Compression mechanism of $HoBaCo_4O_7$, a compound with oxygen absorption/desorption capabilities

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Recently, a new family of isostructural cobaltates ($MBaCo_4O_7$, M = In, Y, Ln) has been synthesized [1]. These cobaltates belong to a new class of geometrically frustrated magnets which not only exhibit interesting magnetic-, electronic-, thermoelectric- and electrochemical-properties; but they also have a remarkable low-temperature oxygen absorption/desorption capability which makes them suitable as oxygen sensors, oxygen permeation membranes and solid oxide fuel cells (SOFCs) [2-3]. For example, $YBaCo_4O_{7+\delta}$ reversibly absorb and desorb oxygen up to $\delta \approx 1.5$ in a narrow temperature range, 470-673 K [2]. Hence, an amount of oxygen that corresponds to ~20% of the total oxygen content is readily loaded or removed being triggered by just a tiny change in temperature or atmosphere. This oxygen capability substantially exceeds in the overall magnitude and in the response sensitivity to those achieved with, for example, $SrFeO_3$ (perovskite structure) and $YBa_2Cu_3O_7$ (perovskite-like structure) [3]. It is well known that the oxygen diffusion properties of perovskite-like compounds are affected not only by the temperature and surrounding oxygen partial pressure but also by their crystal structures. Therefore, a different crystal structure will result in different oxygen diffusion properties. There is currently a discussion about whether the $MBaCo_4O_7$ crystallizes in the space group $P6_3mc$ or in the trigonal subgroup $P3_1c$ at room temperature; or whether $MBaCo_4O_7$ undergoes temperature-induced structural phase transitions at low temperature or not. Nothing is known about the influence of pressure on $MBaCo_4O_7$ compounds, but the apparent thermal instability suggests that these compounds will undergo structural phase transitions at elevated pressure.

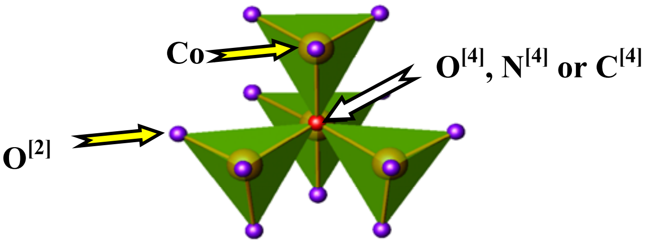

Figure 1. $MBaCo_4O_7$ star-shaped building blocks.

At room temperature the $MBaCo_4O_7$ crystal structure can be described by star-shaped $[O^{[4]}(CoO^{[2]}_3)_4]$ building blocks (Fig. 1), where the central $O^{[4]}$ atom simultaneously links four Co atoms. These building blocks are interconnected forming stable three-dimensional networks. We have already performed high-pressure X-ray diffraction experiments on isotypic compounds where the crystallographic site $X^{[4]}$ is fully occupied by nitrogen (nitridosilicates ($MASi_4N_7$) and oxonitridoaluminosilicates ($MASi_{4-x}Al_xO_xN_{7-x}$)) or carbon (carbidonitridosilicates ($M_2Si_4N_6C$)) [4-5]. Therefore, we will determine the effect of $O^{[4]}$ links on the compressibility of these compounds and compare the high-pressure properties with those of the already investigated silicates that exhibit $N^{[4]}$ or $C^{[4]}$ links.

We have performed *in situ* high-pressure single-crystal synchrotron X-ray diffraction experiments on $HoBaCo_4O_7$ at pressures up to 9 GPa. We collected intensity data at beamline D3 at HASYLAB. A black-metallic single-crystal of 133 x 107 x 52 μm^3 was loaded together with ruby chips for pressure determination into a DAC. A methanol-ethanol (4:1) mixture was used as a pressure-transmitting medium. Intensity data were collected in fixed-phi mode on a HUBER four-circle diffractometer using a point detector and a wavelength of 0.45 Å. Full intensity data of $HoBaCo_4O_7$ were collected at 3.0(1), 6.3(3) and 8.8(1) GPa while just cell parameters were determined at 1.0(1), 4.2(3) and 7.2(1) GPa. From the analysis of data the space group $P6_3mc$ was found to describe better the $HoBaCo_4O_7$ crystal structure. Refinements of the high-pressure data sets were carried out with isotropic and anisotropic displacement parameters.

Table 1. Refinement parameters of $HoBaCo_4O_7$ at 8.8(1) GPa. S.G. $P6_3mc$.

a / Å	6.168(5)
c / Å	9.976(5)
V / Å^3	328.6(4)
Z (formula units)	2
$R_{int}(F^2)$	0.05(4)
Observed reflections	1161
Unique reflections	353
Reflections with $I > 4\sigma$ (I)	337
Parameters	33
$R1$ [$I > 4\sigma$ (I)]	0.0267
$wR2$	0.0563
GooF	1.193

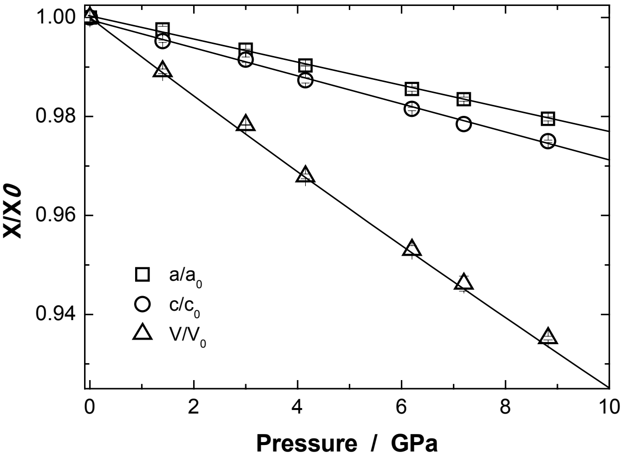

Figure 2. Pressure-dependencies of the normalized unit-cell parameters of $HoBaCo_4O_7$, up to 9 GPa. Fits of 3rd order B-M EOS are plotted by solid lines.

The $HoBaCo_4O_7$ crystal structure is stable up to 9 GPa. Results of the structure refinements of $HoBaCo_4O_7$ at 8.8(1) GPa are shown in Table 1. The structural compression is mainly driven by pure bond length compression. A fit of a 3rd order B-M EOS to the p,V-data results in a bulk modulus of B_0 = 123(2) GPa with its pressure derivative B' = 1.5(2). The pressure dependence of the unit-cell parameters shows that the c-axis is slightly more compressible than the a-axis (Fig. 2).

In summary, this study presents the first experimentally determined structural compression of a $HoBaCo_4O_7$ cobaltate. Further experiments at even higher pressures are needed in order to establish the phase stability limit. Such studies are currently underway by our group and, in conjunction with the present study, will serve as a basis for the understanding of the pressure dependence of the structure–property relationship of this class of compounds.

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