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Thermodynamic stability of various phases of zinc tin oxides from *ab-initio* calculations

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A grid-based Bader charge analysis[1,2] was performed in order to determine the variation of the charge transfer between oxygen and cation along the bond path in the various phases of zinc tin oxides. Table S1 shows the net Bader charges (BC) and net Bader charges per coordination number (BCCN) in zinc tin oxides. The BC was counted as the difference between the charge of an isolated atom and that in the compound. Then, the BCCN was obtained by dividing the BC by the CN.

The BCs of Sn were all higher than those of Zn due to the higher valence electron state of Sn (Sn^{4+}) than that of Zn (Zn^{2+}) in the compound. The BC for a given cation is all similar irrespective of the phase and pressure. On the other hand, the BCCN depends on the CN. Therefore, the deviation of the BCCN was more significant for Zn due to its dual preference of the occupancy sites whereas that for Sn was negligible with respect to the phase transition. These analyses agree with the larger deviation of the bond length of Zn-O which was discussed in chapter 4.6.

Table S1 The net Bader charge and the net Bader charge per CN in zinc tin oxides.

	Space Group	Zn			Sn		
		CN	BC	BCCN	CN	BC	BCCN
ZnO	$P6_3mc$	4	1.20 (1.21) [a]	0.30 (0.30) [a]			
ZnO	$Fm3m$ [b]	6	1.19 (1.26)	0.20 (0.21)			
SnO_2	$P4_2/mnm$				6	2.42 (2.45)	0.40 (0.41)
$ZnSnO_3$	R3c (LN-)	6	1.25 (1.26)	0.31 (0.31)	6	2.36 (2.39)	0.39 (0.40)
Zn_2SnO_4	$P4_122$ (tetra-)	4	1.25 (1.25)	0.31 (0.31)			
		6	1.23 (1.25)	0.20 (0.21)	6	2.30 (2.31)	0.38 (0.39)

[a] The value in the parentheses is the BC and BCCN at the hydrostatic pressure of 14 GPa.

[b] This phase was not involved in the paper.

[1] W. Tang, E. Sanville and G. Henkelman, G, *J. Phys.: Condens. Matter*, 2009, **21**, 084204.

[2] R. F. W. Bader, *Atoms in Molecules: a Quantum Theory*, Oxford University Press, New York, 1990.