Physics of the Earth and Planetary Interiors 189 (2011) 171–175

Contents lists available at SciVerse ScienceDirect

Physics of the Earth and Planetary Interiors

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

Towards better analogues for $MgSiO_3$ post-perovskite: $NaCoF_3$ and $NaNiF_3$, two new recoverable fluoride post-perovskites

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ARTICLE INFO

Article history:
Received 26 May 2011
Received in revised form 10 August 2011
Accepted 29 August 2011
Available online 5 September 2011

Keywords:
Post-perovskite
ABF_3 fluorides
Multi-anvil press

ABSTRACT

We present details of two new quenchable post-perovskite-structured $NaBF_3$ compounds, where B is Co or Ni. Both post-perovskites are readily synthesised in the multi-anvil-press pressure range and have unit cells with axial ratios similar to $MgSiO_3$ post-perovskite ($NaCoF_3$ a = 3.07035(7) Å, b = 10.1291(3) Å, c = 7.4664(1) Å, V = 232.20(1) Å^3; $NaNiF_3$ a = 3.0247(2) Å, b = 10.0543(7) Å, c = 7.3989(3) Å, V = 225.01(3) Å^3). For $NaCoF_3$, we have synthesised post-perovskite single crystals and determined the phase diagram: the perovskite-post-perovskite transition occurs at 18 GPa and 700 °C, with a Clapeyron slope of 15.5 MPa/K. On the basis of the above factors, combined with (1) the fact that ABF_3 compositions also have stable perovskite phases and (2) the relatively small differences in the mass ratios of their constituent atoms, we suggest that these systems might prove to be better analogues for $MgSiO_3$ post-perovskite than the currently used $CaBO_3$ (where B is Ir, Pt, Rh, Ru) compositions.

1. Introduction

The $CaIrO_3$-structured phase of $MgSiO_3$ (hereafter called post-perovskite) is thought to be the majority phase in the D″ region of the lowermost mantle (e.g. Oganov and Ono, 2004; Murakami et al., 2004; Tsuchiya et al., 2004) and to control much of the dynamics of this region; knowledge of the physical properties of post-perovskite is, therefore, of great importance. However the high stabilization pressure of $MgSiO_3$ post-perovskite (~125 GPa at 2500 K; Tateno et al., 2009) precludes many types of measurement which might be of interest. In determining properties which are not currently measurable at the high pressure of $MgSiO_3$ post-perovskite thermodynamic stability, low-pressure analogue systems could be useful. $CaIrO_3$ is the structure-type material and can be produced in both perovskite and post-perovskite forms at atmospheric pressure. In consequence it has been extensively studied, for its thermoelastic and crystal chemical properties (Martin et al., 2007; Boffa Ballaran et al., 2007; Lindsay-Scott et al., 2007, 2010, 2011; Hustoft et al., 2008a; Liu et al., 2011), its mechanical properties (Yamazaki et al., 2006; Walte et al., 2007, 2009; Miyagi et al., 2008; Hunt et al., 2009), its thermal conductivity (Kewaprak et al., 2009) and its grain growth (Yoshino and Yamazaki, 2007). However, it has also been suggested that $CaIrO_3$ is a poor analogue for $MgSiO_3$ on crystal chemical grounds and on the basis of differences between the observed behaviour of the two compounds (Ohgushi et al., 2008; Lindsay-Scott et al., 2007, 2011).

In all studies of structural analogue materials it is preferable to use a suite of analogue compositions so that systematic variations can be determined in order to more confidently predict the properties of the material of interest. While a range of recoverable oxide and sulphide post-perovskites are documented they have not proven to be popular for analogue studies, either because of their high stabilization pressure, their poor chemical stability, or because the perovskite structure cannot be produced. The ABF_3 fluoride perovskites, where A is either Na or K and B is a 2^+ cation, have proven to be good analogues for $MgSiO_3$ perovskite (e.g. Poirier et al., 1983; Street et al., 1997; Chakhmouradian et al., 2001; Umemoto et al., 2006; Grocholski et al., 2010) and the ABF_3 fluorides would, therefore, seem also to be ideal candidates as analogues to PPV-$MgSiO_3$, provided that their PPV phases are readily synthesized and recoverable to room pressure and temperature. This is especially true if such phases can be synthesized at pressures accessible with a multi-anvil press (MAP), i.e. below ~25 GPa. Two fluoride perovskite systems have been reported to transform to PPV at, or close to, pressures attainable in a MAP: $NaMgF_3$ (13–38 GPa: Liu et al., 2005; Martin et al., 2006a; Umemoto et al., 2006; Hustoft et al., 2008b) and $NaZnF_3$ (14–22 GPa: Yakovlev et al., 2009); $NaMgF_3$ post-perovskite was also recovered to ambient conditions (Hustoft et al., 2008b). Here we describe the synthesis of two new post-perovskites, $NaNiF_3$ and $NaCoF_3$, which are both recoverable

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doi:10.1016/j.pepi.2011.08.010

to ambient conditions. The P-T conditions of synthesis are well within standard multi-anvil capabilities and single crystals of $NaCoF_3$ are readily produced.

2. Experimental

High-pressure experiments were performed in multi-anvil presses at UCL (10,000 kN, Walker-type press; 10/5 assembly) ETH Zurich (10,000 kN, Walker-type press; 10/3.5 assembly) and Stony Brook (17,792 kN, split sphere press; 8/3 assembly). Chrome-doped MgO octahedra of edge length 10 or 8 mm were compressed by tungsten carbide anvils with truncations of 5, 3.5 or 3 mm depending on the target pressure. Ten millimetre cells had straight cylindrical furnaces of graphite (10/5; $P < 19$ GPa) or $LaCrO_3$ (10/3.5; $P = 22$ GPa) inside zirconia thermal insulation and internal MgO insulating sleeves. Eight millimetre cells used 75 μm Re-foil furnaces inside $LaCrO_3$ thermal insulation ($P = 20$ GPa). Finely ground stoichiometric mixtures of NaF and either CoF_2 or NiF_2 were used as starting material. For the 10/5 (or 10/3.5) assemblies this fluoride mixture was packed into cylindrical Au (Pt) capsules 2.5 (1.2) mm in diameter and 2 (1.3) mm in length, and loaded into the MgO insulating sleeves inside the furnace. For the 8/3 assembly the starting fluoride mixture was packed directly into the Re furnace along the central 2 mm length of the furnace, with Re discs at the sample ends. Temperature was measured using W/Re thermocouples with their hot junctions terminating on the end of the sample capsule (10/5 and 10/3.5 assemblies), or separated from the Re disc by a thin (~100 μm) Al_2O_3 disc (8/3 assembly). Experiments were performed by cold compression to the desired end-load followed by rapid heating (taking ~20 min) to the target temperature. Temperature was maintained for durations of between 12 h and 7 days, depending on the temperature. Experiments were terminated by rapidly cutting power to the furnace followed by slow decompression over a period of ~15 h.

The recovered samples were gently disaggregated and a small (~2 mg) portion of each was dispersed on 180 μm thick soda-glass plates (microscope slide coverslips) using propanol. These samples were analysed by optical microscopy and, once the propanol had fully evaporated, powder X-ray diffraction. Powder diffraction measurements were performed in Bragg–Brentano reflection geometry on a PANalytical X'Pert Pro diffractometer with Co $K\alpha_1$ radiation (40 kV, 30 mA), monochromated using an incident-beam focusing Ge (1 1 1) Johansson monochromator. Diffraction patterns were collected over the range $10° < 2\theta < 120°$ and analysed using the Rietveld method as implemented in the GSAS suite of programmes (Larson and Von Dreele, 1994; Toby, 2001).

3. Results

3.1. $NaCoF_3$

The conditions of synthesis of $NaCoF_3$ and the recovered phases are given in Table 1. At 400 °C the reaction kinetics were very slow, such that some unreacted starting material remained even after 7 days at temperature, but by 700 °C the reaction was complete in 14 h. Fig. 1 shows a selected region of the diffraction pattern from the sample recovered from 18 GPa and 700 °C. The sample consists mainly of post-perovskite-structured $NaCoF_3$ with a minor amount of perovskite-structured $NaCoF_3$ and a trace of MgO (from the insulating sleeve). Unit cell parameters determined by Rietveld refinement are: $a = 3.07035(7)$ Å, $b = 10.1291(3)$ Å, $c = 7.4664(1)$ Å, $V = 232.20(1)$ Å^3 for the post-perovskite; $a = 5.4187(4)$ Å, $b = 5.6087(4)$ Å, $c = 7.7969(6)$ Å, $V = 236.96(2)$ Å^3 for the perovskite and $a = 4.2121(3)$ $V = 74.72(2)$ for the MgO; errors in brackets are one ESD in the last unit. The weighted profile R-factor, R_{wp}, for the refinement is 0.073 and the χ^2 value is 7.6. The atomic coordinates of the post-perovskite phase are consistent with those of the oxide post-perovskites (within, for example, 2–7 estimated standard deviations of the $MgGeO_3$ post-perovskite structure (Kubo et al., 2008) and 2–15 estimated standard deviations of the $CaPtO_3$ post-perovskite structure (Lindsay-Scott et al., 2011) but we have chosen not to report the crystal structure of post-perovskite $NaCoF_3$ here since the specimen preparation in the present study was not suitable for accurate determination of atomic coordinates, being too thin and quite strongly oriented. We believe that the perovskite in this sample formed by partial decomposition of metastable post-perovskite during recovery and preparation of the sample. Even gentle grinding of recovered $NaCoF_3$ post-perovskite crystals at ambient conditions causes their transformation to the stable perovskite structure. However, X-ray diffraction of bulk sample at the National Synchrotron Light Source (Beamline X17B2) confirmed that perovskite was present in the recovered sample only at trace levels prior to preparation for the laboratory X-ray source. The difference in volume of the PV and PPV phases of $NaCoF_3$ synthesised in their respective stability fields and measured at ambient pressure is 1.8% ($V_{PV} = 236.66(7)$ Å^3 from Lütgert and Babel (1992) and $V_{PV} = 236.868(5)$ Å^3 from the present study).

Fig. 2 shows photomicrographs of coexisting perovskite and post-perovskite $NaCoF_3$ synthesised at 14 GPa, 450 °C for 33.5 h. The post-perovskite grains are substantially larger than those of perovskite and typically grow with a needle-habit. One of the large crystals was identified as post-perovskite by single-crystal X-ray diffraction at the Bayerisches Geoinstitut, but due to strong twinning the crystal was not studied beyond an initial peak indexing and orientation. Similar shape anisotropy is also observed in $CaIrO_3$ and $CaPtO_3$, where the long direction of crystals corresponds to the crystallographic a-axis. Despite no particular efforts being made to

Table 1
Synthesis conditions of $NaCoF_3$ and recovered phases.

P (GPa)	T (°C)	Duration (h)	Recovered phases
14	450	33.5	PV + PPV
15.5	400	77	PPV[a]
16	400	172	PPV[a]
16	600	51	PV
18	700	14	PPV

[a] There was incomplete reaction in these two experiments; NaF and CoF_2 were recovered in addition to post-perovskite $NaCoF_3$.

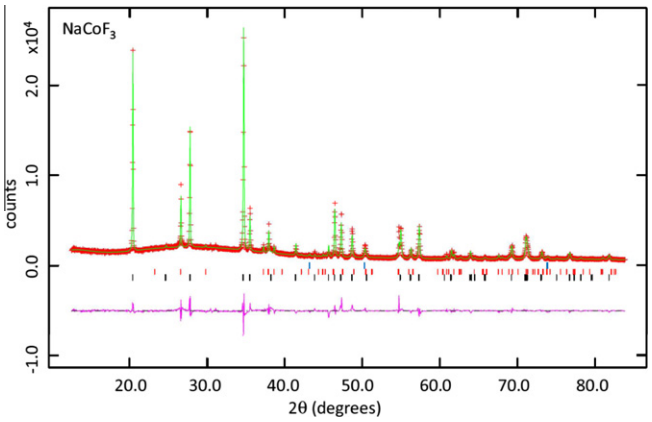

Fig. 1. X-ray diffraction pattern of $NaCoF_3$ (Co $K\alpha_1$ radiation) synthesised at 18 GPa and 700 °C. The data (crosses) have been fitted using the Rietveld method (solid line). Tickmarks show the positions of reflections for post-perovskite (lower series), perovskite (middle series) and MgO (upper series). The lower trace shows the difference between the observed and calculated intensities.