Journal of Solid State Chemistry 258 (2018) 72–78

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Cesium immobilization in (Ba,Cr)-hollandites: Effects on structure

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ARTICLE INFO

Keywords:
Hollandites
Powder diffraction
Cs immobilization
Superstructures

ABSTRACT

Hollandites with compositions $Ba_{1.15-x}Cs_{2x}Cr_{2.3}Ti_{5.7}O_{16}$ ($0 \le x \le 1.15$) intended for the immobilization of cesium (Cs) from nuclear waste have been prepared, characterized, and analyzed for Cs retention properties. Sol-gel synthesized powders were used for structural characterization using a combination of X-ray, neutron, and electron diffraction techniques. Phase-pure hollandites adopting tetragonal (I4/m) or monoclinic symmetry (I2/m) were observed to form in the compositional range $0 \le x \le 0.4$. Structural models for the compositions, $x = 0$, 0.15, and 0.25 were developed from Rietveld analysis of powder diffraction data. Refined anisotropic displacement parameters (β_{ij}) for the Ba and Cs ions in the hollandite tunnels indicate local disorder of Ba/Cs along the tunnel direction. In addition, weak superlattice reflections were observed in X-ray and electron diffraction patterns that were due to the compositional modulation i.e., ordering of ions and vacancies along tunnel direction. Our overall observations suggest the phase-pure hollandites studied assumed supercell structures with ordered tunnel cations, which in turn have positional disorder in individual supercells.

1. Introduction

Synthetic hollandites structurally analogous to natural mineral Hollandite $Ba_xMn_8O_{16}$ [1] have been developed for several potential applications, such as battery anode materials [2,3], multiferroics [4,5], nuclear waste hosts [6,7] etc. The crystal structure is made of continuous network of edge-shared and corner-shared oxygen octahedra that form one-dimensional tunnels. Hollandite family can be represented with the general formula $A_xB_yO_{16}$, with B cations forming the BO_6 oxygen octahedra and A cations occupying the tunnel sites. The hollandite lattice can accommodate monovalent and divalent cations (e.g. Li^+, Na^+, Ba^{2+}, Cs^+, Rb^+) on the A site and a wide range of elements with varying sizes and oxidation states (e.g. Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Ti^{3+}, Ti^{4+}, Ni^{2+}) on the B site. In general, depending on the choice of A and B cations, the unit cell can adopt tetragonal symmetry with the tunnels along the crystallographic c-axis or monoclinic symmetry with the tunnels along the b-axis when using the commonly reported unit cell settings. The extensive flexibility in the chemistry of hollandites enables the tuning of electronic and magnetic properties, ionic conductivities, etc. for various applications.

Hollandites of the family $BaO - M_2^{3+}O_3 - TiO_2$ are considered potential ceramic hosts for radioactive Cs immobilization. Hollandite is one of the major phases of Synroc – a multiphase ceramic material intended to incorporate radioactive elements from nuclear waste [8–10]. In Synroc formulations, hollandite is specifically targeted to immobilize Cs, which has been one of the challenging waste elements to confine due to its high volatility during processing and its high mobility that poses a threat to the biosphere when the waste form is altered in the geologic repository [11,12]. The general composition of the Synroc hollandite $[Ba_aCs_b][M^{3+}{}_{2a+b}Ti^{4+}{}_{8\text{-}2a\text{-}b}O_{16}]$ is also intended to be stable to the redox reactions induced by the β-decay of Cs, $^{137}Cs \rightarrow {}^{137}Ba + \beta(e^-)$ and $Ti^{4+} + \beta(e^-) \rightarrow Ti^{3+}$ [11]. The choice of the trivalent cation is crucial because it affects the lateral dimension of the tunnels and thereby influences the amount of Cs loading in the lattice [11,13]. Further, depending on the ratio of average radius of tunnel cations (Ba and Cs) and octahedral cations (M^{3+} and Ti^{4+}), the hollandite unit cell symmetry can be tetragonal (I4/m) or monoclinic (I2/m) [11,14]. One of the characteristic features of hollandites is that, when Ba and/or Cs are used as tunnel cations, the tunnel sites are always only partially occupied due to the electrostatic repulsions between neighboring sites [15]. In such situations, the cations along with the vacancies can have an ordered arrangement along the individual tunnels resulting in the formation of superstructures [16–20]. In addition to this intratunnel arrangement, correlation might exist between different tunnels that would result in 3-dimensional superstructures [11,20]. The multiplicities of these superstructures are directly related to the occupancy of the tunnels, which in turn depend on the cation combinations used in hollandite formulations.

The effects of the identity of the M^{3+} cation on the structural stability, Cs loading and the effectiveness of Cs retention of the hollandite lattice has been the subject of many studies [11,12,17,20–22]. Recent works showed that Cr-hollandites (M^{3+}=Cr^{3+}) (i) had the highest Cs retention

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http://dx.doi.org/10.1016/j.jssc.2017.10.008
Received 9 March 2017; Received in revised form 3 October 2017; Accepted 5 October 2017

after leaching tests [12] and (ii) form at relatively low temperature of ~900 °C with no secondary phases [21] when compared to the Al and Fe counterparts. Even after processing in a multiphase material, the majority of the Cs-containing hollandite phase was found to also host Cr [23,24]. Based on these findings, $Ba_aCr^{3+}{}_{2a}Ti^{4+}{}_{8-2a}O_{16}$ is expected to be a suitable host lattice for effective Cs immobilization. Within the hollandite formation domain of $Ba_aCr^{3+}{}_{2a}Ti^{4+}{}_{8-2a}O_{16}$ $(0 < a < 1.34)$ [25,26], we selected the composition $Ba_{1.15}Cr_{2.3}Ti_{5.7}O_{16}$ as the base composition for this study. A series of Cs-substituted specimens of the form $Ba_{1.15-x}Cs_{2x}Cr_{2.3}Ti_{5.7}O_{16}$ $(0 \le x \le 1.15)$ were prepared to determine the solubility of Cs and the effects of Cs substitution on Ba sites. Here, we present the structural analysis of phase-pure hollandites of the system $Ba_{1.15-x}Cs_{2x}Cr_{2.3}Ti_{5.7}O_{16}$. The structural characteristics of the host lattice $Ba_{1.15}Cr_{2.3}Ti_{5.7}O_{16}$ are discussed and, the effects of Cs substitution on the octahedral framework and the order/disorder of the tunnel cations are reviewed.

2. Materials and methods

2.1. Material synthesis

Solution-based routes such as alkoxide or sol-gel methods have been reported for the synthesis of different hollandite compositions [11,27], with the latter used to prepare single-phase $Ba_{1.15-x}Cs_{2x}Cr_{2.3}Ti_{5.7}O_{16}$ powders. Barium acetate ($Ba(O_2C_2H_3)_2$), cesium nitrate ($CsNO_3$), chromium nitrate ($Cr(NO_3)_3{\cdot}9H_2O$), and titanium isopropoxide ($Ti(OC_3H_7)_4$) were used as starting materials and dissolved individually in suitable solvents – Ba and Cs precursors in acetic acid, chromium nitrate in isopropanol and, titanium isopropoxide in a mixture of acetic acid and ethanol – and mixed together. The resultant solution was dried using a rotary evaporator at 90 °C to form a homogeneous solidified gel-like material that was calcined at 400 °C for 4 h to remove all the volatile organics. The calcined powder was then compacted (uniaxial pressure ~ 35 MPa) into pellets (20 mm diameter, ~3 mm thickness) for subsequent sintering at 1050 °C/4 h. Cs volatilization is a potential risk associated with attempts to increase Cs uptake by using higher sintering temperatures or extended sintering times [15,17]. The Cs loss behavior with sintering parameters was not studied systematically, however, the mentioned thermal parameters for the material synthesis were validated by verifying the target compositions after different trials.

2.2. Characterization

Sintered pellets were crushed and ground using an agate mortar and pestle, and sieved (−200 mesh) for powder X-ray diffraction (XRD) measurements using a D8 Advance diffractometer (Bruker AXS, USA) equipped with CuKα radiation (40 kV, 40 mA). Diffraction patterns were collected over the range 10 – 140° 2θ using a Lynxeye linear position-sensitive detector. Structural analysis of phase-pure samples was also carried out using neutron diffraction measurements. Time-of-flight (TOF) neutron powder diffraction (NPD) experiments were performed at Oak Ridge National Laboratory (ORNL) using the POWGEN powder diffractometer at the Spallation Neutron Source (SNS). Powder samples were placed in vanadium cans of 6 mm diameter and TOF diffraction patterns were collected at 300 K with neutron center-wavelength, $\lambda = 1.066$ Å that covers reflections from the planes with d-spacing in the range 0.28–5.26 Å.

Microstructures of the polished surfaces of sintered pellets were observed using a FEI™ Quanta 200 F scanning electron microscope (SEM) (FEI, Oregon, USA). The compositions of the powder samples used for diffraction studies were measured by X-ray fluorescnce (XRF) method using a S4 PIONEER - XRF Spectrometer (Bruker AXS, Karlsruhe, Germany).

To extract the structural features, Rietveld refinement of XRD and NPD data was carried out using TOPAS 4.2 (Bruker AXS, Karlsruhe, Germany) software package. Starting with the tetragonal (I4/m) and monoclinic (I2/m) structural models, powder XRD data was refined using TOPAS in GUI mode. Fig. 1 shows a standard I2/m hollandite unit cell with one tunnel site for Ba/Cs (*A* site), two distinct crystallographic octahedral sites for Cr/Ti (M1 and M2) and four distinct oxygen sites (O1, O2, O3 and O4). In the corresponding tetragonal model, M1 and M2, O1 and O2, and O3 and O4 sites are equivalent. Fig. 2 shows the oxygen coordination of different cations. A typical XRD refinement procedure is performed as follows. A Chebyshev polynomial with 7 coefficients was used to describe the background and the peak profiles are described using a pseudo-Voight function. Oxygen sites were assumed to have full occupancy and their atomic positions were not refined. The occupancies and positions of tunnel cation sites were refined first followed by octahedral sites. The sum of occupancies of Cr and Ti on the overall octahedral sites was constrained to 1 in tetragonal models, while for monoclinic models the sum on each of the sites M1 and M2 was assumed equal to 1 (Fig. 1). Finally, isotropic displacement parameters were refined for all cation sites.

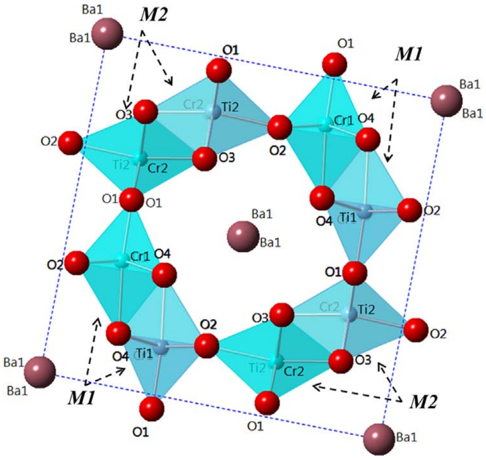

Fig. 1. Hollandite unit cell with I2/m symmetry with all crystallographic sites labeled. M1 and M2 are the two distinct crystallographic sites for octahedral cations (Cr and Ti).

For NPD refinement, appropriate executable input files that were run by TOPAS were created. The structural models generated from the XRD refinement were used as starting models. The background was described using a Chebyshev polynomial with 10 coefficients and the peak profiles using a pseudo-Voight function. Occupancies/atomic positions were refined starting with strongest neutron scatterers to the weakest ones. All oxygen sites were assumed to have full occupancy and are only refined for positions. Occupancies and positions of all cations were refined in a similar fashion to that of XRD refinement. While isotropic displacement parameters were used for Cr, Ti and O sites, anisotropic displacement parameters (ADPs) were used for the tunnel cations to account for any disorder in their locations since they are located along one-dimensional tunnels in the structure.

3. Results and discussion

3.1. Solubility of Cs

Phase-pure hollandite samples were obtained for the compositions only in the range $0 \le x \le 0.4$ as observed from powder XRD data (Fig. 3). For compositions with higher Cs loadings, $x > 0.4$, secondary phases appeared that could be indexed as $BaCrO_4/Cs_2CrO_4$. The formula unit of $A_xB_8O_{16}$ hollandite can accommodate a maximum of two tunnel cations. This limits the theoretical Cs solubility in $Ba_{1.15-x}Cs_{2x}Cr_{2.3}Ti_{5.7}O_{16}$ to $x = 0.85$. The observed lower Cs solubility indicates partial occupancy of tunnel sites. Fig. 4 shows the SEM