



# A New Cation-Ordered Structure Type with Multiple Thermal Redistributions in $\text{Co}_2\text{InSbO}_6$

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**Abstract:** Cation ordering in solids is important for controlling physical properties and leads to ilmenite ( $\text{FeTiO}_3$ ) and  $\text{LiNbO}_3$  type derivatives of the corundum structure, with ferroelectricity resulting from breaking of inversion symmetry in the latter. However, a hypothetical third  $\text{ABO}_3$  derivative with  $R32$  symmetry has never been observed. Here we show that  $\text{Co}_2\text{InSbO}_6$  recovered from high pressure has a new, ordered- $R32$   $\text{A}_2\text{BCO}_6$  variant of the corundum structure.  $\text{Co}_2\text{InSbO}_6$  is also remarkable for showing two cation redistributions, to  $(\text{Co}_{0.5}\text{In}_{0.5})_2\text{CoSbO}_6$  and then  $\text{Co}_2\text{InSbO}_6$  variants of the ordered- $\text{LiNbO}_3$ ,  $\text{A}_2\text{BCO}_6$  structure on heating. The cation distributions change magnetic properties as the final ordered- $\text{LiNbO}_3$  product has a sharp ferrimagnetic transition unlike the initial ordered- $R32$  phase. Future syntheses of metastable corundum derivatives at pressure are likely to reveal other cation-redistribution pathways, and may enable  $\text{ABO}_3$  materials with the  $R32$  structure to be discovered.

Cation ordering within extended oxide structures is an important way to control physical properties such as introduction of ferroelectricity and multiferroism from arrangements that break inversion symmetry.<sup>[1,2]</sup> This is notably illustrated by the corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) type  $\text{A}_2\text{O}_3$  structure which has a simple centrosymmetric arrangement with rhombohedral space group symmetry.  $\text{A}_2\text{O}_9$  dimer units of two octahedra sharing a common face are separated by single vacant octahedra to form AA\_AA chains (Figure 1).

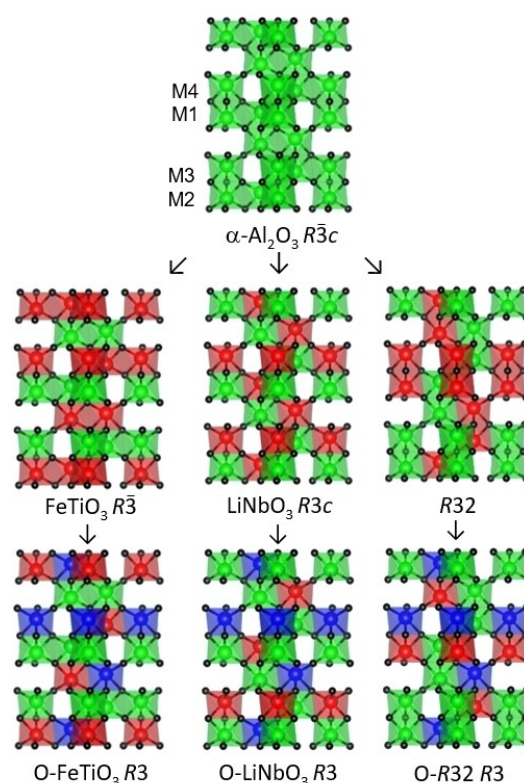
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Two cation-ordered  $\text{ABO}_3$  derivatives are known—the ilmenite ( $\text{FeTiO}_3$ ) and  $\text{LiNbO}_3$  types with centric and acentric  $R3c$  symmetry respectively. Both have AB cation pairs in the dimer units with antiparallel AB\_BA alignment in ilmenite but parallel AB\_AB order leading to polarity in the  $\text{LiNbO}_3$  type. It is intriguing to note that a third  $\text{ABO}_3$  cation ordering type is also possible within the corundum unit cell as shown in Figure 1. This structure has  $R32$  symmetry with AA\_BB chains of dimer pairs, and no examples have been reported. Further cation ordering within the  $\text{ABO}_3$  structures leads to  $\text{A}_2\text{BCO}_6$  derivatives, referred to in the literature as “ordered- $\text{ABO}_3$ ” types. These were first found in  $\text{Li}_2\text{MTeO}_6$  phases which adopt the



**Figure 1.** Crystal structures of the corundum type  $\text{A}_2\text{O}_3$  structure (top), and  $\text{ABO}_3$  (middle row) and  $\text{A}_2\text{BCO}_6$  (“ordered- $\text{ABO}_3$ ”, bottom row) derivatives obtained through cation ordering. Symmetry descents are indicated by the arrows and space groups are shown. Colours indicate the cation occupancies of octahedra in each structure (A/B/C = green/red/blue). The four site labels shown by the  $\text{A}_2\text{O}_3$  structure are used throughout this paper, where  $\text{M4} = \text{Sb}$  in  $\text{Co}_2\text{InSbO}_6$ .

ordered-LiNbO<sub>3</sub> structure for M=Zr and Hf,<sup>[3]</sup> and the ordered-ilmenite type for M=Ge.<sup>[4]</sup> The “ordered-R32” A<sub>2</sub>BCO<sub>6</sub> derivative of the R32-type has not been reported. These three A<sub>2</sub>BCO<sub>6</sub> arrangements all have R3 symmetry with four symmetry-independent octahedral cation sites. This structure is known as the Ni<sub>3</sub>TeO<sub>6</sub> (NTO) type and represents a special case of all three A<sub>2</sub>BCO<sub>6</sub> types (Figure 1) where A=B=Ni and C=Te.

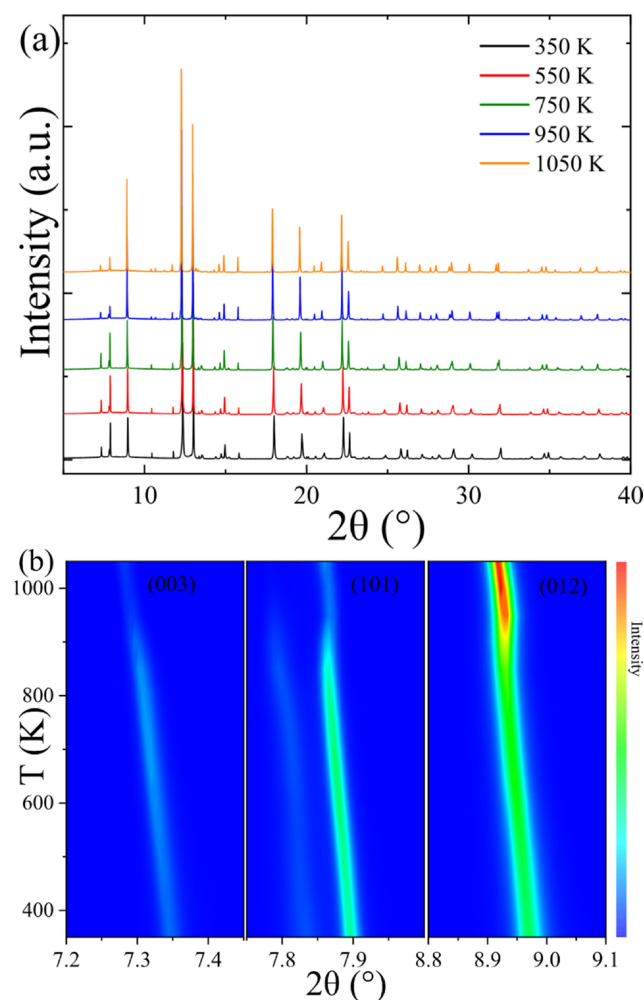
The non-centrosymmetric cation ordered corundum derivatives offer a rich variety of properties<sup>[5–7]</sup> according to their point group symmetry.<sup>[8]</sup> R3c LiNbO<sub>3</sub>-types (C<sub>3v</sub> point group) have allowed polar and piezoelectric activity, and LiNbO<sub>3</sub> itself is an important ferroelectric, piezoelectric and non-linear optical material.<sup>[9]</sup> The R32 ABO<sub>3</sub> structure (D<sub>3</sub>) is notable as belonging to the class of space groups that are non-polar but allow enantiomorphic and piezoelectric activity, so discovered examples would be of great interest. The ordered A<sub>2</sub>BCO<sub>6</sub> (NTO-type) structures (C<sub>3</sub>) have allowed polar, chiral and piezoelectric properties arising from their R3 symmetry. Further coupling of these structural orders to magnetism (multiferroism) can be introduced by use of magnetic cations that adopt long-range spin orders at low temperatures.<sup>[10]</sup> High pressure is often used to stabilise these acentric cation-ordered corundum derivatives, for example, MnTiO<sub>3</sub> changes from a centric ilmenite type at ambient pressure to an acentric LiNbO<sub>3</sub>-type high-pressure polymorph where weak ferromagnetism offers a mechanism for multiferroic switching.<sup>[11]</sup> Mn(Fe<sub>0.5</sub>M<sub>0.5</sub>)O<sub>3</sub> (M=Nb, Ta) are further examples of ABO<sub>3</sub> LiNbO<sub>3</sub>-types, with Fe/M disorder.<sup>[12]</sup> Within the R3 A<sub>2</sub>BCO<sub>6</sub> types, β-Mn<sub>2</sub>InSbO<sub>6</sub> has the ordered-ilmenite arrangement<sup>[13]</sup> while M<sub>2</sub>ScSbO<sub>6</sub> (M=Mn,<sup>[14]</sup> Co,<sup>[15]</sup> Ni<sup>[16]</sup>) and Mn<sub>2</sub>FeWO<sub>6</sub><sup>[17]</sup> are ordered-LiNbO<sub>3</sub> types. Mn<sub>2</sub>FeMoO<sub>6</sub> recovered from high pressure synthesis has an ordered-LiNbO<sub>3</sub> structure but this changes to an ordered-ilmenite type on heating and the stabilisation of these two types was rationalised from band structure calculations.<sup>[18]</sup> Magnetoelectric effects are reported in Ni<sub>3</sub>TeO<sub>6</sub><sup>[19–21]</sup> and ternary NTO-type analogues have recently been discovered for A<sub>3</sub>TeO<sub>6</sub> (A=Mn, Co)<sup>[22]</sup> and Mn<sub>3</sub>WO<sub>6</sub><sup>[23]</sup> at high pressure. In this communication, we report the synthesis of the new double-corundum material Co<sub>2</sub>InSbO<sub>6</sub> and thermal cation redistributions of unprecedented complexity from the previously unobserved ordered-R32 type to two different ordered-LiNbO<sub>3</sub> types.

A mixture of CoO, In<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>5</sub> in stoichiometric proportions for product Co<sub>2</sub>InSbO<sub>6</sub> was treated under high pressure and temperature conditions using a multi-anvil apparatus. Further details are in Supporting Information. A sample recovered from 6 GPa and 1373 K was found to contain a CaCl<sub>2</sub>-type product with an orthorhombic structure that is unrelated to the corundum types and characterisation of this phase is described in Supporting Information. Synthesis under 8 GPa and 1373 K led to a recovered Co<sub>2</sub>InSbO<sub>6</sub> product with R3 symmetry (lattice parameters  $a = 5.2882(3)$  Å and  $c = 14.029(1)$  Å) consistent with A<sub>2</sub>BCO<sub>6</sub> structures shown in Figure 1.

Synchrotron powder X-ray diffraction data from the Co<sub>2</sub>InSbO<sub>6</sub> sample were collected in situ while heating from 300 to 1073 K to determine the structure and any thermal

changes. Refinement of the recovered Co<sub>2</sub>InSbO<sub>6</sub> product structure at 300 K (fit and results in Supporting Information) gave cation site occupancies M1=Co<sub>0.3</sub>In<sub>0.7</sub>, M2=Co<sub>0.7</sub>In<sub>0.3</sub>, M3=Co and M4=Sb. Remarkably, the two Co-rich sites M2 and M3 are present in the same dimer units so that the cation distribution is close to the ordered-R32 type rather than the ordered-ilmenite or LiNbO<sub>3</sub> types. This is an important structural discovery given that no ordered-R32 A<sub>2</sub>BCO<sub>6</sub> or R32 ABO<sub>3</sub> structures have been reported amongst many known corundum-derived phases. The present compound thus represents a new structural type within the corundum group (Figure 1).

Comparison of the variable temperature patterns in Figure 2 shows that Co<sub>2</sub>InSbO<sub>6</sub> persists as a R3 corundum-derived material up to 1073 K but changes in peak positions and intensities near 900 K reveal structural rearrangement. Initial unconstrained fits (summarised in Supporting Information) demonstrated that while one cation site (M4) remains occupied by Sb throughout, Co/In occupancies at



**Figure 2.** a) Selected powder X-ray diffraction data from the high pressure Co<sub>2</sub>InSbO<sub>6</sub> sample collected in situ while heating from 300 to 1073 K. b) Diffraction intensity map for low-angle (003), (101) and (012) peaks. Changes between 850 and 950 K reflect the evolving cation distributions.



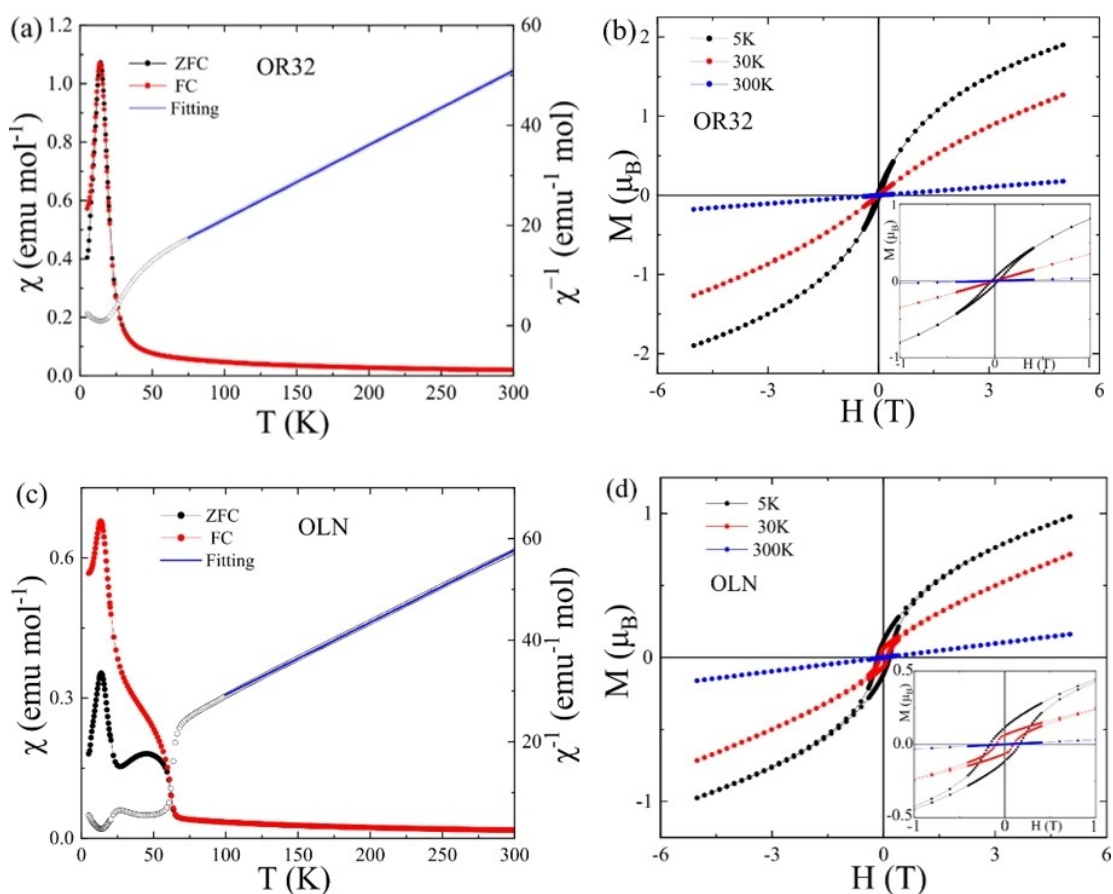
The second transition, from a cation-disordered to a cation-ordered structure on heating, is unusual given the loss of configurational entropy and evidences likely metastability of the intermediate  $(\text{Co}_{0.5}\text{In}_{0.5})_2\text{CoSbO}_6$  phase.

Average metal–oxygen bond lengths (Figure 3c) are consistent with the Co/In occupancy rearrangements, given the cation sizes (6-coordinate ionic radii are  $\text{Co}^{2+}=0.745$ ,  $\text{In}^{3+}=0.80$ , and  $\text{Sb}^{5+}=0.60$  Å).<sup>[24]</sup> M1–O and M2–O distances both decrease on heating from 850 to 950 K as their Co-populations increase, while an increase in the M3–O distance reflects the almost complete replacement of  $\text{Co}^{2+}$  by  $\text{In}^{3+}$ . The similar sizes and charges of  $\text{Co}^{2+}$  and  $\text{In}^{3+}$  cations allow the changing cation distributions at M1–M3 sites while the smaller and more highly charged  $\text{Sb}^{5+}$  occupies only the M4 site throughout.

Interplay between cation sizes and charges provides a likely explanation for the observed sequence of structures for  $\text{Co}_2\text{InSbO}_6$ . Efficient cation packing is favoured under the high pressure (8 GPa) at which the initial sample was synthesised. The ordered-*R32* structure with  $\text{Co}^{2+}\text{Co}^{2+}\text{In}^{3+}\text{Sb}^{5+}$  chains of cation pairs is thus stabilised as  $\text{Co}^{2+}$  (0.745 Å) is similar in size to the average (0.70 Å) of the larger  $\text{In}^{3+}$  and smaller  $\text{Sb}^{5+}$  cations. Thermal relaxation at ambient pressure leads to  $(\text{Co}_{0.5}\text{In}_{0.5})^{2.5+}\text{Co}^{2+}(\text{Co}_{0.5}\text{In}_{0.5})^{2.5+}\text{Sb}^{5+}$  and then to  $\text{Co}^{2+}\text{In}^{3+}\text{Co}^{2+}\text{Sb}^{5+}$  sequences of cation

pairs in the successive ordered- $\text{LiNbO}_3$  type products. This reduces electrostatic repulsions between cations in the dimer pairs which becomes more significant at ambient pressure where packing constraints are less important. Repulsions between cation charges  $q_i$  in the dimer pairs can be quantified in a simple nearest-neighbour approximation as  $E=q_Aq_B+q_Cq_D$  for AB\_CD cation order in the chains assuming fixed cation-cation separations. The sequence of structures shown above as (1) have  $E=19\rightarrow 17.5\rightarrow 16$  and the  $\text{Co}^{2+}\text{In}^{3+}\text{Co}^{2+}\text{Sb}^{5+}$  sequence in the final ordered- $\text{LiNbO}_3$  product has the lowest possible electrostatic repulsion energy within the family of  $\text{A}_2\text{BCO}_6$  structures (Figure 1), as the ordered-ilmenite alternative would have greater repulsion across  $\text{Co}^{2+}\text{In}^{3+}\text{Sb}^{5+}\text{Co}^{2+}$  pairs. This lowering of cation-cation repulsion is consistent with the decrease in thermal expansion of  $a$  and  $V$  cell parameters on heating across the two transitions seen in Figure 3a.

The effects of the cation rearrangement on the magnetic properties of  $\text{Co}_2\text{InSbO}_6$  were explored by comparing the original sample recovered from high pressure with ordered-*R32* structure type (OR32 sample), with a sample subsequently heated to 1073 K having the final ordered- $\text{LiNbO}_3$  cation arrangement (OLN sample). Magnetic susceptibility measurements show that both samples are Curie–Weiss paramagnets at high temperatures (Figure 4), with effective



**Figure 4.** Magnetic measurements for a) and b) the OR32, and c) and d) the OLN, samples of  $\text{Co}_2\text{InSbO}_6$ . a) and c) ZFC and FC susceptibilities and inverse ZFC susceptibilities with high-temperature Curie–Weiss fits. b) and d) Magnetisation-field loops with insets showing low field regions.

paramagnetic moment  $\mu_{\text{eff}}=5.19 \mu_{\text{B}}$  per  $\text{Co}^{2+}$  and Weiss temperature  $\theta=-43 \text{ K}$  for the OR32 sample, and  $\mu_{\text{eff}}=5.30 \mu_{\text{B}}$  and  $\theta=-106 \text{ K}$  for OLN. The moments are in excess of spin-only values showing that strong orbital contributions are present, and similar values up to  $\approx 5.20 \mu_{\text{B}}$  have been reported for other  $\text{Co}^{2+}$  oxides such as  $\text{Co}_2\text{ScSbO}_6$ .<sup>[15]</sup> Negative values of  $\theta$  indicate that dominant spin-spin interactions are antiferromagnetic. Both samples show deviation of the susceptibility above the Curie–Weiss variation at temperatures below  $\approx 65 \text{ K}$  suggesting antiparallel but ferrimagnetic spin alignments, given the negative values of  $\theta$ . The OR32 sample shows no discontinuity or divergence of zero-field cooled and field cooled (ZFC and FC) susceptibilities, which suggest short range ferrimagnetism. However, the OLN sample has a sharp Curie transition at  $T_{\text{C}}=65 \text{ K}$ , similar to  $T_{\text{C}}=59 \text{ K}$  for isostructural ferrimagnetic  $\text{Co}_2\text{ScSbO}_6$ .<sup>[15]</sup> This contrasting behaviour reflects a key difference in cobalt spin distributions in the two structures. In the *R32* structure, the Co spins are located in dimers which results in frustration between successive dimer layers, but in the ordered- $\text{LiNbO}_3$  structure the spins are distributed in a less frustrated, three-dimensional network. Both samples have susceptibility peaks at  $15 \text{ K}$  indicative of a possible antiferromagnetic or a spin-glass transition. The latter could result from the 20–25 % Co/In disorder between two sites observed for both samples. Neutron diffraction will be needed to confirm the spin orders or their absence. Magnetization-field loops show substantial magnetization for the two samples at low temperatures (Figure 4). The moments at  $5 \text{ K}$  and  $5 \text{ T}$  approach  $2$  and  $1 \mu_{\text{B}}$  per  $\text{Co}_2\text{InSbO}_6$  formula unit for OR32 and OLN samples, respectively. The OR32 sample exhibits a small hysteresis at  $5 \text{ K}$  (remnant magnetization  $M_{\text{r}}=0.04 \mu_{\text{B}}$  and coercive field  $B_{\text{c}}=0.03 \text{ T}$ ) but hysteresis for the OLN sample is more substantial ( $M_{\text{r}}=0.12 \mu_{\text{B}}$  and  $B_{\text{c}}=0.16 \text{ T}$ ), consistent with the well-defined ferrimagnetic transition for this phase.

These results demonstrate that a new  $\text{A}_2\text{BCO}_6$  ordered-*R32* variant of the corundum structure is stabilised in  $\text{Co}_2\text{InSbO}_6$  prepared at high pressure. This discovery of dimer units containing the same cations is unprecedented in  $\text{ABO}_3$  or  $\text{A}_2\text{BCO}_6$  corundum derivatives and likely results from similar average cation sizes in the  $\text{Co}_2\text{O}_9$  and  $\text{InSbO}_9$  dimer units minimising volume at pressure. High pressure may thus enable discovery of  $\text{ABO}_3$  phases with the as-yet unreported *R32* structure. These would be of interest for the stabilization of spin-dimer materials with A/B = magnetic/non-magnetic cation combinations.  $\text{Co}_2\text{InSbO}_6$  is also remarkable for showing an unprecedented sequence of two cation rearrangements on heating: first to  $(\text{Co}_{0.5}\text{In}_{0.5})_2\text{CoSbO}_6$  and then to  $\text{Co}_2\text{InSbO}_6$  phases with the ordered- $\text{LiNbO}_3$  structure. These rearrangements reduce cation-cation repulsions and favour the ordered- $\text{LiNbO}_3$  structure that is often observed in corundum-derived  $\text{A}_2\text{BCO}_6$  materials. The cation distributions change magnetic properties as the final ordered- $\text{LiNbO}_3$  product has a sharp ferrimagnetic transition at  $65 \text{ K}$  whereas the initial ordered-*R32* phase has a broader feature indicative of short-range spin ordering. Both samples have susceptibility peaks at  $15 \text{ K}$  indicative of an antiferromagnetic or spin-glass tran-

sition. All of the  $\text{Co}_2\text{InSbO}_6$  phases have acentric *R3* symmetry, and so are of interest for future exploration of acentric and multiferroic properties.

In conclusion,  $\text{Co}_2\text{InSbO}_6$  and previously-reported  $\text{Mn}_2\text{FeMoO}_6$ <sup>[18]</sup> demonstrate that high pressure may be used to recover metastable cation arrangements within the corundum family that can be thermally relaxed to new structures. This enables dependence of physical properties on the cation-ordering patterns to be explored. Further syntheses of high-pressure corundum derivatives are likely to reveal other cation-redistribution pathways, and may enable  $\text{ABO}_3$  materials with the as-yet unreported *R32* structure type to be discovered.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are openly available in Edinburgh DataShare at <https://datashare.ed.ac.uk/handle/10283/838>.

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