**Experimental report:**

'In situ determination of the phase diagram and structures

of the industrially relevant oxide conductor In_2O_3'
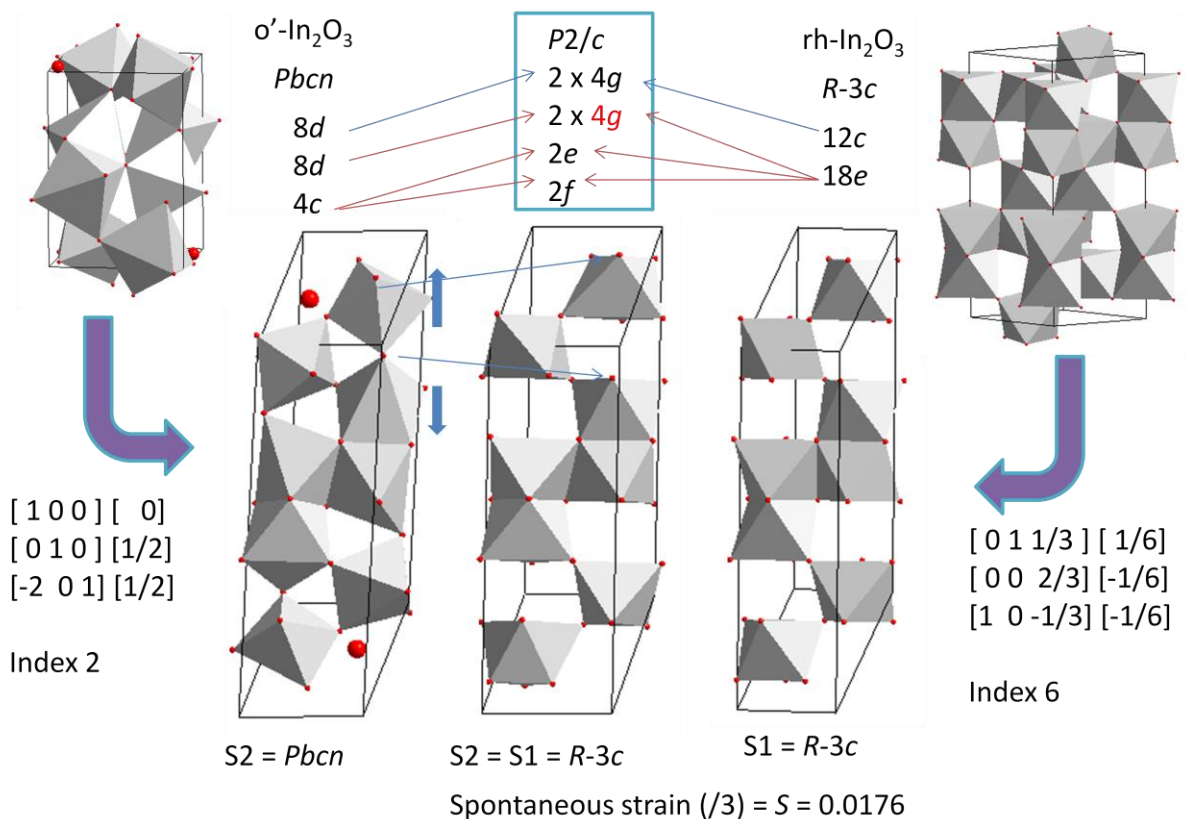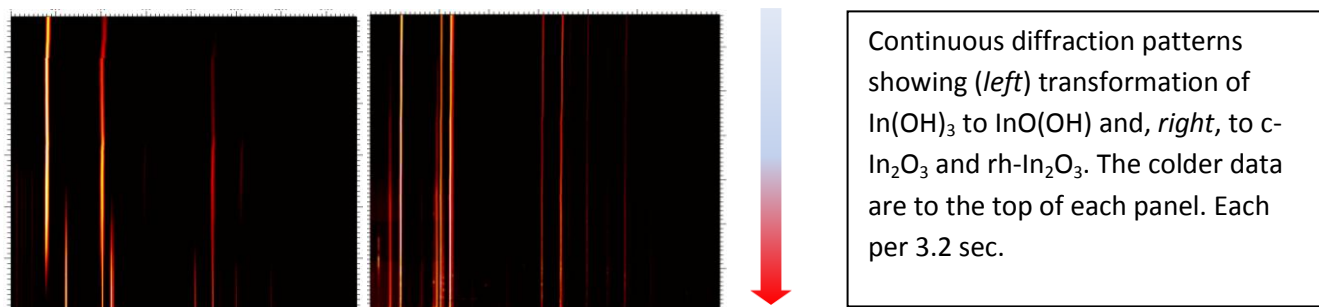
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The purpose of the experiment was to delineate any phase boundaries occurring between the o', rh and cubic structures of In_2O_3. There is some considerable debate on this topic, highlighted in recent work of Bekheet and others, which concludes that the rh-In_2O_3 phase (corundum type) is stable. Unfortunately, this current work suggests otherwise; that o' is stable at high p, T and that rh is recovered only on decompression having transformed to o', except perhaps in one very limited p, T region between cubic and o' phases. Therefore, o' is not metastable but rh may be, although it can be prepared reliably. Having formed o' it will invariably transform to rh at all pressures less than o' except at highest temperatures, where it will transform directly to the stable cubic phase. The region of where rh-In_2O_3 will form is delineated. Roughly (work in progress):
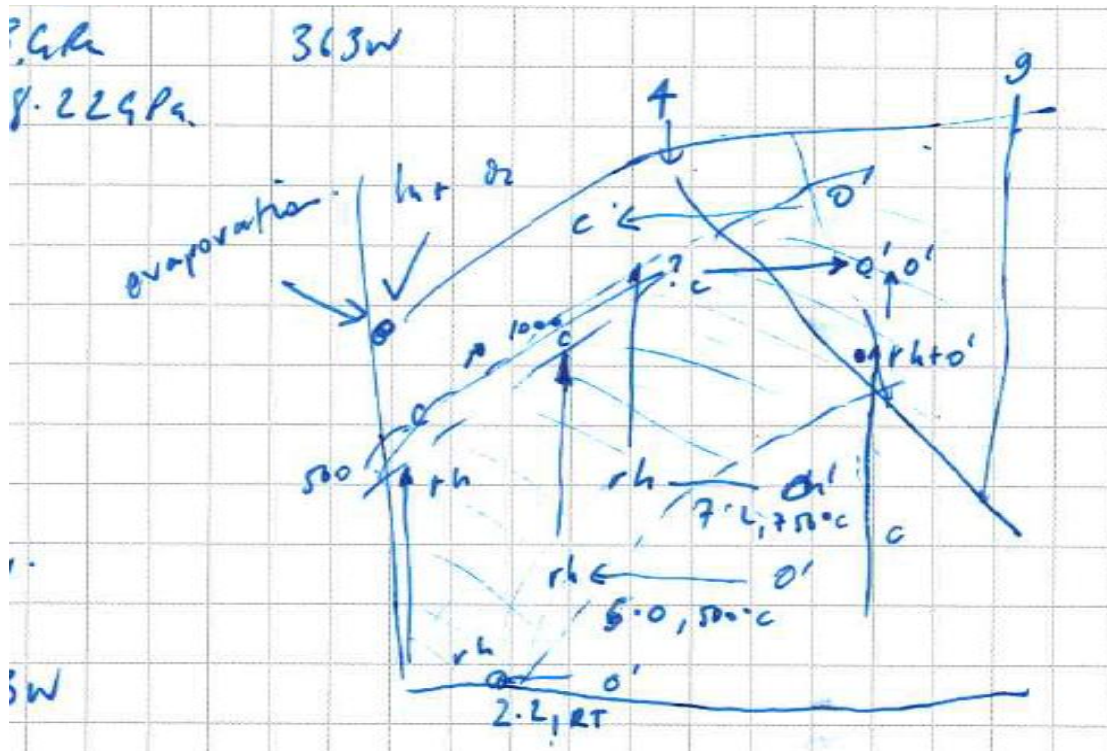
This may be due to the relationship shown below, based in in situ data a transformation, which maps the rh and the o' to a common subgroup, from which inferences on the mechanism of transformation can be established:

o'-In₂O₃
Pbcn
8d
8d
4c

P2/c
2 x 4g
2 x 4g
2e
2f

rh-In₂O₃
R-3c
12c
18e

[1 0 0] [0]
[0 1 0] [1/2]
[-2 0 1] [1/2]

Index 2

[0 1 1/3] [1/6]
[0 0 2/3] [-1/6]
[1 0 -1/3] [-1/6]

Index 6

S2 = Pbcn   S2 = S1 = R-3c   S1 = R-3c

Spontaneous strain (/3) = S = 0.0176

Inspection of the subgroup structure S2, derived from o'-In₂O₃, we see that the atom that is required to move most is that involved in the splitting is the 8d positions to 2 x 4g of S1 and S2, which are equivalent, eventually, to the 18e of rh-In₂O₃. In moving, this oxygen causes significant polyhedral rotation and bond breaking and brings the eventual corundum sheet to in-plane O 18e positions. In other systems, this mechanism might provide a way by which bixbyite-type structures transform to corundum. The o' is elsewhere known as Rh₂O₃-II-type. Each of these are rather widespread.

Continuous diffraction patterns showing (*left*) transformation of In(OH)₃ to InO(OH) and, *right*, to c-In₂O₃ and rh-In₂O₃. The colder data are to the top of each panel. Each per 3.2 sec.

In short: 8 runs were made on both In₂O₃ and In(OH)₃ starting materials. In(OH)₃ transforms to InO(OH) to c-In₂O₃ to rh-In₂O₃ with increasing temperature. Therefore (and following known transformations) rh-In₂O₃ is favourably obtained in from the hydroxide in a system where it is not otherwise obviously stable. The following transformations were observed c → o', o' → c; c → rh+o'(and possible triple point); rh+o' → o'; o' → rh; rh → c; c→ In + O₂ (it effectively evaporates). Transformations were, as much as allows, observed by both changing pressure and changing temperature conditions.

A manuscript is currently in prep.