

A comparison of the X-ray single-crystal structure of Li_3SbO_4 with the Rietveld refinement

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The X-ray single-crystal structure of trilithium antimony tetraoxide, Li_3SbO_4 , is compared with the Rietveld refinement previously reported for the same material. An analysis of the geometric parameters and s.u.'s extracted from both refinements shows that, as expected, powder data yield a less accurate structure. Nevertheless, both refinements give correct geometric parameters within s.u.'s characteristic of each technique.

Comment

The crystal structure of Li_3SbO_4 was first reported from X-ray powder diffraction data (Blasse, 1963), but was refined in an incorrect space group. A more recent study determined the correct structure of this oxide (Skakle *et al.*, 1996) and described it as an ordered rocksalt-type compound with distorted MO_6 octahedra ($M = \text{Sb, Li}$). The compound crystallized in the $P2/c$ space group and the structure was refined by the Rietveld method using X-ray powder diffraction data from a Stoe Stadi/P psd-based system (psd is an abbreviation for position sensitive detector). This work has now been extended by a single-crystal structure refinement (Fig. 1) to assess the accuracy of both methods in the determination of geometric parameters. Reflections that were omitted for the powder refinement could be included in the present study, which resulted in some adjustments of the cell parameters and the atomic coordinates. Apparent discrepancies between both refinements are discussed.

A direct comparison of the s.u.'s for the geometric parameters clearly favours the single-crystal refinement; the observed range for the uncertainties of the 12 independent bond lengths is 0.002–0.009 Å for the present study (see Table 1) *versus* 0.01–0.08 Å for the Rietveld refinement. Moreover, the differences in bond lengths seem to be large for both methods, ranging from 0 to 0.128 Å. However, the application of a classical probabilistic test (Glusker *et al.*, 1994)

shows that these differences are not significant. Computing the parameter q , which measures the relationship of the difference between two bond lengths (Δd) with respect to the s.u.'s (σ_1 and σ_2), *i.e.* $q = \Delta d / (\sigma_1^2 + \sigma_2^2)^{1/2}$, it can be seen that only two differences in bond lengths between refinements are probably significant [$q = 3.63$ for $\text{Sb1}—\text{O1} = 2.047$ (2) Å and $q = 3.10$ for $\text{Li1}—\text{O1} = 2.214$ (7) Å], one difference is borderline [$q = 2.63$ for $\text{Li1}—\text{O2} = 2.107$ (7) Å], while the remaining differences are not significant (q in the range 0–2.06).

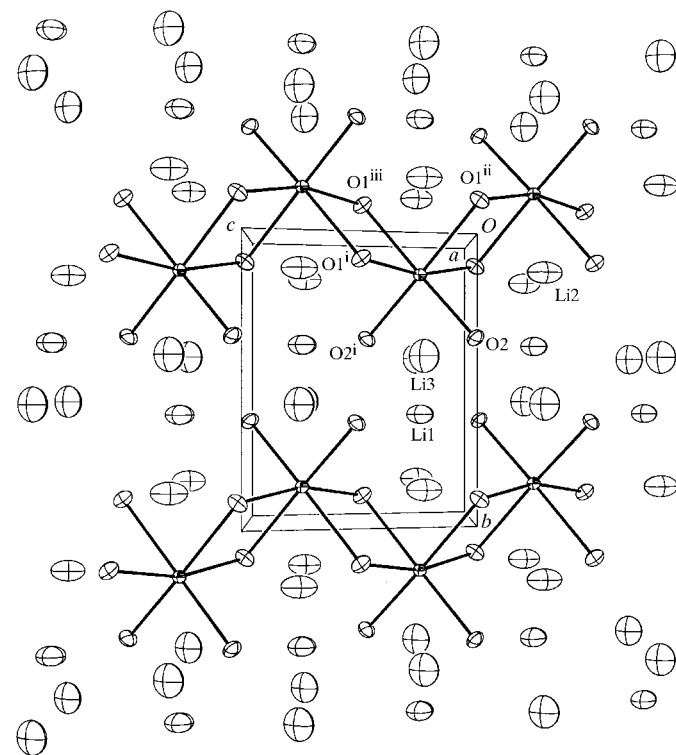


Figure 1

The structure of the title compound in a projection normal to [100]. SbO_6 octahedra form zigzag infinite chains parallel to $c \sin \beta$. Displacement ellipsoids are drawn at the 75% probability level [symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-x, -y, -z$; (iii) $x, -y, \frac{1}{2} + z$].

The same test applied separately for each refinement indicates the significance of the differences in bond lengths, regardless of the technique used. It is clear that for the single-crystal refinement, the three $\text{Sb}—\text{O}$ bond lengths are not equivalent, with q values ranging from 15.56 to 41.72, while for the Rietveld data, the test is somewhat ambiguous, with a range of 1.41–4.24 for q . In the same way, the refinement based on single-crystal data indicates that the geometries around the Li atoms are severely distorted from ideal octahedral values; the calculated q ranges are 5.25–10.81, 1.34–27.13 and 1.40–49.33 for Li1, Li2 and Li3, respectively. In the case of the Rietveld refinement data, corresponding ranges are substantially smaller (3.88–6.01, 0.71–1.82 and 0.95–12.13, respectively), leading to a less accurate description of the structure. For instance, the three $\text{Li2}—\text{O}$ bond lengths determined by the Rietveld method are not significantly different, leading to a poor description of the coordination geometry for this atom.

Similar observations can be made for the O—M—O angles ($M = \text{Sb, Li}$). The s.u.'s are in the range 0.5–4.0° for the Rietveld data and 0.10–0.18° for the present work, with a more accurate description of the structure in the latter case.

Finally, it should be mentioned that the differences observed in the lattice parameters are too small to account for the differences observed in the geometric parameters, even though it has been claimed many times that the cell-constant s.u.'s obtained from a four-circle diffractometer may be over-optimistic (Jones, 1984; Sheldrick, 1997). In the present case, the relative difference between the cell volumes is under 0.6%.

In conclusion, the geometric parameters for the title compound are the same for the Rietveld and single-crystal refinements. Nevertheless, the geometry based on the Rietveld data is not as accurate, especially for the light atoms. This point justifies, in general, that a Rietveld refinement should be complemented, if possible, by a single-crystal study.

Experimental

Crystals of Li_3SbO_4 were grown by total synthesis from appropriate amounts of the high-purity reagents Li_2CO_3 and Sb_2O_5 . Details of the procedure have been reported previously (Skakle *et al.*, 1996).

Crystal data

Li_3SbO_4	$D_m = 4.354 \text{ Mg m}^{-3}$
$M_r = 206.57$	D_m measured by pycnometer
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.1456$ (5) Å	Cell parameters from 44 reflections
$b = 6.0794$ (5) Å	$\theta = 4.2\text{--}13.8^\circ$
$c = 5.1291$ (6) Å	$\mu = 8.90 \text{ mm}^{-1}$
$\beta = 108.859$ (8)°	$T = 293$ (2) K
$V = 151.84$ (3) Å ³	Needle, white
$Z = 2$	$0.7 \times 0.1 \times 0.1 \text{ mm}$
$D_x = 4.518 \text{ Mg m}^{-3}$	

Data collection

Siemens P4 diffractometer	$R_{\text{int}} = 0.026$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: ψ scan (XSCANS; Fait, 1991)	$h = -6 \rightarrow 6$
$T_{\text{min}} = 0.782$, $T_{\text{max}} = 0.899$	$k = -7 \rightarrow 7$
774 measured reflections	$l = -6 \rightarrow 6$
355 independent reflections	2 standard reflections every 48 reflections
342 reflections with $I > 2\sigma(I)$	intensity decay: 1.7%

Table 1

Selected bond lengths (Å).

Sb1—O2 ($\times 2$)	1.929 (2)	Li2—O2 ^{iv} ($\times 2$)	2.032 (6)
Sb1—O1 ($\times 2$)	2.003 (2)	Li2—O1 ⁱ ($\times 2$)	2.205 (6)
Sb1—O1 ⁱ ($\times 2$)	2.047 (2)	Li2—O1 ^v ($\times 2$)	2.214 (3)
Li1—O2 ⁱⁱ ($\times 2$)	2.107 (7)	Li3—O2 ^{vi} ($\times 2$)	2.050 (3)
Li1—O2 ⁱⁱⁱ ($\times 2$)	2.174 (3)	Li3—O2 ⁱⁱⁱ ($\times 2$)	2.062 (8)
Li1—O1 ⁱⁱⁱ ($\times 2$)	2.214 (7)	Li3—O1 ⁱⁱ ($\times 2$)	2.518 (9)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, y, \frac{1}{2} - z$; (iii) $x, 1 - y, \frac{1}{2} + z$; (iv) $-1 - x, y, -\frac{1}{2} - z$; (v) $-x, y, -\frac{1}{2} - z$; (vi) $-1 - x, y, \frac{1}{2} - z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0110P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.015$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.036$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
355 reflections	$\Delta\rho_{\text{min}} = -1.04 \text{ e \AA}^{-3}$
40 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.024 (2)

Data collection: XSCANS (Fait, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1995); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-Plus; software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1318). Services for accessing these data are described at the back of the journal.

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