increase of the hexagonal–orthorhombic phase transition temperature and improvement of oxygen storage properties. The

compounds with $M^{3+} = \text{Gd} \rightarrow \text{La}$ may be expected to be progressively more difficult to prepare; on the other hand we identified a number of M^{2+} and M^{3+} cations of the size suitable for the ${}^3\text{Co}_4^{[4t]}\text{O}_7$ framework.

Acknowledgments

This work was partially supported by FCT, Portugal (Projects PTDC/CTM/64357/2006 and SFRH/BPD/28629/2006). The authors are grateful to the anonymous reviewers for useful comments and suggestions.

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