

symmetry and structure of TAHSe in both phases I and II allows us to discuss the mechanism of the I–II phase transition. SeO_4 tetrahedra in phase II are deflected from the symmetrical position required by space group $R\bar{3}m$. The potential barrier preventing SeO_4 tetrahedra from switching to the other side of the (210) planes decreases with increasing temperature and both orientations of SeO_4 tetrahedra become equally probable. The problems of anharmonic potentials and pseudo-potential have been discussed by Bachmann & Schulz (1984). They have demonstrated that one cannot distinguish between ordered and disordered structures with just one data set measured at one temperature. The temperature range of phase I of TAHSe is rather small nevertheless, we have also determined the crystal structure of phase I at 366 K. Although atomic parameters did not change significantly, the distance between two angular positions of disordered SeO_4 tetrahedra became smaller with increasing temperature. We attribute this to the dependence of pseudo-potential on temperature and a decrease of the potential barrier in a double energy well.

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Redetermination of the Structure of Barium Peroxide by Single-Crystal X-ray Diffraction*

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Abstract. BaO_2 , $M_r = 169.3$, tetragonal, $I4/mmm$, $a = 3.8016(4)$, $c = 6.7786(8)$ Å, $V = 97.97(2)$ Å³, $Z = 2$, $D_x = 5.74$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 198.5$ cm⁻¹, $F(000) = 144$, $T = 293$ K, final $R = 0.0092$ for 58 unique reflections. BaO_2 adopts the CaC_2 structure; Ba is bound to ten O atoms, eight at 2.788 (1) Å and two at 2.648 (5) Å. The O—O bond length in the peroxide ion is 1.482 (10) Å.

Introduction. The structure of BaO_2 has been studied several times in the past (Abrahams & Kalnajs, 1954, and references therein) owing to interest in the nature of the peroxide bond, but never by single-crystal methods. More recently, Roth, Rawn & Hill (1991) examined the reactivity, non-stoichiometry and decomposition of BaO_2 . They also grew crystals of BaO_2 from a $\text{Ba}(\text{NO}_3)_2$ melt under pure O_2 and

found the crystals were typically twinned. Although they reported precession photographs on the crystals, no single-crystal structure determination was carried out. In this paper, the structure of BaO_2 based on a crystal grown from a $\text{Ba}(\text{OH})_2$ – BaCl_2 flux in air is reported.

Experimental. The crystal of BaO_2 used in this study was obtained during the synthesis of a new barium molybdate aluminate, whose structure will be published shortly. However, crystals of BaO_2 occasionally appeared in other preparations with the $\text{Ba}(\text{OH})_2$ – BaCl_2 flux. 0.33 g Al_2O_3 and 2.0 g MoO_3 were mixed with 14 g $\text{Ba}(\text{OH})_2$ and 2.5 g BaCl_2 and placed in an alumina crucible with a tightly fitting lid. The crucible was heated in air at 300 K h⁻¹ to 1073 K, held for 5 h at 1073 K and slowly cooled to 923 K at 4.2 K h⁻¹. Colorless rectangular plate, 0.16 × 0.10 × 0.01 mm, sealed in a capillary to prevent

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decomposition from moisture. Enraf-Nonius CAD-4 diffractometer at room temperature. Density not measured. Lattice parameters from 25 reflections with $21 < 2\theta < 28^\circ$ averaged with Friedel pairs. ω scans, scan width $1.3\text{--}2.6^\circ$, scan speed $1.80\text{--}5.00^\circ \text{ s}^{-1}$. 353 data collected, $6 < 2\theta < 60^\circ$; $h = 5$ to 5 , $k = 0$ to 5 , $l = 0$ to 9 . Two intensity control reflections (112 and $\bar{1}2\bar{1}$) measured every hour of X-ray exposure; data normalized for 2% decay. Lorentz, polarization and analytical absorption corrections (de Meulenaer & Tompa, 1965). Faces indexed [distance to center in mm]: (110) [0.079]; ($\bar{1}\bar{1}0$) [0.079]; ($\bar{1}10$) [0.051]; ($1\bar{1}0$) [0.051]; (001) [0.0058]; (00 $\bar{1}$) [0.0058]. Transmission factors 0.17–0.79. 175 weak reflections with $h + k + l = 2n + 1$ removed. All 59 unique reflections remaining after merging data ($R_{\text{int}} = 1.60$) had $I > 24\sigma$. The structure was refined by full-matrix least squares on F . Crystallographic calculations were performed on a DEC computer network using a system of programs developed by Dr J. C. Calabrese. Plot made with ORTEP (Johnson, 1976). Ba refined with anisotropic thermal parameters (refining O with anisotropic thermal parameters did not improve wR significantly). The occupancy of O was refined. Although the occupancy is within 3σ of 100%, refining it gave a significant improvement in wR according to the Hamilton test (Hamilton, 1965). Statistical weights employed with $\sigma(F) \propto 1/[\sigma(I)^2 + (0.03I)^2]$. No secondary-extinction correction. Strongest reflection (110) removed from refinement owing to poor agreement. Final residuals for 6 parameters and 58 reflections: $R = 0.0092$, $wR = 0.0122$, $S = 0.72$, maximum $\Delta/\sigma = 0.00005$, maximum difference Fourier peak height $\pm 0.46 \text{ e } \text{Å}^{-3}$. Scattering factors for neutral atoms including corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Table 1* lists atomic positions, thermal parameters and occupancies. Fig. 1 shows the unit cell of BaO_2 , with bond lengths labelled. The structure agrees with those published previously, although the a lattice parameter differs since the non-standard space group $F4/mmm$ was used in these reports. The structural formula is $\text{BaO}_{1.76(10)}$, taking into account the refined occupancy of O. The c axis and the degree of non-stoichiometry in the peroxide ion agree well with the findings of Roth, Rawn & Hill for BaO_2 which had been quenched in air from 923 K. But if there is missing peroxide, there must be

Table 1. Final atomic coordinates, thermal parameters (Å^2) and occupancies, with e.s.d.'s in parentheses

	x	y	z	Occupancy		
Ba	0	0	0	1.0		
O	0	0	0.3907 (7)	0.88 (5)		
	B_{11}/B_{iso}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba	0.37 (1)	0.37	0.69 (2)	0	0	0
O	0.8 (1)					

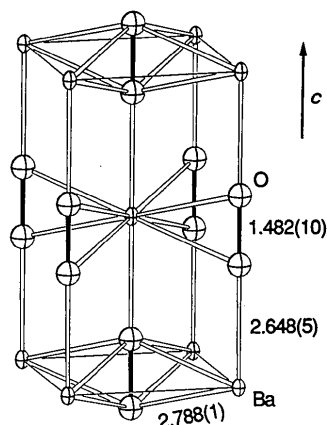


Fig. 1. ORTEP view of unit cell of BaO_2 . Peroxide bonds are shaded; Ba—O bonds are unshaded. Thermal ellipsoids are drawn at the 75% probability level.

oxide ions to balance the charge. The formula would then be approximately $\text{BaO}_{0.25}(\text{O}_2)_{0.75}$. The oxide ion might be expected to occupy the position 0.0,0.0,0.5, as in the rocksalt structure of BaO . However, that site showed a difference Fourier peak of only $0.46 \text{ e } \text{Å}^{-3}$, and an atom could not be refined there. From this, we can conclude that either the compound is stoichiometric (or nearly so), or the oxide ions occupy one of the oxygen sites of the peroxide ion they displace, leaving the Ba atom above or below with an incomplete coordination sphere. Owing to the large error on the O occupancy, these two possibilities cannot be distinguished. The author eagerly awaits the results of the neutron powder diffraction analysis of BaO_{2-x} mentioned by Roth, Rawn & Hill to clarify the nature of the non-stoichiometry.

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* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55641 (2 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1011]