Systematic study on new dense structures in A_2O_3 compounds

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Since Goldschmidt and his co-workker established the systematics of phase transitions from C rare earth sesquioxides structure (RES) to B- and A-RES in sesquioxides, the A-RES possessing seven oxygen-coordinated polyhedra is believed to be the densest phase. Namely, no sesquioxides structure having eight oxygen-coordination numbers was reported to date. In recent years, the another kind of dense structure, $CaIrO_3$ phase (so-called post perovskite phase[1]), has been found in a few sesquioxides[2-5] as the post Rh_2O_3(II) phase. The structure possesses six and eight oxygen-coordinated polyhedra and the density is comparable to that of the A-RES phase. Last year, two kind of dense sesquisulfide structures were reported on the post-$CaIrO_3$ phases of sesquioxides, one is the U_2S_3 structure predicted in Al_2O_3 at 370 GPa by ab initio calculation[6], another is the Gd_2S_3 structure stabilizing in In_2O_3 at 40 GPa which is based on both experimental and theoretical studies[7]. Interestingly, both structures are characterized by seven and eight oxygen-coordinated polyhedra. In this report, we present Sc_2O_3 as the second sesquioxide compound crystallized into Gd_2S_3 structure under high P-T conditions by indicating in-situ x-ray diffraction experiments and ab initio calculations[8]. Furthermore, based on the results, we propose new systematics of the phase transition in rare earth sesquioxides. The fact that the Gd_2S_3 structure stabilized not only in IIIB sesquioxides but also in rare earth sesquioxides is striking. It is highly possible that the new transition systematics to the Gd_2S_3 structure would be universal in most sesquioxides.

[1] M. Murakami et al., Science 304, 855 (2004)
[2] S. Ono et al., J. Phys. Chem. Solids 65, 1527 (2004)
[3] J. Tsuchiya et al., Phys. Rev. B72, 020103(R) (2005).
[4] S. Ono et al., Earth Planet. Sci. Lett., 246, 326 (2006).
[5] T. Tsuchiya et al., Phys. Rev. B76, 174108(2007)
[6] K. Umemoto et al, Proc. Natl. Acad. Sci., 105, 6526 (2008)
[7] H. Yusa et al., Phys. Rev. B78, 092107(2008).
[8] H. Yusa et al., under review.