Rapid Communication

Geometric parameterization of the \( \text{YBaCo}_4\text{O}_7 \) structure type: Implications for stability of the hexagonal form and oxygen uptake

M. Avdeev\textsuperscript{a,*}, V.V. Kharton \textsuperscript{b}, E.V. Tsipis \textsuperscript{c}

\textsuperscript{a} Bragg Institute, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kurraba, NSW 2232, Australia
\textsuperscript{b} Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
\textsuperscript{c} Chemistry Department, Instituto Tecnológico e Nuclear, CPMC-UL, EN10, 2686-953 Sacavém, Portugal

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\textbf{A B S T R A C T}

We explore the stability of the hexagonal form of \( \text{MBaCo}_4\text{O}_7 \) 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 \( \text{CoO}_4 \) 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 \( \text{MBaCo}_4\text{O}_7 \) structure.

\( 1.00 \, \text{Å}(\text{Y}) \), Below some critical temperature (ranging from 170 K for \( \text{Lu} \) \cite{20} to 300–310 K for \( \text{Y} \) \cite{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 \cite{18,22} rather than by magnetostriiction \cite{23} or \( \text{Co}^{2+/3+} \) charge ordering \cite{15}. It is therefore of interest to investigate geometry of the \( \text{YBaCo}_4\text{O}_7 \) structure type in more details.

In this communication, we explore geometric characteristics of the \( \text{YBaCo}_4\text{O}_7 \) structure type and quantify the mismatch between the size or bond valence sum requirements of \( \text{Ba}^{2+} \), \( \text{M}^{3+/2+} \) and the framework consisting of \( \text{CoO}_4 \) 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 \( \text{LnBaCo}_4\text{O}_{7+\delta} \) (\( \delta=1–1.5 \)) \cite{5,19,24}.

\textbf{2. Calculations}

There is some debate whether the correct space group of the high symmetry modification of \( \text{MBaCo}_4\text{O}_7 \) is \( \text{P6}_3\text{mc} \) (No. 186) or \( \text{P31c} \) (No. 159). However, in the context of our analysis both space groups lead to the same result and therefore, we will consider the \( \text{P6}_3\text{mc} \) as a higher symmetry group. In the \( \text{P6}_3\text{mc} \) model, \( \text{M, Ba, Co, and O} \) atoms occupy \( 2h \), \( 2h, (2a+6c), \) 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 \( 2a(0,0,2) \) or \( 2h(1/3,2/3,2) \) position. Here, we follow the original report of Valldor \cite{2} and place the \( \text{Ba} \) atoms.
to the position at \( z=0 \), i.e. at \( 2b(1/3,2/3,3/0) \), or equivalently at \( (2/3,1/3,1/2) \).

Examination of the experimentally determined atomic coordinates reveals that the completely undistorted \( \text{MBaCoO}_2 \) structure type with an ideal \( \text{CoO}_4 \) tetrahedra, \( \text{MO}_6 \) octahedra, and \( \text{BaO}_{12} \) anti-cuboctahedra will have atoms located at the positions listed in Table 1.

Considering \( \text{CoO}_4 \) tetrahedra as the primary structural blocks, it is trivial to show that in the undistorted structure the dimensions of the unit cell and \( \text{MO}_6 \) and \( \text{BaO}_{12} \) polyhedra may be expressed in terms of a \( \text{CoO}_4 \) tetrahedron size or \( \text{Co}–\text{O} \) distance \( (d_{\text{Co–O}}) \) as

\[
c_{\text{hex}}^\text{ideal} = \frac{4\sqrt{6}}{3} d_{\text{Co–O}}, \quad c_{\text{hex}}^\text{ideal} = \frac{16}{3} d_{\text{Co–O}}, \quad d_{\text{Mo–O}}^\text{ideal} = \frac{2}{3\sqrt{3}} d_{\text{Co–O}}.
\]

That suggests that a simple parameter

\[
\tau = \frac{\sqrt{3} R_{\text{M}} + R_{\text{O}}}{2 R_{\text{Co}} + R_{\text{O}}}
\]

where \( R_{\text{M}}, R_{\text{Co}}, \) and \( R_{\text{O}} \) are ionic radii, may serve as an indicator of suitability of an \( M^{2+} \) cation to the octahedral site in \( \text{MBaCoO}_2 \), analogously to the “tolerance factors” widely used for other structural types, e.g. perovskites [25]. The more \( \tau \) deviates from unity, the more tensile or compressive strain \( M \) will exert on six tetrahedra connected to the \( \text{MO}_6 \) 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]

\[
\text{GII} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( \sum_{j=1}^{N} s_{ij} - V_{i} \right)^{2}}/N
\]

where \( s_{ij} = \exp\left( R^*-d_{ij} \right)/0.37 \) 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 valence parameter for cobalt, \( R^*(\text{Co}^{2+}) \), was calculated by averaging the parameters for \( \text{Co}^{2+} \) and \( \text{Co}^{3+} \) ions with respect to their fractions in \( \text{MBaCoO}_2 \), i.e. \( R^*(\text{Co}^{2.25+}) = 0.75 R^*(\text{Co}^{2+}) + 0.25 R^*(\text{Co}^{3+}) = 1.694 \) Å, with \( R^*(\text{Co}^{2+}) \) and \( \text{Co}^{3+} \) being 1.692 and 1.700 Å, respectively [29]. Then, the same parameter \( R^*(\text{Co}^{2.25+}) \) was used to derive the unstrained \( \text{Co}^{2.25+}–\text{O} \) distance by reversing Eq. (3), i.e. \( d_{\text{Co–O}} = R^*(\text{Co}^{2.25+}) - 0.37 \ln(2.25/4) = 1.907 \) Å. The \( R^* \) values for \( \text{Ba}^{2+} (2.285 \) Å) and \( M^{2+} \) 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 \( \text{La}^{3+} \) 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. 1. General view of the \( \text{MBaCoO}_2 \) structure type. Polyhedra of two colours represent the inequivalent Co1 and Co2 sites, blue and red spheres show the positions of \( \text{Ba} \) and \( \text{M} \) 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>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
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<tbody>
<tr>
<td>( M )</td>
<td>2b(2/3,1/2)</td>
<td>2/3</td>
<td>1/3</td>
<td>7/8</td>
</tr>
<tr>
<td>( Ba )</td>
<td>2b(2/3,1/2)</td>
<td>2/3</td>
<td>1/3</td>
<td>1/2</td>
</tr>
<tr>
<td>Co1</td>
<td>2a(0,0,2)</td>
<td>0</td>
<td>0</td>
<td>7/16</td>
</tr>
<tr>
<td>Co2</td>
<td>6c(x,—x,z)</td>
<td>1/6</td>
<td>5/6</td>
<td>11/16</td>
</tr>
<tr>
<td>O1</td>
<td>6c(x,—x,z)</td>
<td>1/6</td>
<td>1/2</td>
<td>3/4</td>
</tr>
<tr>
<td>O2</td>
<td>2a(0,0,2)</td>
<td>0</td>
<td>0</td>
<td>1/4</td>
</tr>
<tr>
<td>O3</td>
<td>6c(x,—x,z)</td>
<td>1/6</td>
<td>5/6</td>
<td>1/2</td>
</tr>
</tbody>
</table>
then that, as was noted before, the $\text{MBa}_2\text{Co}_4\text{O}_7$ materials are kinetically stabilized and annealing at temperatures below $900–950^\circ \text{C}$ results in phase decomposition \([5,19,28]\).

2. GII dependence on $R^*(\text{M}^{3+})$ well reproduces the reported increase of the hexagonal–orthorhombic phase transition temperature with increasing $R^*(\text{M}^{3+})$ (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→Dy (Fig. 4). Fig. 2(a) suggests that materials with higher $R^*(\text{M}^{3+})$, i.e. Gd→La, might be expected to demonstrate even further improvement in oxygen storage properties, essentially becoming less and less stable. However, it may be progressively more and more difficult, if not impossible, to prepare single $\text{MBa}_2\text{Co}_4\text{O}_7$ phases with $\text{M} = \text{Gd}$–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 $\text{M}^{2+}\text{BaCo}_4\text{O}_7$ phases with $\text{M} = \text{Gd}$–La. Only In$^{3+}$ and Tl$^{3+}$ appear to lie within the explored structure type stability domain.

4. Conclusions

The $\text{YBaCo}_4\text{O}_7$, or "114," hexagonal crystal structure type has been parameterized in terms of its specific tolerance factor $t$, based on ionic radii, and the Global Instability Index. For the $\text{MBa}_2\text{Co}_4\text{O}_7$ family, the structure is severely strained even in the case of $\text{M}^{3+}=\text{Lu}$ having the most optimal size. Cations $\text{M}^{2+}$ 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 $\text{Co}_3^{3+}(\text{O})_7$ framework.

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