



Pressure-induced phase transitions of hexagonal perovskite-like oxides



Tomoya Aoba^{a,b,c}, Taneli Tiittanen^a, Hisayuki Suematsu^b, Maarit Karppinen^{a,*}

^a Department of Chemistry, Aalto University, FI-00076 Espoo, Finland

^b Extreme Energy-Density Research Institute, Nagaoka University of Technology, Niigata 940-2188, Japan

^c Department of Mechanical Engineering, Toyohashi University of Technology, Aichi 441-8580, Japan

ARTICLE INFO

Article history:

Received 3 August 2015

Received in revised form

13 November 2015

Accepted 15 November 2015

Available online 17 November 2015

Keywords:

Double-perovskite

Complex oxide

High-pressure synthesis

Tolerance parameter

ABSTRACT

We have stabilized two new cubic (3C structured) $A_2B'B''O_6$ -type double-perovskite phases, Ba_2CoSbO_6 and Ba_2ZnTeO_6 , by means of a high-pressure heat-treatment of corresponding hexagonal (6H and 12R structured, respectively) non-perovskite phases at 4 GPa and 1000 °C. Similar treatments on hexagonal Ba_2TiMnO_6 (12R) and Ba_2NiTeO_6 (12R) phases did not yield the 3C double-perovskite structure but converted the 12R structure to the 6H structure. The pressure-induced phase conversion in each $A_2B'B''O_6$ system apparently goes from the 12R structure towards the 6H and 3C structures with increasing pressure, where the pressure ranges required most likely depend (among other possible factors) on the tolerance factor for the particular combination of A, B' and B''. We foresee that yet a number of novel B-site ordered double-perovskite compounds are to be discovered through the high-pressure high-temperature treatment.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Perovskite oxides form one of the most *protean* inorganic material families. The single-perovskite ABO_3 structure itself is a highly flexible *chameleon* allowing a wide range of A and B cation combinations. Yet another freedom of expanding the material variety is realized through co-occupation of one of the two cation sites in ABO_3 with multiple cation species. The cation substituent may occupy the original single-perovskite cation site either randomly or in an ordered manner; with one-to-one stoichiometry of the two A-site (A' and A'') or B-site (B' and B'') constituents and (ideally) complete ordering so-called A- and B-site ordered double perovskites are realized. The latter structure in particular allows hundreds of cation compositions and thus extensive materials property tailoring [1].

In a perfectly B-site ordered double perovskite, $A_2B'B''O_6$, the octahedral B-cation site is alternatively occupied with two cations, B' and B'' , such that each BO_6 octahedron is surrounded by six corner-sharing $B''O_6$ octahedra, and vice versa. The ideal face-centered cubic unit cell is $2 \times 2 \times 2 = 8$ times larger than the primitive cubic cell of the ABO_3 single perovskite. Empirically, the larger the difference between the charges of the two B-site cations is, the higher is the equilibrium degree of order at the B site, such that for B' and B'' cation combinations with the charge difference

larger than two complete ordering is commonly achieved, whereas for the $A_2^I B^II B^V O_6$ -type compounds various degrees of order are observed depending on the synthesis conditions [2–5].

Double-perovskite oxides of the $A_2B'B''O_6$ type were first studied already in 1960s [6–8]. Since the B-site ordered perovskite structure is adopted by hundreds of different cation combinations of A, B' and B'' [1], the phases possess a wide variety of attractive material properties, the most interesting ones from the application point of view being the room-temperature halfmetallicity and intergrain tunneling magnetoresistance effect first discovered for Sr_2FeMoO_6 [9–11] and the excellent performance as a SOFC anode material for Sr_2MgMoO_6 and related compounds [12–14]. Of the more fundamental interest, intriguing magnetic properties are seen for various B-site ordered double perovskites; the Cu^{II} -based $Sr_2CuB''O_6$ system is an exciting example where low-dimensional and/or frustrated magnetic behaviors may be found depending on the B'' cation *d*-orbital occupancy [15–17].

The ideal crystal structure of the simple ABO_3 perovskite is built up by alternating AO layers of the larger 12-fold oxygen-coordinated cation A and BO_2 layers where the smaller cation B is surrounded by an oxygen octahedron; the ideal structure can be abbreviated as 3C (3-layered cubic) structure. The so-called Goldschmidt tolerance factor

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

where r_A , r_B and r_O are the ionic radii of A, B and O, respectively, is an excellent indicator for the stability and distortions of the perovskite structure. For the $A_2B'B''O_6$ double perovskite, an average

* Correspondence to: Department of Chemistry, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland.

E-mail address: maarit.karppinen@aalto.fi (M. Karppinen).

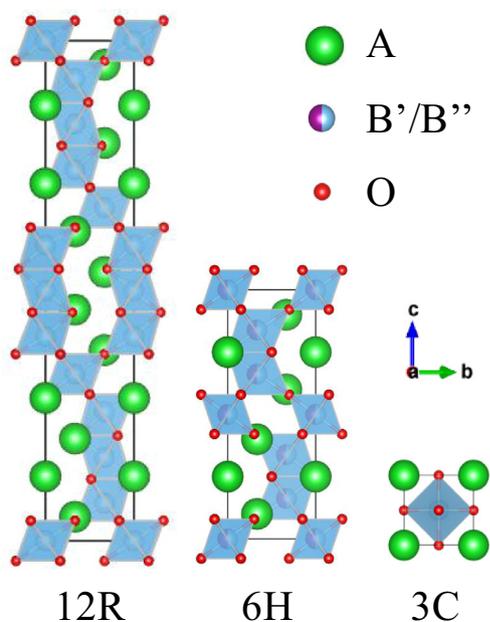


Fig. 1. Schematic illustration of the crystal structures of 12R, 6H and 3C (drawn with VESTA [18]).

value of the B-cation radii is often employed. The ideal cubic perovskite structure is expected for $t \approx 1.0$; for $t < 1$ the (octahedrally) tilted perovskite structure is usually observed down to $t \approx 0.9$. On the other hand, when $t > 1.0$ many $A_2B'B''O_6$ compounds form related hexagonal non-perovskite structures where part of the oxygen octahedra share a face with another octahedron to release the strain caused by the cation radius mismatch at ambient pressure (AP), the most common being the 12R (12-layered rhombohedral) and 6H (6-layered hexagonal) structures shown in Fig. 1.

High-pressure (HP) treatment of a sample with $t > 1$ could provide us with a means to decrease the apparent tolerance factor as the A–O bond typically possesses a larger compressibility compared to the B–O bond [1,19]. Hexagonal perovskites are known to exhibit sequential structural changes from 2H to 9R, 4H, 6H, and finally to 3C as the high pressure stabilizes the high-density phase [20]. The same applies to the double-perovskite materials, for example, 4H Ba_2CuTeO_6 and Jahn–Teller distorted Sr_2CuIrO_6 change to 3C at ca. 5 GPa [21,22]. There should yet be plenty of novel $A_2B'B''O_6$ -type double perovskites to be discovered through the HP conversion technique [1]. Here we explore the possibility to stabilize such “missing” double perovskites among four materials previously reported to form a related hexagonal structure at AP, i.e. 12R Ba_2TiMnO_6 [23,24], 6H Ba_2CoSbO_6 [25,26], 12R Ba_2NiTeO_6 [27,28] and 12R Ba_2ZnTeO_6 [28,29], with the AP tolerance factors ranging from 1.04 to 1.08.

2. Experimental

First we prepared the four hexagonal Ba_2TiMnO_6 , Ba_2CoSbO_6 , Ba_2NiTeO_6 and Ba_2ZnTeO_6 samples through AP solid-state synthesis from appropriate mixtures of $BaCO_3$, TiO_2 , MnO , Co_3O_4 , Sb_2O_3 , NiO , ZnO and TeO_2 powders. The powder mixtures were calcined in air at 1250 °C/45 h, 1150 °C/30 h, 1250 °C/10 h and 1100 °C/15 h, respectively, followed by a thorough grinding in an agate mortar. The thus obtained precursor powder for the HP heat-treatment was compacted into a gold capsule covered with a NaCl separator and placed in a pyrophyllite pressure media equipped with an internal graphite sleeve heater. The HP heat-treatment was carried

out in a cubic-anvil apparatus (Riken-Seiki) at ca. 4 GPa and 1000 °C for 1 h, followed by quenching to room temperature.

X-ray powder diffraction (XRD) patterns were recorded using PANanalytical X'Pert PRO MPD Alpha-1 (Cu $K_{\alpha 1}$ radiation; 45 kV and 40 mA) diffractometer for both the hexagonal-structured precursor powders and the corresponding HP-converted products. The crystal structure parameters were refined using the Rietveld refinement program RIETAN-FP [30], in space groups $Fm\bar{3}m$ (#225) and $P6_3/mmc$ (#194) for the HP-synthesized samples.

Diffuse reflectance UV/vis/NIR spectra were recorded for both the ambient-pressure synthesized and high-pressure treated samples under ambient conditions using PerkinElmer LAMBDA 950 UV/vis/NIR spectrophotometer with integrating sphere. The sample powders were dispersed on quartz glass plates using ethanol and allowed to dry before measurement. Data were collected over the 200–2500 nm range.

3. Results and discussion

The four hexagonal phases were obtained through the ambient-pressure (AP) synthesis in air in essentially phase-pure forms; X-ray patterns for these materials are shown in Fig. 2 revealing that Ba_2TiMnO_6 , Ba_2NiTeO_6 and Ba_2ZnTeO_6 exhibit the 12R structure (plus a trace of Ba_3TeO_6 impurity in the Ba_2NiTeO_6 sample), while Ba_2CoSbO_6 is of the 6H structure (with a trace of the Sb-rich $Ba_3CoSb_2O_9$ phase), all in line with the original reports [23,26–28]. The crystal structure information obtained from the Rietveld refinements are summarized in Table 1 together with the nominal tolerance factors calculated from the Shannon's ionic radius values [32] for the targeted cubic perovskite structures. The refined lattice parameters are in accordance with the previous reports. With increasing average B-site ionic radius both the unit-cell volume and the tolerance factor increase.

Upon the HP heat-treatment the hexagonal 6H-structured Ba_2CoSbO_6 and 12R-structured Ba_2ZnTeO_6 phases were found to transform to the 3C structure, while a change from the 12R structure to the 6H structure was observed for Ba_2TiMnO_6 and Ba_2NiTeO_6 . Colors for these HP-treated phases were: Ba_2CoSbO_6 black, Ba_2ZnTeO_6 pale gray, Ba_2TiMnO_6 dark brown and Ba_2NiTeO_6 pale yellow. All HP samples included traces of the non-reacted hexagonal precursor phase. Rietveld refinement of the structural

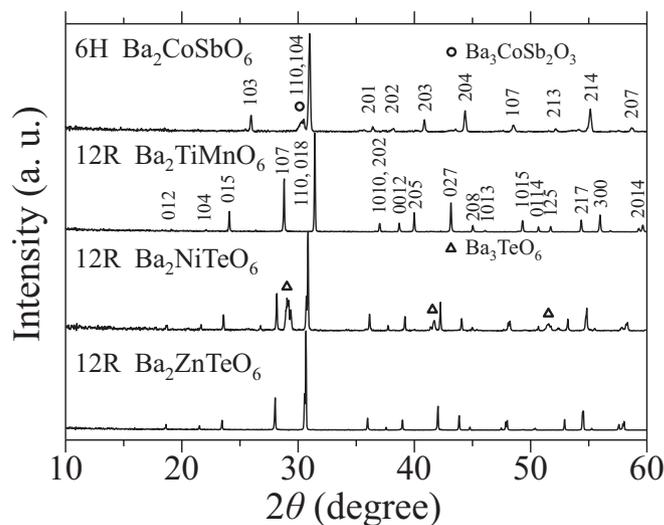


Fig. 2. XRD patterns for the AP-synthesized hexagonal materials; the patterns for Ba_2TiMnO_6 and Ba_2CoSbO_6 are indexed in space groups $R\bar{3}m$ and $P6_3/mmc$, respectively, while the peaks for the $Ba_3CoSb_2O_9$ [31] and Ba_3TeO_6 phases are marked by a circle and a triangle, respectively.

Download English Version:

<https://daneshyari.com/en/article/1329724>

Download Persian Version:

<https://daneshyari.com/article/1329724>

[Daneshyari.com](https://daneshyari.com)