



Swansea University
Prifysgol Abertawe



Cronfa - Swansea University Open Access Repository

This is an author produced version of a paper published in:

Mineralogical Magazine

Cronfa URL for this paper:

<http://cronfa.swan.ac.uk/Record/cronfa29037>

Paper:

Margadonna, S. (2016). Observation of Sb₂S₃-type post-post-perovskite in NaFeF₃. Implications for ABX₃ and A₂X₃ systems at ultrahigh pressure. *Mineralogical Magazine*, 80(4), 659-674.

<http://dx.doi.org/10.1180/minmag.2016.080.017>

This item is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Copies of full text items may be used or reproduced in any format or medium, without prior permission for personal research or study, educational or non-commercial purposes only. The copyright for any work remains with the original author unless otherwise specified. The full-text must not be sold in any format or medium without the formal permission of the copyright holder.

Permission for multiple reproductions should be obtained from the original author.

Authors are personally responsible for adhering to copyright and publisher restrictions when uploading content to the repository.

<http://www.swansea.ac.uk/library/researchsupport/ris-support/>

Observation of Sb_2S_3 -type post-post-perovskite in NaFeF_3 . Implications for ABX_3 and A_2X_3 systems at ultrahigh pressure.

W. A. CRICHTON ^{1*}, F. L. BERNAL ², J. GUIGNARD ¹, M. HANFLAND ¹ AND S. MARGADONNA ^{2†*}

¹ ESRF - The European Synchrotron, 71, rue des Martyrs, Grenoble cedex, 38043, France.

² Department of Chemistry and Center for Materials Science and Nanotechnology, University of Oslo, Oslo, Norway.

† Now at: College of Engineering, Swansea University, Singleton Park, Swansea SA2 8PP, U.K.

* E-mail: crichton@esrf.fr and s.margadonna@swansea.ac.uk

KEYWORDS: Perovskite, post-perovskite, GdFeO_3 , single-crystal diffraction, high pressure

Running title: Sb_2S_3 -type post-post-perovskite

Abstract

We describe the structures and transformations that lead to the crystallisation of a post-post-perovskite of Sb_2S_3 -type in a GdFeO_3 -type fluoroperovskite system at high pressure conditions, through use of large-volume powder and single-crystal x-ray diffraction techniques. The results of this analysis gives unique access to the relative crystallographic orientations of all polymorphs encountered (GdFeO_3 -type, CaIrO_3 -type and Sb_2S_3 -type). We use this information to extend this description to include other calculated and observed forms that are competitive in ABX_3 and A_2X_3 stoichiometries (*e.g.* α - Gd_2S_3 - and Be_3N_2 -types) and provide substantial information on inter-relationships between these structures. Such information is critical to the interpretation of transition mechanisms, predicting transition sequences and to the expression of directional properties in those transformed structures. The transformation from CaIrO_3 -type to Sb_2S_3 -type is group-subgroup, from $Cmcm$ with fc^2a , to $Pnma$ c^5 , with no observable volume change, but considerable change to the morphology of the lattice, with an increase in coordination and average bond length compared to the post-perovskite form of NaFeF_3 .

Introduction

It has been a decade since one of the most significant scientific breakthroughs in our understanding of the structure of the deep Earth (Murakami *et al.*, 2004; Oganov and Ono, 2004; Tsuchiya *et al.*, 2004). The seismic discontinuity observed at the D" layer is attributed to the transformation of MgSiO₃ perovskite (pv, of GeFeO₃-type) to its post-perovskite form (ppv, of CaIrO₃-type). While much experimental and theoretical work has been devoted to the study of this transition, further advances are impeded by the extreme conditions of temperature and pressure that are needed to reproduce the real conditions at, and beyond, the D" layer. For this reason, studies of the behaviour of related systems, such as the fluoroperovskites and noble-metal oxides systems, which also undergo a pv to ppv transition but at much more easily accessible conditions, have been undertaken to establish the phase diagrams, stability and physio-chemical properties of these ppv phases together with possible post-post-perovskite forms (Oganov *et al.*, 2005; Martin *et al.*, 2006a; Martin *et al.*, 2006b; Umemoto and Wentzcovitch, 2006; Martin *et al.*, 2007; Hustoft *et al.*, 2008; Grocholski *et al.*, 2010; Dobson *et al.*, 2011; Shirako *et al.*, 2012b; Yusa *et al.*, 2012; Dobson *et al.*, 2012; Dobson *et al.*, 2013; Hunt *et al.*, 2013). Taken together, these have a direct bearing on our understanding and interpretation of possible deep Earth and super-Earth processes.

In parallel, other research has made significant ground in extending comparable A₂X₃ systems to similar extremes of pressure and temperature; notably in the Fe₂O₃, Al₂O₃ and lanthanide sesquioxides and sulfide systems (Oganov and Ono, 2005; Caracas and Cohen, 2007; Tsuchiya *et al.*, 2007; Umemoto and Wentzcovitch, 2008; Yusa *et al.*, 2008a; Yusa *et al.*, 2008b; Shim *et al.*, 2009; Yusa *et al.*, 2009; Umemoto and Wentzcovitch, 2011; Ovsyannikov *et al.*, 2012). Recently a hexagonal lattice 'H-phase' was proposed for Fe-rich phase produced (with ppv) during a decomposition reaction of (Mg,Fe)SiO₃ (Zhang *et al.*, 2014), which is further implied to have a structure related to the PPV-II proposition of Cohen and Lin (2014). More recently, Xu *et al.* (2014) have proposed the existence of another post-post-perovskite form, which we interpret as identical to the α-Gd₂S₃-type, and have extended its application as a systematically occurring structure in highly compressed oxide and fluoride perovskites, as well as in generalized sesquioxide systems. While the determination of the crystallographic structures of pv, ppv and allied forms is fundamental, information on how the orientation of their unit cells is affected by their successive transitions is equally valuable. The inheritance of directional and tensor properties that accompany these transformations are pivotal for the full description, interpretation and preservation of textural and rheological response in the deep Earth.

Compounds, such as Fe_2O_3 , have been observed to transform, with increasing pressure, from corundum-type structures, through the $\text{Rh}_2\text{O}_3(\text{II})$ - to the CaIrO_3 -type (Shim *et al.*, 2009). In the case of Fe_2O_3 , the high pressure form is characterized by distinct 6 and 8-fold coordinated Fe^{3+} cation sites and a similar situation is also observed in Al_2O_3 (Oganov and Ono, 2005; Umemoto and Wentzcovitch, 2008). This structure is shared by all these chemistries and is the highest-pressure single-phase polymorph observed in these and oxide ABX_3 systems, such as MgSiO_3 . It follows that, while neither Al_2O_3 nor Fe_2O_3 form a pv they do stabilize as ppv and this allows comparisons to be drawn anew, between ABX_3 and A_2X_3 stoichiometries. Al_2O_3 and other sesquioxide structures are then further predicted to transform to other higher density structures; *viz.* the Sb_2S_3 - and/or the α - Gd_2S_3 -types (the case of Sc_2O_3 , In_2O_3 and Y_2O_3) at high pressures (Oganov and Ono, 2005; Caracas and Cohen, 2007; Tsuchiya *et al.*, 2007; Umemoto and Wentzcovitch, 2008; Yusa *et al.*, 2008a; Yusa *et al.*, 2008b; Shim *et al.*, 2009; Yusa *et al.*, 2009; Umemoto and Wentzcovitch, 2011; Ovsyannikov *et al.*, 2012, Xu *et al.*, 2014). The sequence of corundum, $\text{Rh}_2\text{O}_3(\text{II})$, CaIrO_3 , Sb_2S_3 (and/or to α - Gd_2S_3) has been predicted to cover a range of pressures of approximately 5 Mbar - pressures well exceeding those available to oxides in the Earth, and to static experimentation (Oganov and Ono, 2005; Umemoto and Wentzcovitch, 2008). Therefore, a clear link between ABX_3 systems and the sesquioxides (or other A_2X_3 system) and its extension, through the common CaIrO_3 -type, remains a significant challenge to observe. The formation of equivalent structures at these pressures (or at least the accessibility of analogous forms) as CaIrO_3 - and post-post-perovskites has significant implications for the mutual solubility of A_2X_3 and ABX_3 at the extremes of terrestrial stability of oxide phases. The search for suitable analogues to extend the systematics of these A_2X_3 and ABX_3 systems will also overcome the requirement for a "...perovskite compound in which both the 6-fold- and the 8-fold-coordination sites are occupied by the same cation" (Liu and Bassett, 1986) and offer the possibility of unified account of these systems to the highest pressures under which oxides are stable in the Earth's interior, and beyond.

In this study, we provide complete refinements of the different crystal structures observed in compressed NaFeF_3 and express the crystallographic orientations of the ppv and post-post perovskite Sb_2S_3 -type structure with respect to the pv form. We interpret the structural sequence through matrix transformations to underscore the transition mechanisms from pv, to ppv and Sb_2S_3 -type, as well as to the related α - Gd_2S_3 -type and Be_3N_2 -type structures. The former is most-commonly observed in high pressure sesquioxide structures (Oganov and Ono, 2005; Caracas and Cohen, 2007; Tsuchiya *et al.*, 2007; Umemoto and Wentzcovitch, 2008; Yusa *et al.*, 2008a; Yusa *et al.*, 2008b; Shim *et al.*, 2009; Yusa *et al.*, 2009; Umemoto and Wentzcovitch, 2011;

Ovsyannikov *et al.*, 2012, Xu *et al.*, 2014), and the latter is calculated as a further potential post-ppv form in ABX_3 (Umemoto and Wentzcovitch, 2006), but is also known as a polymorphic form of compounds that also show perovskite, and the ante-perovskite bixbyite and Al_2O_3 structures. Our work then highlights and extends the similitude between sesquioxide and perovskite-like systems beyond ppv, through their mutual expression as Sb_2S_3 - and/or α - Gd_2S_3 -types (which can both be related to the $CaIrO_3$ -type, but, as our work suggests, by different twin mechanisms). As these transformation matrices and the twinning descriptions included herein are crystallographic descriptions, they are of significant value in transferring any symmetry or directionally affected tensor properties from one phase to the next as a first-order estimate of how bulk properties are altered at any transition. In addition, given that all post-pv structures yet expected in ABX_3 and A_2X_3 structure can be related, it is now possible to use a broader base from which to construct an overall systematic for these anticipated high density structures and to establish which and why any particular trend may be exhibited over another. As such these model structures, and the details of their transformations, are fundamental in modelling a wider range of potential phase diagrams and for estimating the rheology (and other physical properties) of deep- and super-Earth environments.

Experimental

Synthesis of $NaFeF_3$ perovskite

NaF, Fe and FeF_3 powders were finely ground and mixed in a 3:2:1 ratio according to the synthesis method of Brenner and Hoppe (1990) and of the same batch as used by Bernal *et al.* (2014). The so-obtained mixtures were then pelletised and loaded into a Fe-tube which was used as a reaction vessel. All the manipulations were carried out in an Ar-filled glove-box given the hygroscopic nature of NaF and to avoid exposure to oxygen and/or moisture. The Fe-tube was tightly closed and then heated under a constant nitrogen flow at 750 °C for 8 days before recovery.

Single-crystal diamond-anvil cell techniques

Single-crystal samples were loaded in a membrane-driven diamond-anvil cell, together with a ruby sphere for pressure measurement and a He pressure-transmitting medium. Single-crystal datasets were collected at a wavelength of 0.41458 Å, selected by a horizontally focusing Laue monochromator at beamline ID09A of the ESRF, by ω -slicing from -30° to 30° with an integrated interval of 0.5° per frame (Merlini and Hanfland, 2013). The exposure time per frame was 1 second and the beam size was approximately 0.01 x 0.01 mm. The sample-

detector distance and wavelength were refined using a Si powder sample, following the method described in Hammersley *et al.* (1995). Data were reduced using the CrysAlis software of Oxford Diffraction. In general, the model system (laboratory and crystal orientation) was refined with sample-detector distance fixed at that determined by Fit2D (Hammersley *et al.*, 1995). The data reduction followed averaging in the centred lattice of the eventual space group assignment and the frame data were rescaled using ABSPACK correction for absorption. The data were refined using Jana2006 (Petříček *et al.*, 2006), following averaging and culling of $>20\%$ I/\bar{I} for equivalents. Further corrections to the assembled *hkl* dataset were made on an individual basis and were dependent on lattice and averaged Laue symmetry, degree of overlap, interception of peaks with diamond reflections, gasket shadow, detector edges etc.

Powder diffraction from large-volume press

In situ high pressure x-ray diffraction data were taken with the large-volume press and recorded at beamline ID06LVP, ESRF, using a linear pixelated GOS detector from Detection Technology, running sequential exposures for 3.2 seconds at 10 Hz at 32 seconds interval and mounted to intercept the downstream diffraction from the horizontal anvil gap at 1180 mm distance. The detector-beam normal plane was mechanically corrected for tilt and rotation and the detector position for zero-offset and calibrated against SRM660a, using Fit2D (Hammersley *et al.*, 1995), at a monochromatic wavelength of 03757 Å, selected from the emission of a U18 undulator (6.1 mm gap) by a Cinel Si(111) double-crystal monochromator. Data for refinement were collected using a Tl:NaI scintillator counter, with a 0.2 mm pinhole and receiving slits at intermediate distance, which acted as collimators of background scattering coming from the cell assembly. The effective radius of the pseudo-rotation detector arm is 1350 mm. These data were fitted with Jana2006 (Petříček *et al.*, 2006). Collimated beam sizes were 0.5 mm horizontal by 1 mm, or the vertical anvil gap, if smaller. Data for tilt estimations were sequentially refined using GSAS (Larson and Von Dreele, 2000) via EXPGUI (Toby, 2001). In each case the NaFeF₃ sample was finely ground in a corundum mortar and loaded into an h-BN (Goodfellow) capsule, before being included into the 10/4 windowed Cr-doped MgO assembly (Ceramic Substrates). Pressure was generated using the 2000 ton MAVO press in 6/8(x32 mm) mode, with carbide anvils. Pressures were estimated using the equation of state of h-BN described by Le Godec *et al.*, 2000.

Results and Discussion

Structural aspects of the transition sequence

Compression of GdFeO₃-type NaFeF₃ pv (Fig.1a) has been investigated by single-crystal methods (pv, ppv and Sb₂S₃-type) and by large-volume techniques, pv and ppv only, on polycrystalline samples of the same batch. The lower-pressure large-volume data are discussed in greater detail in Bernal *et al.* (2014). It is sufficient to illustrate that further pv diffraction patterns (Fig. 2) taken with the press show rapid evolution up to the transition boundary, as evidenced by the continuous increase in separation of the Bragg reflections corresponding to $d_{(200)}$, $d_{(020)}$ and $d_{(002)}$ (Fig. 2c.). Consequently, the degree of anisotropy increases with pressure, as reflected by the value of the tilting angle that quickly reaches the approximate limiting value (Tateno *et al.*, 2010) of $\phi = 26.9^\circ$ at 9.5 GPa (see also Table 1, from single-crystal refinement, and the powder diffraction results of Bernal *et al.*, 2014).

Through further increase in pressure the ppv NaFeF₃ is formed (Table 2, Fig. 1b), between 9.5 (cold-pressed LVP data) and 13.5 GPa (single-crystals in He). PPv also exhibits significant anisotropy, with the a - and c -lengths at approximately 95% of ambient values and b having been reduced to 92% at 21.2 GPa (cf. $a = 3.13774(4)$ Å, $b = 10.2087(1)$ Å, $c = 7.4587(1)$ Å; Bernal *et al.*, 2014.). Normalisation of the cell parameters, shows that the b -axis stiffens with pressure, such that both b/a and b/c diminish, while c/a increases linearly with pressure, at reduced rates of $b/a:b/c:c/a \approx -6:-3:+1$. With this pattern of stiffening of b relative to the a - c plane, the bulk anisotropy decreases with pressure. The same pattern, though more pronounced, is seen in both calculation and experimental studies of NaMgF₃ (Martin *et al.*, 2006a; Umemoto and Wentzcovitch 2006; Martin *et al.*, 2007). This is a consequence of the location of the highly compressible Na-sites, which align parallel to b and perpendicular to the corrugation of comparatively rigid edge- and corner-sharing FeF₆ octahedra that form stacked sheets in the a - c plane. Any a -axis lattice compression must require bond length changes, particularly as the edge-sharing F1 sites are fixed at $a/2$, the Fe sites are lattice-bound and Na are located at $(0,y, \frac{1}{4})$ (Fig. 1b). Therefore, and illustrated by the single-crystal data, the larger part of the compression comes from displacement of F2, by a combination of rotation (the Fe-F-Fe angle increases to $\sim 150^\circ$) and bond length change (the longer Na-F distance reduces to 2.80 Å at 21.2 GPa, while the shorter Na-F1 distances reduce to 2.16 Å). As compression results in significant bond-length shortening, it is not unexpected that the more rapid b -axis compression will tend to saturate, leading to a consequent reduction in out-of-plane anisotropy with increasing pressure. The ppv form is recoverable in bulk, Bernal *et al.* (2014), though the single-crystal samples do back-transform to pv.

Through continued reduction of atom distances and lattice dimensions the ppv form undergoes a transition, at between 21.2 and 22 GPa (Table 3, Fig. 1c). The occurrence of the new structure was clearly identifiable

through the loss of reflections limited by the C lattice centering condition. Reflections were harvested using a constrained primitive orthorhombic lattice with mmm Laue symmetry. Assessments of the symmetry based on likely subgroups, lattice extinctions and electron density distribution all suggested $Pnma$ being most likely. Refinement of a model based on charge-flipping (Palatinus and Chapuis, 2007), supplemented by additional Fourier difference map cycles, confirmed this adoption (Table 3). Similar lattice metrics ($\pm 20\%$) and c^5 Wyckoff sequence uniquely describes the Sb_2S_3 -type structure, according to the ICSD classification (such a search highlights the In_2O_3 , Ti_2O_3 and U_2S_3 chemistries of Yusa *et al.*, 2008b; Ovsyannikov *et al.*, 2012 and Umemoto and Wentzcovitch, 2011). There is little or no volume change on transition (to the subgroup) and it is completely reversible, with very little hysteresis (~ 1 GPa). This transition affords an increase in coordination over both Na and Fe sites, through the combination of lattice distortion and reduction in site symmetries from fc^2a to c^5 . The topotactic relationship between these two structures is evident from the map of observed electron densities (Fig. 3).

Transition mechanisms

With the aid of the STRUCTURE RELATIONS (Kroumova *et al.*, 2003) code of the Bilbao Crystallographic Server (Aroyo *et al.*, 2006) we have reconstructed the high symmetry form (post-perovskite in $Cmcm$) from the low symmetry structure (Sb_2S_3 -type in $Pnma$). Structures in $Cmcm$ can transform to those in (subgroup) $Pnma$ via a mechanism that would allow for Wyckoff site splitting; so that two $4c_{Pnma}$ sites are formed from one $8f_{Cmcm}$. The correct stoichiometry is retained as other site multiplicities are unaffected, becoming $4c$ sites in $Pnma$ (Fig. 4). Inspection of the site symmetries, using SAM (Tasci *et al.*, 2012), identifies that this transition should be detectable by Raman scattering experiments as a significant increase in both active A_g (4 to 10) and B_g (8 to 20) modes is expected. This general $Cmcm$ to $Pnma$ mechanism is not unusual and a similar group/subgroup description with f - to c -site splitting can be used, for instance, to describe a (back)transformation from $CaTi_2O_4$ - to $CaFe_2O_4$ -type; e.g. in $MgAl_2O_4$ (f^2c^2b to c^7 ; Ono *et al.*, 2008), or, in $FeCr_2O_4$ (Ishii *et al.*, 2014). In $NaFeF_3$, the application of this mechanism, via matrix description (1):

$$\begin{pmatrix} 0 & 1 & 0 & : & 1/4 \\ 0 & 0 & 1 & : & 1/4 \\ 1 & 0 & 0 & : & 1/2 \end{pmatrix} \quad (1)$$

leads, with lattice compression, to the formation of a new Fe-F-Fe liaison between adjacent octahedral ‘sheets’ and an increase in coordination about the Fe site from 6 to 7 (Fig. 1c). This results in shorter, and average, Fe-F distances of 1.98 and 2.08 Å in the Sb_2S_3 -type. Both of these distances are longer than those in the ppv, which is

a consequence of the increase in coordination. This is also coincident with the displacement and reduction in symmetry of the Fe site (Fig. 5), from the inversion centre at $4a$ ($2/m..$) to $4c$ ($.m.$) $Pnma$, along the new bond direction. This effect is visible in the electron density distribution as horizontal displacement from the previously vertically aligned ppv Fe positions (Fig. 3). It is also reflected by the significant reduction of the cell parameter along the former long ppv b dimension. There are strictly no atomic displacements in the structure relative to the short CaIrO₃-type a direction, as the $4c$ lattice sites retain their mirror symmetry. The average displacements of the atomic sites are of the order of 0.4 \AA , including any lattice distortion. The spontaneous lattice strain is 0.07. An illustrated description of atomic displacements necessary, available from the STRUCTURE RELATIONS code, and shown in Figure 5, is also directly comparable to static calculations of the soft mode displacements in unstable ppv NaMgF₃ (Umemoto and Wentzcovitch, 2006).

Taken together, the increase in coordination by cross-linking one Fe site to the 7-fold polyhedra of the adjacent layer is expected to stiffen the structure (and reduce anisotropy). It then follows that this will result in a higher incompressibility and, following the same arguments as those presented by Umemoto and Wentzcovitch (2006) for NaMgF₃, increased acoustic phonon frequencies in NaFeF₃. At the same time the observed higher coordination will directly lead to the expansion of the cell parameters (we determine that a is longer in Sb₂S₃) and continuing Umemoto and Wentzcovitch (2006)'s discussion, lead to softening of the high optical frequencies. This may lead to a positive Clapeyron slope, which is contrary to the expectation from the increased coordination between the CaIrO₃-type and Sb₂S₃-type. In Al₂O₃, this transition line is predicted to be highly vertical (Umemoto and Wentzcovitch, 2008).

Influence on topology

The topotactic relationships between pv and ppv structures is of significant importance in determining the mechanisms possible for the transition to take place (Oganov *et al.*, 2005; Dobson *et al.*, 2013), and, to establish in what way any stratification in the Earth's interior through deformation (or transition mechanism) could give rise to observable seismic anisotropy, particularly at D'' (Oganov *et al.*, 2005; Merkel *et al.*, 2007; Dobson *et al.*, 2013). The intrinsic topotactic relationship between the successive crystalline structures can also be investigated via the comparison of lattice dimensions and orientations in laboratory space (the UB matrices). These are derived directly from the distribution of diffraction peaks of each form in reciprocal space - from the same original crystal which has not otherwise moved. This information is a powerful, inherent, feature of the

single-crystal technique, which is not available to regular powder diffraction analysis. The following UB matrices are obtained, and correspond to unconstrained volumes of 212.8, 205.5 and 186.36 Å³, for the pv, ppv and Sb₂S₃ structures:

$$\begin{pmatrix} -0.07867 & -0.01255 & -0.00828 \\ 0.00615 & -0.06473 & 0.02701 \\ -0.01713 & 0.03440 & 0.04780 \end{pmatrix} \quad \text{pv in } Pbnm \text{ setting} \quad (2)$$

$$\begin{pmatrix} -0.01758 & -0.04270 & -0.00779 \\ 0.12001 & -0.00740 & 0.02658 \\ -0.06571 & -0.00286 & 0.05054 \end{pmatrix} \quad \text{post - perovskite in } Cmcmm \quad (3)$$

$$\begin{pmatrix} -0.06656 & -0.00705 & -0.04533 \\ -0.11097 & 0.02402 & 0.01969 \\ 0.04699 & 0.04654 & -0.01722 \end{pmatrix} \quad \text{Sb}_2\text{S}_3 \text{ type in } bac \text{ setting } (Pmnb) \text{ of spacegroup 62} \quad (4)$$

Comparison of the spatial orientation information contained within the UB construction shows that the pv, the ppv and the Sb₂S₃-type structures share a common axis, and that the common diagonal lattice plane of the two high pressure phases is normal to a principle lattice direction of the original pv (see Fig. 6). This results in (001)_{pv} *Pbnm* || (001)_{ppv} || (010)_{Sb₂S₃} *Pmnb* and, for example, the (100)_{pv} is orthogonal to the (001) and (-110) of the ppv and (010) and (-110) of the Sb₂S₃ structure (Fig. 6). Angles calculated using TWIN CALCULATOR (of R.J. Angel) from the UB matrices vary by up to ~1° from ideal values, due to significant pressure-induced differences in the lattice parameters which form part of the UB matrix construction. The angle calculated from the UBs between the (100)_{pv} and (010)_{ppv} is equal to 16.49° (angle *a*, Fig 6a.), entirely consistent with previous observations from TEM measurements, geometrical reconstruction and the predictions of Oganov *et al.*, (2005) and Dobson *et al.*, (2013). An equivalent angle between the (010)_{pv} and (100)_{Sb₂S₃} is 19.77° (angle *b*, Fig 6b.), again including a significant proportion of lattice compression. Figure 6c highlights these relationships between the reciprocal lattices of pv, ppv and Sb₂S₃-type structures, shown here along *c** of the pv (*Pbnm*), ppv (*Cmcmm*) lattices and *b** (*Pmnb*) Sb₂S₃, with the green line along to the <010> direction of the pv (*Pbnm*) lattice. It is natural that twinning is expected, with the high degree of coincident lattice points and the high symmetry between principle lattice planes and directions noted above, and indeed twinning is observed.

Related structures and chemistries

Given that the high pressure structures in the Sc₂O₃, In₂O₃ and Y₂O₃ species are proposed to share the α-Gd₂S₃-type structure (Yusa *et al.*, 2008b; Yusa *et al.*, 2009; Umamoto and Wentzcovitch, 2011; Xu *et al.*, 2014), we have also investigated the possibility of generating further twins of α-Gd₂S₃-type lattices from ppv lattice points. One possible mechanism that will transform the *Cmcmm* lattice of ppv NaFeF₃, via *cab* and origin shift of (3/4|40)

to $Pnma$, generates pairs of oP lattices of 5.597(2), 3.016(2) and 11.171(9) Å at 90° to each other about their common c^* (Fig. 6d). These dimensions are consistent with those detailed elsewhere for oxide structures (e.g. Yusa *et al.*, 2008b; Yusa *et al.*, 2009; Umemoto and Wentzcovitch, 2011). We tested this against the data and, while symmetry was estimated as $Pnma$ (*i.e.*, a lattice metric and symmetry as per the α -Gd₂S₃-type), no successful solution or refinement was retained. We nonetheless infer that any volumetric difference between possible competing α -Gd₂S₃-types and Sb₂S₃-types is minimal given the common lattice direction and the $\sqrt{2}$ relationships between the other dimensions (resulting in approximate Sb₂S₃-equivalent lattice of $a = 3.016$ Å, $b = 7.900$ Å, $c = 7.914$ Å, or less than 1% from that in the UB matrix above, determined from our observed lattice points). The spontaneous strain for the notional ppv to α -Gd₂S₃ transition is estimated at ~ 0.1 and the average distance that paired atoms must move during the transformation is roughly 1.5 Å, nearly two and three times that of the Sb₂S₃-type description, respectively. Consequently, a notional α -Gd₂S₃-type derivative of the ppv structure has a compatibility, Δ , of 1.734 compared to our solution in Sb₂S₃, with a more favourable $\Delta = 0.473$. Similar values are estimated for the transition pv to α -Gd₂S₃-type; where the transformation (identity, plus origin shift of $\frac{1}{2} 0 \frac{1}{2}$), requires significant movement of F and Fe to fulfill our expectation of higher coordinated Fe polyhedra (to 1.6 Å, with average of 1.08 Å) and has a compatibility of $\Delta = 2.505$. It can, nonetheless, be expected that in some systems these structures may be competitive; *e.g.* in Dy₂S₃, which is described at ambient conditions in Ho₂S₃-, α -Gd₂S₃- and Sb₂S₃-types (Meetsma *et al.*, 1991). The Ho₂S₃-type is equivalent to the intermediate CaRhO₃ phase between perovskite and post-perovskite, Shirako *et al.* (2012a), and Y₂S₃ transforms from Ho₂S₃-type to Sb₂S₃-type, at high pressure (Range and Leeb, 1975). The predominance of the α -Gd₂S₃ structure in A_2X_3 stoichiometries and the twinning expected by Fig. 6d, suggests that for ABX_3 structures to crystallize in this type, a significant reduction in contrasting cation sizes must be achieved, but not at the expense of limiting oxygen-packing in this higher (than CaIrO₃) coordinated structure. It is not necessary (by site symmetry) to invoke $B = A$ stoichiometries or site-disorder (*i.e.*, AAX_3 or $(A,B)_2X_3$) to crystallize as α -Gd₂S₃-type (with c^5 symmetry) as all atom sites are symmetrically inequivalent. It does, however, make the suggestion more realisable. Alternatively, it perhaps indicates why only A_2X_3 stoichiometries have been yet determined to undergo the CaIrO₃- to α -Gd₂S₃-type transition, as the twinning involved requires that the orthogonal twins produced have coincident anion sites. Therefore, while the cation coordination is different in both sites in the CaIrO₃-type A_2X_3 compounds, for the α -Gd₂S₃-type to subsequently crystallise by a mechanism that generates orthogonal twins the cation-anion distances must have the *potential* to match in both c site anion polyhedra. This is most simply achieved in A_2X_3 stoichiometries, where nil contrast the ionic radii would allow

this. As the Sb_2S_3 - and the $\alpha\text{-Gd}_2\text{S}_3$ -type structures are so evidently closely-related but appear to require this distinction, the application of further pressure (and consequent reduction of differences in unlike ionic radii) may lead to an Sb_2S_3 -to- $\alpha\text{-Gd}_2\text{S}_3$ -type transition at higher loads in ABX_3 systems, as per that calculated for Al_2O_3 , Umemoto and Wentzcovitch (2008), or predicted as semi-ubiquitous in compressed perovskites and sesquioxides (Xu *et al.*, 2014). Further investigations to confirm the systematic appearance of $\alpha\text{-Gd}_2\text{S}_3$ and, as dimorphism is known, Sb_2S_3 -type, should be undertaken following the outcome of recent work.

Extending the scheme

Calculations have predicted another probable higher pressure phase in the NaMgF_3 system (Umemoto and Wentzcovitch, 2006). It has been proposed in symmetry $P6_3/mmc$, with NiAs stacking of cations and Na and F filling an IrAl_3 -like sublattice, with *fdba* Wyckoff symmetry. This proposed model is identical to Nodari *et al* (1988)'s InFeO_3 (after $\text{Na} \rightarrow \text{Fe}$ and $\text{Fe} \rightarrow \text{In}$) and the InMnO_3 described by Giaquinta and zur Hoye (1992). Both are also equivalents to the Be_3N_2 structure-type after an origin shift of $(0\ 0\ \frac{1}{2})$ is applied (to transform *fdba* \leftrightarrow *fdca*). Other structures classified as Be_3N_2 include Shannon and Prewitt (1968)'s GaInO_3 (whose components and solid-solutions are also known in bixbyite and corundum structures, both ante-perovskites) and YAlO_3 and YMnO_3 , both with known GdFeO_3 -type polymorphs (Bertaut and Mareschal, 1963; Gibbs *et al.*, 2011). As this probable higher pressure Be_3N_2 - and the CaIrO_3 -type structures share a common subgroup in $Pnma$, it is of value to determine the common transformations between these structures, to test if there is a common $Pnma$ subgroup that coincides with the Sb_2S_3 -type, also $Pnma$. The proposed Be_3N_2 structure transforms, using TRANPATH (Capillas, *et al.*, 2007), from $P6_3/mmc$, with an index of 6, via matrix (5), to $Pnma$ with the F on $4f$ site-splitting to c^5 . The transformation from ppv to the common subgroup, in $Pnma$, is via matrix (6) with index 2, which in splits the $8f$ F sites to give a near-identical c^5 subgroup structure (Fig. 7).

$$\begin{pmatrix} 0 & 1 & 1 & : & 1/2 \\ 0 & 0 & 2 & : & 1/2 \\ 1 & 0 & 0 & : & 0 \end{pmatrix} \quad P6_3/mmc \rightarrow Pnma \quad (5)$$

$$\begin{pmatrix} 0 & 1 & 0 & : & 3/4 \\ 0 & 0 & 1 & : & 3/4 \\ 1 & 0 & 0 & : & 1/2 \end{pmatrix} \quad Cmc \rightarrow Pnma \quad (6)$$

It is quite apparent that this transition path between our experimentally determined ppv structure and our assignment of the Be_3N_2 -type classification to the $P6_3/mmc$ description of Umemoto and Wentzcovitch (2006) results in the closely-related subgroups S1 and S2 (Fig. 7). These subgroups bear strong resemblance to our

experimentally derived Sb_2S_3 -type definition for post-ppv NaFeF_3 . This reinforces the higher pressure description proposed for NaMgF_3 , Umemoto and Wentzcovitch (2006), even in spite of the substantial lattice compression and distortion required for this transition to occur. We estimate, from symmetry and bond length considerations, that this transformation may occur at about 55 % total compression, per formula unit, from ambient (or, $a \sim 3.34 \text{ \AA}$, $c \sim 6.25 \text{ \AA}$, $Z = 2$).

Discussion

The use of high-pressure X-ray techniques has allowed the study of a series of phase transitions in NaFeF_3 , leading to a detailed in-situ structural characterisation of pv, ppv and Sb_2S_3 -type post-post-perovskite phases. This Sb_2S_3 -type post-ppv structure (a continuously variable structure-type that can be subcategorised into Th_2S_3 -, Sb_2S_3 - and U_2S_3 -types, depending on lattice metrics) has been calculated and observed as high density form of Al_2O_3 and Ti_2O_3 (Umemoto and Wentzcovitch, 2008; Ovsyannikov, 2011). Alternatively, in other A_2X_3 systems (e.g. In_2O_3 , Sc_2O_3 ; Yusa *et al.*, 2008*a*; 2008*b*), the α - Gd_2S_3 -type is preferred and a new systematic was proposed for high density C -type sesquioxides based on this; and further differentiated, in appropriate systems, by the effect of d -electrons on related observations (Umemoto and Wentzcovitch, 2011). The Sb_2S_3 -type structure was also proposed as a possible model for a post-ppv form in NaMgF_3 (Umemoto and Wentzcovitch, 2006). More recently, a structure that we interpret as α - Gd_2S_3 -type is calculated as semi-ubiquitous across wide ranges of perovskite and sesquioxide series (Xu *et al.*, 2014). None of these propositions have been observed in *any* oxide perovskite, fluoride perovskite or as a post- CaIrO_3 -type sesquioxide. The lack of any such observation and the interpretation, particularly, of soft phonon behaviour in NaMgF_3 (Umemoto and Wentzcovitch, 2006, not the case for the identical transition in Al_2O_3 ; Umemoto and Wentzcovitch, 2011) has lead to the suggestion that the ppv-to- Sb_2S_3 transition is metastable with respect to decomposition to NaF and cotunnite-type MgF_2 (Umemoto and Wentzcovitch, 2006). However, according to those calculations and the conclusions therein, the enthalpy difference between the dissociation is sufficiently low to possibly allow overstepping decomposition (by as little as 2.5 GPa in NaMgF_3) and observing the Sb_2S_3 -type structure directly. Similarly, the expected small energetic differences between competitive fluoride perovskites are apparently sufficient to allow for exploration of the complete high pressure, temperature phase diagram of pv and ppv forms of NaNiF_3 without any impediment from decomposition, which plagues the same exploration in, e.g., NaCoF_3 (Yusa *et al.*, 2012). Once the transition occurs further decomposition can be precluded, as suggested by the phase diagram of NaMgF_3 , Umemoto and Wentzcovitch (2006), and the highly vertical transition expected for CaIrO_3 -to- Sb_2S_3 -type in

Al_2O_3 (Umemoto and Wentzcovitch, 2008). Such advantageous use of small energetic differences may, in the future, permit the study of the higher pressure transition to Be_3N_2 -type at >200 GPa, if, at increased density, packing and polyhedral volumes are commensurate with predictions. While it is evident that Al_2O_3 has no such decomposition, the ppv-to- Sb_2S_3 and Sb_2S_3 -to- α - Gd_2S_3 transitions are expected at pressures exceeding 370 GPa, Umemoto and Wentzcovitch (2008), and are also, consequently, beyond all conventional static experimentation.

Our description of pv and ppv structures, is also further evidence of the continued development of inherited texture during the transformation process from pv to ppv, as previously discussed elsewhere (Oganov *et al.*, 2005; Merkel *et al.*, 2007; Dobson *et al.*, 2013). This effect is extended into the Sb_2S_3 -type structure, and can be pushed further using our descriptions of the transformations to Be_2N_3 - or α - Gd_2S_3 -types to assess the structure-property relationships over a wider range of proposed A_2X_3 - ABX_3 topologies. Regarding the ppv-to- Sb_2S_3 transition; as the crystallographic orientations are preserved, the low values for both atomic displacement and spontaneous strain, coupled with a more equant Sb_2S_3 -type lattice, imply that anisotropy will be maintained, at a reduced level. Studies that are capable of extracting the elastic constants of these materials can elucidate this further and allow for derivation of rheological properties while making use of the relative geometries, and associated texture development with preferred orientation of these subsequent crystal structures.

One other aspect of the topotactic relationships is that the CaIrO_3 -type forms part of a homologous series of structure types that includes spinels, post-spinels and oxides (Goutenoire *et al.*, 1995; Bertastegui *et al.*, 2004; Guignard and Crichton, 2014) and these have been demonstrated to be capable of forming intergrowths with other members of the series, and with rocksalt structures (Kusinsky *et al.*, 1994). The importance of such an assemblage is obvious given that $(\text{Mg,Fe})_2\text{SiO}_4$ will decompose towards pv + rocksalt prior to the transition to ppv. The other salient point that arises from inspection of this series is that all more complex forms *tend* towards topologies based on decoration of a sesquioxide- or ppv-like structural basis. Upon increasing coordination, and forming the Sb_2S_3 -type structure, these A_2X_3 and ABX_3 can then continue in an analogous manner, with only a minor effect on the solubility or capacity to be intergrown, within this series of stoichiometries. This generalism may indeed extend further than previously supposed, and beyond structures limited by 6-fold coordinated cations, in line with arguments for other sesquioxides (Umemoto and Wentzcovitch, 2008; Xu *et al.* 2014) and given the evident parallels between the Be_3N_2 structure (most easily viewed along the $\langle 110 \rangle$ direction; Fig. 2c of Umemoto and Wentzcovitch, 2006) and, e.g. Figs. 3 and 5 of Guignard and Crichton (2014). Similar

comments are made regarding possible intermixing of ppv and PPV-II types elsewhere Cohen and Lin (2014) and could be assumed, given the proposed twin relationships between CaIrO_3 -, Sb_2S_3 - and $\alpha\text{-Gd}_2\text{S}_3$ -types.

Conclusions

We provide a full in-situ structural description for all observed structures in the NaFeF_3 system up to a post-post-perovskite phase. This Sb_2S_3 -type phase is, to the best we can determine via single-crystal methods at RT, stable. Whether the occurrence of the Sb_2S_3 -type structure in the fluoride system truly reflects silicate oxide systems is beyond all static experimentation; as that transition is expected at 1.6 TPa (Umemoto *et al.*, 2006). Nonetheless, the topotactic relationship between this and the lower density structures is maintained and can be extended, using our crystallographic orientations (UB or transformation matrices) combined with calculated tensor information to describe the rheological response of the observed Sb_2S_3 structure. Our experimental evidence is aligned with the results of calculations regarding the mechanism for such a transition (Umemoto and Wentzcovitch, 2006). Similar transformation matrices provide for transitions to and from the $\alpha\text{-Gd}_2\text{S}_3$ and Be_3N_2 -type models, which permit further such investigation and modeling, built upon a strict crystallographic basis, particularly in sesquioxide and double-sesquioxide perovskites, where these assemblages are more likely. The observation of the Sb_2S_3 and our description of a possible mechanism, via orthogonal twinning of a post- CaIrO_3 -type to form the $\alpha\text{-Gd}_2\text{S}_3$ structure, provides a link between the generalized transition sequences of A_2X_3 and ABX_3 structures that have been observed to crystallize in the ppv structure under extreme conditions. With the full suite of matrix and twinning descriptions included, we promote that the full range of pv, ppv, Sb_2S_3 , $\alpha\text{-Gd}_2\text{S}_3$ and Be_3N_2 -type structures can be then reproduced from any other starting point; given that the perovskite to $\text{Rh}_2\text{O}_3(\text{II})$ relationship is known already (*e.g.* Shim *et al.*, 2009). We also offer reasoning for why the $\alpha\text{-Gd}_2\text{S}_3$ structure may be preferred over the Sb_2S_3 -type in certain A_2X_3 compounds. Finally, given that CaIrO_3 -, Sb_2S_3 - and $\alpha\text{-Gd}_2\text{S}_3$ -types can all be related through twinning and matrix descriptions that involve little or no volume change, we expect that any constraints from the structures themselves on the solubility and continued transfer of elements upon transition to the post-post-perovskite forms to be minimal. Any transition to a higher pressure phase may preclude any retrograde transformation at higher temperatures, and/or decomposition to its components. The derivation of a common subgroup between our observed ppv and Be_3N_2 -type NaFeF_3 that closely matches our observed data for Sb_2S_3 provides further justification for the use of this structural sequence in modeling higher density environments in any related system. Indeed, the only catalogued other Be_3N_2 -type oxide structures are also known in corundum-, perovskite- and bixbyite-type structures, all commonly occurring

as ante-ppv or ante- α -Gd₂S₃ structures in A₂X₃ systems. These descriptions can be generalized for further exploration, by experiment or otherwise, for both ABX₃ and A₂X₃ systems, and extended using the inherited directional properties that come with these UB descriptions and further tested against expected, e.g. anisotropic signatures or inherited textures.

The search for similar experimental descriptions of the higher pressure transitions of perovskites towards possible α -Gd₂S₃- and/or Be₃N₂-types is, at in excess of 210 GPa in the nearest calculated, NaMgF₃ chemistry, Umemoto and Wentzcovitch (2006), beyond current experimental technology in single-crystal measurements. However, as we highlight in this work, the use of analogous compounds is of great utility in experimental exploration of the topology of generalized phase diagrams and transitions. Suggestions, from this work, for such studies are to use those compounds, of ABX₃ stoichiometry, with components found in A₂X₃ systems i.e. double sesquioxides where ABX₃ = A³⁺₂B³⁺₂X₆. In other words, these high density structures, some of which may be precluded in silicates by decomposition, are certainly possible in other sesquioxide-based compounds of an analogous ABX₃ stoichiometry. This then clearly generates a further point of alignment between sesquioxide- and perovskite-like systems and lends further weight to the proposition that ‘multi-megabar crystal chemistry of planet-forming minerals might be related to the rare-earth oxides’ (Umemoto and Wentzcovitch, 2008). This general comment has been put to the test in the recent calculations of Xu *et al.* (2014), and now widens the scope with the experimental evidence here presented for the influence of sesquioxide type-structures in ultrahigh pressure perovskite compositions.

Acknowledgements

The ESRF is thanked for allocation of in-house beamtime at ID06LVP and ID09A. The studentship of FLB was supported by NFR project 214260 of the Norges Forskningsråd to SM.

References

Aroyo, M. I., Perez-Mato, J. M., Capillas, C., Kroumova, E., Ivantchev, S., Madariaga, G., Kirov, A. and Wondratschek, H. (2006) Bilbao Crystallographic Server: I. Databases and crystallographic computing programs. *Zeitschrift für Kristallographie*. **221**, 15-27.

- Berastegui, P., Eriksson, S., Hull, S., García García, F. J., and Eriksen, J. (2004) Synthesis and crystal structure of the alkaline-earth thallates $M_n\text{Tl}_2\text{O}_{3+n}$ ($M = \text{Ca}, \text{Sr}$). *Solid State Science*, **6**, 433-441.
- Bernal, F. L., Yuzenko, K., Sottmann, J., Drathen, C., Guignard, J., Løvvik, O., Crichton, W. A. and Margadonna, S. (2014) Perovskite to postperovskite transition in NaFeF_3 . *Inorganic Chemistry*, **53**, 12205.
- Bertaut, E. F. and Mareschal, J. (1963) Un nouveau type de structure hexagonale AlTO_3 ($T = \text{Y}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$). *Comptes Rendu Hebdomadaire des Seances de l'Academie des Sciences*, **257**, 867-870.
- Benner, G. and Hoppe, R. (1990) Über fluoride des zweiwertigen Eisens: zum Aufbau von NaFeF_3 . *Journal of Fluorine Chemistry*, **46**, 283-295.
- Caracas, R. and Cohen, R. E. (2007) Ppv phase in selected sesquioxides from density-functional calculations. *Physical Review B* **76**, 184101.
- Capillas, S., Perez-Mato, J.M. and Aroyo, M. I. (2007) Maximal symmetry transition paths for reconstructive phase transitions. *Journal of Physics: Condensed Matter*, **19**, 275203.
- Cohen, R. E., and Lin, Y. (2014) Prediction of a potential high-pressure structure of FeSiO_3 . *Physical Review B*, **90**, 140102R.
- Dobson, D. P., Hunt, S. A., Lindsay-Scott, A. and Wood, I. G. (2011) Towards better analogues for MgSiO_3 ppv: NaCoF_3 and NaNiF_3 , two new recoverable fluoride ppvs. *Physics of the Earth and Planetary Interiors*, **189**, 171-175.
- Dobson, D.P., McCormack, R., Hunt, S. A., Ammann, M. W., Weidner, D., Li, L. and Wang, L. (2012) The relative strength of perovskite and post-perovskite NaCoF_3 . *Mineralogical Magazine*, **76**, 925-932.
- Dobson, D. P., Miyajima, N., Nestola, F., Alvaro, M., Casati, N., Liebske, C., Wood, I. G. and Walker, A. M. (2013) Strong inheritance of texture between perovskite and ppv in the D'' layer. *Nature Geoscience*, **6**, 575-578.
- Giaquinta, D. M. and zur Hoyer, H. C. (1992) A new transition metal oxide with an unusual ABO_3 structure. *Journal of the American Chemical Society*, **114**, 10952-10953.
- Gibbs, A. S., Knight, K. S. and Lightfoot, P. (2011) High-temperature phase transitions of hexagonal YMnO_3 . *Physical Review B*, **83**, 094111.
- Goutenoire, F., Caignaert, V., Hervieu, M., Michel, C. and Raveau, B. (1995) Chemical twinning of the rock salt structure: CaTl_2O_4 and $\text{Ca}_2\text{Tl}_2\text{O}_5$, the first two members of the new series $\text{Ca}_n\text{Tl}_2\text{O}_{n+3}$. *Journal of Solid State Chemistry*, **114**, 428-434.
- Grocholski, B., Shim, S. H. and Prakapenka, V. B. (2010) Stability of the MgSiO_3 analog NaMgF_3 and its implication for mantle structure in super-Earths. *Geophysical Research Letters*, **37**, L14204.
- Guignard, J. and Crichton, W. A. (2014) Synthesis and recovery of bulk Fe_4O_5 from magnetite, Fe_3O_4 . A member of a self-similar series of structures for the lower mantle and transition zone. *Mineralogical Magazine*, **78**, 361-371.
- Hammersley, A. P., Svensson, S. O., Thompson, A., Graafsma, H., Kvick, Å and Moy, J. P. (1995) Calibration and correction of distortions in 2D detector systems. *Review of Scientific Instruments*, **66**, 2729-2733.
- Hunt, S. A., Lindsay-Scott, A., Wood, I. G., Ammann, M. W. and Taniguchi, T. (2013) The P-V-T equation of state of CaPtO_3 ppv. *Physics and Chemistry Minerals*, **40**, 73-80.

- Hustoft, J., Catali, K., Shim, S. H., Kubo, A., Prakapenka, V. and Kunz, M. (2008) Equation of state of NaMgF_3 postperovskite: Implication for the seismic velocity changes in the D " region. *Geophysical Research Letters*, **35**, L10309.
- Ishii, T., Kojitani, H., Tsukamoto, S., Fujino, K., Mori, D., Inaguma, Y., Tsujino, N., Yoshino, T., Yamazaki, D., Higo, Y., Funakoshi, K. and Akaogi, M. (2014) High-pressure phase transitions in FeCr_2O_4 and structure analysis of new post-spinel FeCr_2O_4 and $\text{Fe}_2\text{Cr}_2\text{O}_5$ phases with meteoritical and petrological implications. *American Mineralogist*, **99**, 1788-1797.
- Kroumova, E., Aroyo, M.I., Perez-Mato, J.M., Kirov, A., Capillas, C., Irantchev, S. and Wondratschek, H. (2003) Bilbao Crystallographic Server: Useful databases and tools for phase-transition studies. *Phase Transitions*, **76**, 155-170.
- Kusinsky, J., Jasienska, S. and Monty, C. (1994) Microstructural and microanalytical examinations of partially reduced doped wustites. *Solid State Ionics*, **68**, 185-192.
- Larson, A. C. and Von Dreele, R. B. General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748 (2000).
- Le Godec, Y., Martinez-Garcia, D., Mezouar, M., Syfosse, G., Itié, J.P., and Besson, J.M. (2000) Thermoelastic behavior of hexagonal graphite-like boron nitride. *High Pressure Research*, **17**, 35-46.
- Liu, L. G. and Bassett, W. A. (1986) Elements, Oxides, Silicates: High-Pressure Phases with Implications for the Earth's Interior. Oxford University Press, New York.
- Meetsma, A., Wiegers, G. A., Haange, R. J., de Boer, J. L. and Boom, G. (1991) Structure of Two Modifications of Dysprosium Sesquisulfide, Dy_2S_3 . *Acta Crystallographica C*, **47**, 2287-2291.
- Martin, C. D., Crichton, W. A., Liu, H. Z., Prakapenka, V., Chen, J. H. and Parise, J. B. (2006a) Rietveld structure refinement of perovskite and ppv phases of NaMgF_3 (Neighborite) at high pressures. *American Mineralogist*, **91**, 1703 -1706.
- Martin, C. D., Crichton, W. A., Liu, H. Z., Prakapenka, V. B., Chen, J. H. and Parise, J. B. (2006b) Phase transitions and compressibility of NaMgF_3 (Neighborite) in perovskite- and ppv-related structures. *Geophysical Research Letters*, **33**, L11305.
- Martin, C. D., Chapman, K. W., Chupas, P. J., Prakapenka, V., Lee, P. L., Shastri, S. D. and Parise, J. B. (2007) Compression, thermal expansion, structure and instability of CaIrO_3 , the structure model of MgSiO_3 ppv. *American Mineralogist*, **92**, 1048-1053.
- Merkel, S. McNamara, A.K., Kubo, A., Speziale, S., Miyagi, L., Meng, Y., Duffy, T. and Wenk, H. R. (2007) Deformation of (Mg, Fe) SiO_3 ppv and D'' anisotropy. *Science*, **316**, 1729-1732.
- Merlini, M. and Hanfland, M. (2013) Single-crystal diffraction at megabar conditions by synchrotron radiation. *High Pressure Research*, **33**, 511-522.
- Murakami, M., Hirose, K., Kawamora, K., Sata, N., and Ohishi, Y. (2004) Post perovskite phase transition in MgSiO_3 . *Science*, **304**, 855-858.
- Momma, K. and F. Izumi, F. (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, **44**, 1272-1276.
- Nodari, I., Alebouyeh, A., Brice, J. F., Gerardin, R. and Evrard, O. (1998) Caracterisation de nouveaux ferrites d'indium: $\text{In}_2\text{Fe}_4\text{O}_9$ et InFeO_3 . *Materials Research Bulletin*, **23**, 1039-1044.

- Oganov, A. R. and Ono, S. (2004) Theoretical and experimental evidence for a post-perovskite phase of MgSiO₃ in Earth's D'' layer. *Nature*, **430**, 445-448.
- Oganov, A. R. and Ono, S. (2005) The high-pressure phase of alumina and implications for Earth's D'' layer. *Proceedings of the National Academy of Science of the USA*, **102**, 10828-10831.
- Ono, S., Brodholt, J.P., Price, G.D. (2008) First-principles simulation of high-pressure polymorphs in MgAl₂O₄. *Physics and Chemistry of Minerals*, **35**, 381-386.
- Oganov, A. R., Martonak, R., Laio, A., Raiteri, P. and Parrinello, M. (2005) Anisotropy of Earth's D'' layer and stacking faults in the MgSiO₃ ppv phase. *Nature*, **438**, 1142-1144.
- Ovsyannikov, S. V., Xiang, X., Karkin, A. E., Shchennikov, V. V. and Manthilake, G. (2012) Pressure-temperature phase diagram of Ti₂O₃ and physical properties in the golden Th₂S₃-type phase. *Physical Review B*, **86**, 024106.
- Palatinus, L. and Chapuis, G. (2007) Superflip - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *Journal of Applied Crystallography*, **40**, 786-790.
- Petricek, V., Dusek, M. and Palatinus, L. (2006) Jana2006. The crystallographic computing system. Institute of Physics, Praha, Czech Republic.
- Range, K. J. and Leeb, R. (1975) High-pressure modifications of rare-earth sulphides Ln₂S₃ (Ln = Lu-Ho, Y) with U₂S₃-structure. *Zeitschrift für Naturforschung B*, **30**, 889-895.
- Shannon, R. D. and Prewitt, C. T. (1968) Synthesis and structure of phases in the In₂O₃-Ga₂O₃ system. *Journal of Inorganic and Nuclear Chemistry*, **30**, 1389-1398.
- Shim, S. H., Bengtson, A., Morgan, D., Sturhahn, W., Catalli, K., Zhao, J., Lerche, M. and Prakapenka, V. (2009) Electronic and magnetic structures of the postperovskite-type Fe₂O₃ and implications for planetary magnetic records and deep interiors. *Proceedings of the National Academy of Science of the USA*, **106**, 5508-5512.
- Shirako, Y., Kojitani, H., Oganov, A. R., Fujino, K., Miura, H., Mori, D., Inaguma, Y., Yamaura, K. and Akaogi, M. (2012a) Crystal structure of CaRhO₃ polymorph: High-pressure intermediate phase between perovskite and post-perovskite. *American Mineralogist*, **97**, 159-163.
- Shirako, Y., Shi, Y. G., Aimi, A., Mori, D., Kojitani, H., Yamaura, K., Inaguma, Y. and Akaogi, M. (2012b) High-pressure stability relations, crystal structures, and physical properties of perovskite and ppv of NaNiF₃. *Journal of Solid State Chemistry*, **191**, 167-174.
- Tasci, E. S., de la Flor, G., Orobenyo, C., Capillas, C., Perez-Mato, J. M. and Aroyo, M. I. (2012) An introduction to the tools hosted in the Bilbao Crystallographic Server *EPJ Web of Conference Series* 21:00009 doi:10.1051/epjconf/20122200009 .
- Tateno, S., Hirose, K., Sata, N., and Ohisi, Y. (2010) Distortion of CaSnO₃ perovskite under pressure and the quenchable post-perovskite phase as a low-pressure analogue to MgSiO₃. *Physics of Earth and Planetary Interiors*, **181**, 54-59.
- Toby, B.H. (2001) EXPGUI, a graphical user interface for GSAS. *Journal of Applied Crystallography*, **34**, 210-213 (2001).
- Tsuchiya, T., Tsuchiya, J., Umemoto, K. and Wentzcovitch, R. M. (2004) Phase transition in MgSiO₃ perovskite in the earth's lower mantle. *Earth and Planetary Science Letters*, **224**, 241.

- Tsuchiya, T., Yusa, H., and Tsuchiya, J. (2007) Post-Rh₂O₃(II) transition and the high pressure-temperature phase diagram of Gallia: A first-principles and x-ray diffraction study. *Physical Review B*, **76**, 174108.
- Umemoto, K. and Wentzcovitch, R. M. (2006) Potential ultrahigh pressure polymorphs of ABX₃-type compounds. *Physical Review B* **74**, 224105.
- Umemoto, K., Wentzcovitch, R. M. and Allen, P. B. (2006) Dissociation of MgSiO₃ in the cores of gas giants and terrestrial exoplanets. *Science*, **311**, 983-986.
- Umemoto, K. and Wentzcovitch, R. M. (2008) Prediction of an U₂S₃-type polymorph of Al₂O₃ at 3.7 Mbar. *Proceedings of the National Academy of Science of the USA*, **105**, 6526-6530.
- Umemoto, K. and Wentzcovitch, R. M. (2011) Effect of the d electrons on the phase transitions in transition-metal sesquioxides. *Physics and Chemistry of Minerals*, **38**, 387-395.
- Xu, C., Xu, B., Yang, Y., Dong, H., Oganov, A. R., Wang, S., Duan, W., Gu, B. and Bellaiche, L. (2014) Prediction of a stable post-post-perovskite structure from first principles. *Physical Review B*, **91**, 020101.
- Yusa, H., Tsuchiya, T., Sata, N. and Ohishi, Y. (2008a) Rh₂O₃(II)-type structures in Ga₂O₃ and In₂O₃ under high pressure: Experiment and theory. *Physical Review B*, **77**, 064107.
- Yusa, H., Tsuchiya, T., Tsuchiya, J., Sata, N. and Ohishi, Y. (2008b) α -Gd₂S₃-type structure in In₂O₃: Experiments and theoretical confirmation of a high-pressure polymorph in sesquioxide *Physical Review B*, **78**, 092107.
- Yusa, H., Tsuchiya, T., Sata, N. and Ohishi, Y. (2009) High-pressure phase transition to the Gd₂S₃ structure in Sc₂O₃: A new trend in dense structures in sesquioxides. *Inorganic Chemistry*, **48**, 7537-7543.
- Yusa, H., Shirako, Y., Akaogi, M., Kojitani, H., Hirao, N., Oishi, Y. and Kikegawa, T. (2012) Transitions in NaNiF₃ and NaCoF₃ and Disproportionation of NaCoF₃ Postperovskite under High Pressure and High Temperature. *Inorganic Chemistry*, **51**, 6559-6566.
- Zhang, L., Meng, Y., Yang, W., Wang, L., Mao, W. L., Zheng, Q.-S., Jeong, J. S., Wagner, A. J., Mkhoyan, K. A., Liu, W., Xu, R. and Mao, H.-k (2014) Disproportionation of (Mg,Fe)SiO₃ perovskite in Earth's deep lower mantle. *Science* **344**, 877-882.

TABLE 1. Results of single-crystal refinement from data collected at 9.5 GPa, GdFeO₃-type NaFeF₃:

Compound	NaFeF ₃ -I						
Space group	<i>P n m a</i>	62					
Lattice parameters, Å							
	<i>a</i>	<i>b</i>	<i>c</i>				
	5.572 (6)	7.4607 (8)	5.119 (4)				
Unit-cell volume							
	212.802 Å ³						
Atom	X	Y	Z	Occ	U Å ²	Site	Sym
Na	0.0760 (6)	0.25	-0.024 (3)	1	0.0171 (9)	4c	.m.
Fe	0.5	0.0	0.0	1	0.0120 (4)	4b	-1
F1	0.4451 (9)	0.25	0.135 (3)	1	0.0158 (16)	4c	.m.
F2	0.3092 (7)	0.0615 (7)	-0.328 (2)	1	0.0189 (12)	8d	1
Selected distances							
2x	Fe1-F2	1.989 (7) Å	Na1-F1	2.121 (18) Å	Na1-F2	2.183 (8) Å	
2x	Fe1-F1	2.013 (5) Å	Na1-F1	2.213 (10) Å	Na1-F2	2.465 (11) Å	
2x	Fe1-F2	2.038 (9) Å					

Table footnote: 36% completeness to 0.61 Å, 50% to 0.8 Å. Rint 5.7 % and 5.2% over the same ranges, from 465/225 and 347/145 measured/unique reflections. Refined to Robs = 3.67%, wRobs = 4.31%, wRall 4.31%.

TABLE 2. Single-crystal refinement results from NaFeF₃ ppv, from data taken at 12.0 GPa on decompression, after back-transformation from Sb₂S₃-type NaFeF₃.

Compound	NaFeF ₃ -II						
Space group	<i>C m c m</i>	63					
Lattice parameters, Å							
	<i>a</i>	<i>b</i>	<i>c</i>				
	2.9731 (14)	9.453 (12)	7.120 (3)				
Unit-cell volume		200.106 Å ³					
Atom	X	Y	Z	Occ	U Å ²	Site	Sym
Na	0.0	0.229 (7)	0.25	1	0.003 (5)	4c	2/m..
Fe	0.0	0.0	0.0	1	0.019 (5)	4a	m2m
F1	0.0	0.079 (8)	-0.25	1	-0.006 (6)	4c	m2m
F2	0.5	-0.162 (5)	-0.069 (2)	1	-0.010 (5)	8f	m..
Selected distances							
4x	Fe1-F2	1.93 (3) Å	4x	Na1-F2	2.11 (3) Å		
2x	Fe1-F1	2.018 (3) Å	2x	Na1-F1	2.35 (8) Å		

Table Footnote: Rint obs/all 10.63/10.66 from 48/53 averaged from 93/107 reflections extracted from reintegration after solution in *oC* lattice. Four reflections culled at 20% difference from average. Refined on F, with 10*σFobs cutoff (19 reflections). Refines to Robs 16.48 wRobs 11%, wRall = 11.4%.

TABLE 3 Single-crystal refinement results from the post-post-perovskite, Sb₂S₃-type, NaFeF₃ at 20.5 GPa, from data collected upon decompression from maximum pressure (~25 GPa).

Compound	NaFeF ₃ -III						
Space group	<i>P n m a</i>	62					
Lattice parameters, Å							
	<i>a</i>	<i>b</i>	<i>c</i>				
	7.8380 (14)	3.007 (3)	7.901 (5)				
Unit-cell volume		186.218 Å ³					
Atom	X	Y	Z	Occ	U Å ²	Site	Sym
Na	0.326 (2)	0.25	-0.024 (4)	1	0.024 (4)	4c	.m.
Fe	-0.0080 (8)	0.25	0.2047 (10)	1	0.010 (2)	4c	.m.
F1	0.2191 (17)	0.25	0.311 (4)	1	-0.006 (4)	4c	.m.
F2	-0.061 (2)	0.75	0.371 (5)	1	0.013 (5)	4c	.m.
F3	-0.3794 (18)	0.75	0.424 (4)	1	-0.003 (4)	4c	.m.
Selected distances							
1x	Fe1-F1	1.967 (19) Å	1x	Na1-F3	2.01 (3) Å		
2x	Fe1-F3	2.04 (2) Å	2x	Na1-F1	2.02 (3) Å		
2x	Fe1-F2	2.076 (16) Å	2x	Na1-F3	2.12 (3) Å		
1x	Fe1-F1	2.142 (15) Å	2x	Na1-F2	2.34 (2) Å		
1x	Fe1-F2	2.386 (2) Å					

Table Footnote: 147/348 unique reflections. Rint obs/all 12.25/13.14 from 91 reflections averaged from 146/326. Three reflections culled at 20% difference from average. Refined on F with I < 3σI set as unobserved and 15 *σFobs rejection (15 reflections). Refines to Robs 16.7%, wRobs 11.8% and wR(all) of 13.57%.

Figure Legends

Figure 1. The structures of NaFeF₃. The observed structures of NaFeF₃ described in the text and resulting from refinements in Tables 1-3. The Na-atoms and polyhedra are yellow, Fe polyhedra are brown in the (a) GdFeO₃-type perovskite, (b) CaIrO₃-type ppv and (c) Sb₂S₃-type structures. Annotations are referred to in the text. The figures have been prepared (as Figs 4, 5, 7) using VESTA (Momma and Izumi, 2011).

Figure 2. Powder diffraction data. Rietveld refinements of high-pressure x-ray patterns of NaFeF₃ taken with the collimated point-counter, from large-volume samples at about 9.5 GPa, before (a) in the pv structure, and after transition (b) in the ppv structure. Time-lapsed powder diffraction data, using the DT detector, are shown as a stacked waterfall plot (c), taken during compression to 9.5 GPa, to highlight the increase in anisotropy with pressure, which increases upwards.

Figure 3. Experimental electron density distributions. The Fobs maps for the single-crystal specimens calculated in Jana2006 (Petricek *et al.*, 2006) of (a) ppv and (b) Sb₂S₃-type NaFeF₃. These distributions highlight the increased bond distances and the new staggering of the Fe-sites. They are directly comparable to those presented in Umemoto and Wentzcovitch (2006), at 90°.

Figure 4. Schematic structural relations between ppv and Sb₂S₃. Panels (a)-(d) schematically represent the transformation, derived using STRUCTURE RELATIONS, for a transition between refined ppv (a) and Sb₂S₃ (d) structures with parameters here identical to those presented in Tables 2 and 3. Panels (b) and (c) are shown flattened and illustrate the constructions obtained when the high symmetry (*Cmcm*) ppv is transformed into the low symmetry *Pnma* lattice of the Sb₂S₃ structure with ppv dimensions (b). In (c) the Sb₂S₃ structure is lattice distorted to this same metric. The distances the atoms must move and the spontaneous strain for this transformation can be effectively estimated from (b) → (c) and (c) → (d), as discussed in the text.

Figure 5. Atom displacements in the ppv to Sb₂S₃ structure. The atom positions of the Sb₂S₃ structure have been superposed upon the *b*-axis projection of ppv structure to highlight the loss of symmetry and for direct comparison with unstable mode calculations shown in Fig. 4 of Umemoto and Wentzcovitch (2006). High symmetry axis directions and planes are indicated by dashed lines, along which both the Na and Fe are located in ppv. They are displaced from these positions upon transition to Sb₂S₃. Atom movement is indicated by red arrows, so that Na atoms move from yellow to blue positions and F from grey to green. The Fe positions are occluded by the polyhedra.

Figure 6. The relative orientations of observed lattices. Experimentally harvested lattice points and indexed lattices from high pressure single-crystal runs on NaFeF₃. (a) shows the pv lattice points, (b) shows the Sb₂S₃ lattice points. In each case these are overlain by the ppv lattices. (c) Shows a composite reconstruction of the three lattice directions, for pv (black), ppv (blue) and Sb₂S₃(red) lattices, referred to by matrices (2)-(3). Panel (d) demonstrates that a twinned pair of orthogonal α -Gd₂S₃-type lattices can index (but not refine) Sb₂S₃ reflection data. The marked angles are referred to in the text.

Figure 7. Schematic transition paths between post-ppv structures. Clockwise from left: The experimentally determined ppv structure (Table 2) transforms to the Sb₂S₃ structure (Table 3) upon application of pressure. The related chemistry, NaMgF₃, is proposed (Umemoto and Wentzcovitch, 2006) to undergo a transition to a structure here classified as Be₃N₂-type. Using TRANPATH, we can investigate common subgroups of the two high symmetry ppv and Be₃N₂ structures, through their expression in the common subgroup symmetry. It is remarkable that these subgroup intermediates, S1 and S2, coincide rather closely with each other and with the experimentally determined Sb₂S₃-type NaFeF₃.