Various superstructures formed by tin-vacancy ordering in $K_8Sn_{44}\square_2$ and $Rb_8Sn_{44}\square_2$ clathrates

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The $K_8Sn_{44}\square_2$ and $Rb_8Sn_{44}\square_2$ clathrates are Zintl phases stabilized by creating tin vacancies ($\square$) in the covalent clathrate-I framework [1]. Recently, $Rb_8Sn_{44}\square_2$ [2] and $Ba_8Ge_{43}\square_3$ [3] were reported with partial and full vacancy ordering. Both show the same cubic $2a_1\times2a_1\times2a_1$ superstructure (space group $Ia\bar{3}d$), with the vacancies building up a spiral substructure along {100} (similar to that in Fig. 1c).

In contrast to earlier work on $K_8Sn_{44}\square_2$ (Pearson symbol *cP*52, a_1 = 12.03 Å, space group $Pm\bar{3}n$) [1, 4], in our X-ray powder diffraction (XRPD) patterns splitting of the reflections is observed at high 2θ values, indicating a non-cubic unit cell. In addition, weak reflections between the main ones revealed the formation of a superstructure. By studying the samples on a Tecnai 10 electron microscope (equipped with CCD camera TemCam-F224HD from TVIPS), selected area electron diffraction SAED patterns show the existence of three different superstructures. The first one is a tetragonal $2a_1\times2a_1\times2a_1$ superstructure (SAED patterns in Figs. 1a, 1b) observed in a sample annealed at 350 °C (quenched in water). A suitable crystal structure model (a = 24.063(2) Å, c = 24.007(2) Å, $I\bar{4}2d$ space group, Pearson symbol *tI*416) was derived from the structure of $Ba_8Ge_{43}\square_3$. In this superstructure (see Figs. 1c, 1d), 1.5 of 2 vacancies per formula unit are fully ordered. The pairwise ordering of the majority of the vacancies in the basal plain (Fig. 1d) explains the shortening of the c axis. The second superstructure has an orthorhombic $4a_1\times2a_1\times2a_1$ unit cell (*oC*832, SAED patterns in Figs. 2a, 2b) and was found in a furnace cooled sample (after annealing at 350 °C). The third one is a tetragonal $4a_1\times4a_1\times2a_1$ superstructure (*tI*1664; see Figs. 2c, 2d) found in a sample annealed at 200 °C (quenched in water).

TEM study of a $Rb_8Sn_{44}\square_2$ sample annealed at 400 °C (water quenched) revealed a giant orthorhombic $8a_1\times2\sqrt{2}a_1\times2\sqrt{2}a_1$ superstructure (*oC*3328; see Fig. 3). Other superstructures related to the *oC*832 and *tI*1664 variants in $K_8Sn_{44}\square_2$ were also observed in this $Rb_8Sn_{44}\square_2$ sample. No obvious splitting of the reflections in the high 2θ region of $Rb_8Sn_{44}\square_2$ XRPD patterns was observed. Thus, it is expected that in the $Rb_8Sn_{44}\square_2$ superstructures the distribution of the tin vacancies is more homogeneous (no vacancy pair structure) than in the $K_8Sn_{44}\square_2$ superstructure variants. Within the same space group, there are at least two different modes for vacancy arrangement.

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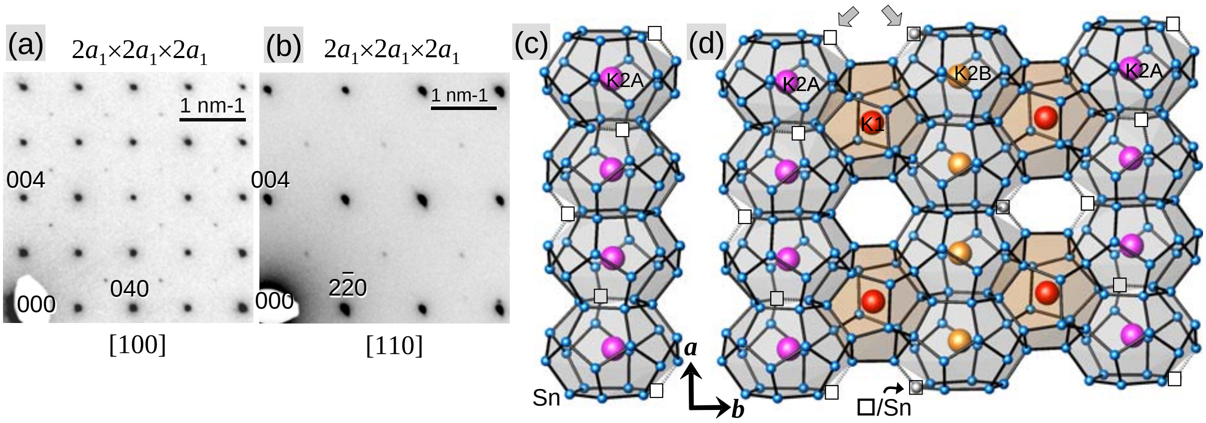

Figure 1. (a) [100] and (b) [110] SAED patterns of the *I*-centered tetragonal $2a_1 \times 2a_1 \times 2a_1$ superstructure (*tI*416) of $K_8Sn_{44}\square_2$. (c), (d) Fragments of the $2a_1 \times 2a_1 \times 2a_1$ structure showing the arrangement of the tin □ vacancies (spiral substructure along *a* axis in (c)). At short-range level, pairs of vacancies are formed on the basal plane (gray arrows in (d)).

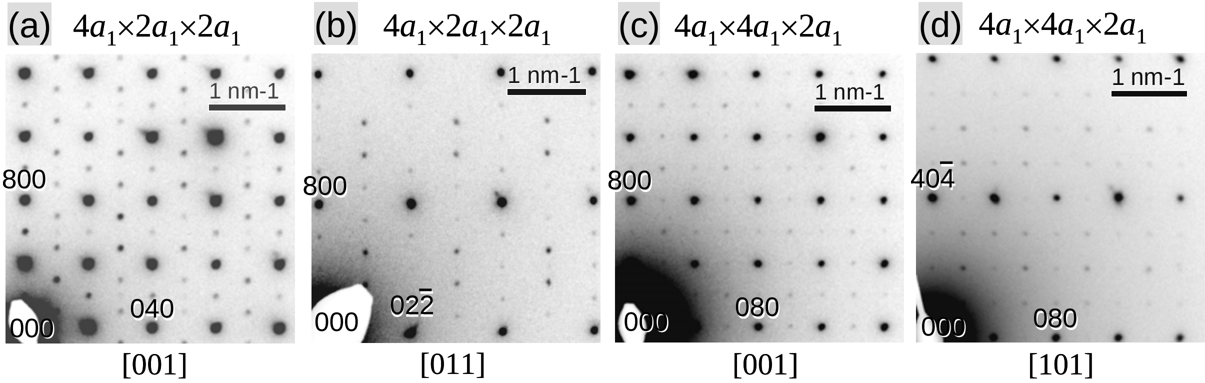

Figure 2. (a) [001] and (b) [011] SAED patterns of the orthorhombic $4a_1 \times 2a_1 \times 2a_1$ superstructure (*oC*832) of $K_8Sn_{44}\square_2$. (c) [001] and (d) [101] SAED patterns of the *I*-centered tetragonal $4a_1 \times 4a_1 \times 2a_1$ superstructure (*tI*1664) of $K_8Sn_{44}\square_2$.

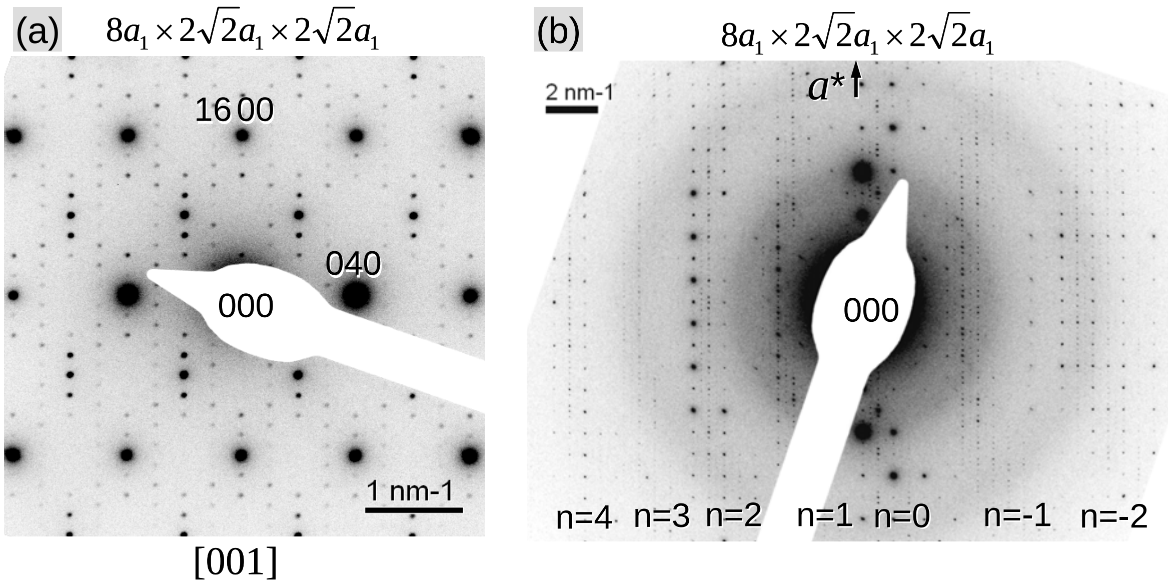

Figure 3. (a) [001] SAED pattern of the orthorhombic $8a_1 \times 2\sqrt{2}a_1 \times 2\sqrt{2}a_1$ superstructure (*oC*3328) of $Rb_8Sn_{44}\square_2$. (b) Tilted [001] SAED pattern (~6° about the *a** axis), showing the different Laue zones, $(uvw)_n$* layers for n = -2, -1, 0, 1, 2, 3, 4.

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