Journal of Solid State Chemistry **147,** 478–484 (1999)
Article ID jssc.1999.8402, available online at http://www.idealibrary.com on IDEAL®

Structural Properties of Nonstoichiometric Barium and Strontium Peroxides: BaO_{2-x} $(1.97 \geq 2-x \geq 1.72)$ and SrO_{2-x} $(1.98 \geq 2-x \geq 1.90)$

Markus Königstein[1]

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

Received May 12, 1998; in revised form May 24, 1999; accepted June 16, 1999

The crystal structures of eight single crystals of barium and strontium peroxide, prepared by high pressure–high temperature synthesis, were determined by X-ray diffraction. The crystallographic data were successfully refined in the calcium carbide structure (space group $I4/mmm$, $Z=2$). The results clearly indicate that the peroxides are nonstoichiometric compounds, MO_{2-x} (M=Ba, Sr), with a peroxide deficiency and that oxide ions are present on interstitial lattice sites. The composition rage extends from near stoichiometry to compounds with a total oxygen content of 1.72 in the barium and 1.90 in the strontium peroxide. We find that the oxide ions, replacing the peroxide molecular ions, occupy an interstitial position that is in the middle of the replaced peroxide molecular ion. A decrease of the peroxide content in the crystals results in a decreased *c*-axis of the tetragonal unit cell of the structure, while the *a*-axis is almost constant. Furthermore, the peroxide bond length decreases, as was confirmed by Raman spectroscopy. © 1999 Academic Press

INTRODUCTION

In recent years there has been considerable interest in both the structures and the stabilities of the alkaline earth metal peroxides. Barium and strontium peroxide have been known for a long time, and their crystal structures were first derived by Bernal *et al.* (1) in 1935 on the basis of powder diffraction data; they possess a tetragonally distorted rock salt structure, usually referred to as the calcium carbide structure—space group $I4/mmm$. The metal ions occupy the regular cation positions and the peroxide dumbbells (O_2^{2-}) are centered on the anion sites, while their alignment is along one of the unit cell axes (*c*-axis) leading to the observed tetragonal distortion, as shown in Fig. 1. Although Bernal's structural model is essentially correct, some refinement is needed: thermoanalytical measurements (2, 3) suggest that barium peroxide is a nonstoichiometric compound, as is supported by the recent single crystal X-ray structure determinations on the compound by VerNooy (4) and on strontium peroxide by Range *et al.* (5), although due to the high standard deviations of the compositions of the peroxide crystals in the two studies this finding cannot be confirmed with certainty. Furthermore, in neither of these studies was it possible to prove the presence of oxide ions in the crystal lattice, as is required for nonstoichiometric compounds. Moreover, we have the single crystal X-ray study by Wong-Nog *et al.* (6), which suggests a stoichiometric composition for barium peroxide. In view of this uncertainty, we have undertaken a systematic study of several single crystals of barium and strontium peroxide to clarify the questions concerning the nonstoichiometry in these materials. An additional aim of our work is to obtain accurate values of the peroxide bond length, as the values reported by Bernal are clearly too short (ca. 1.3 Å) and as the peroxide bond length might depend on the exact composition of the nonstoichiometric peroxides.

EXPERIMENTAL

Sample Preparation

Standard high pressure–high temperature synthesis was conducted using starting materials of "BaO_2"[2] (Merck, p.a.), BaO, "SrO_2," and SrO (Alfa, 99.5%). BaO was prepared using $Ba(NO_3)_2$ (Merck, p.a.) as starting material (7), and "SrO_2" was prepared by the oxidizing of $Sr(NO_3)_2$ using H_2O_2 (8). In order to prepare single crystals of nonstoichiometric barium and strontium peroxides with different compositions, BaO and "BaO_2" or SrO and "SrO_2" were carefully mixed using varying ratios of the oxide and the peroxide; afterward the mixture was placed in a platinum crucible. Each reaction was performed in the modified Belt-apparatus (9) at 10 kbar and 1400–1800°C for 30 min on average. After slowly reducing the temperature by 200–300°C within approximately 30 min, the sample was quenched to ambient pressure and temperature.

---

[1] Present address: Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albermarle Street, London W1X 4BS, U.K.

[2] The quotation marks are used to indicate that the compound is nonstoichiometric.

0022-4596/99 $30.00

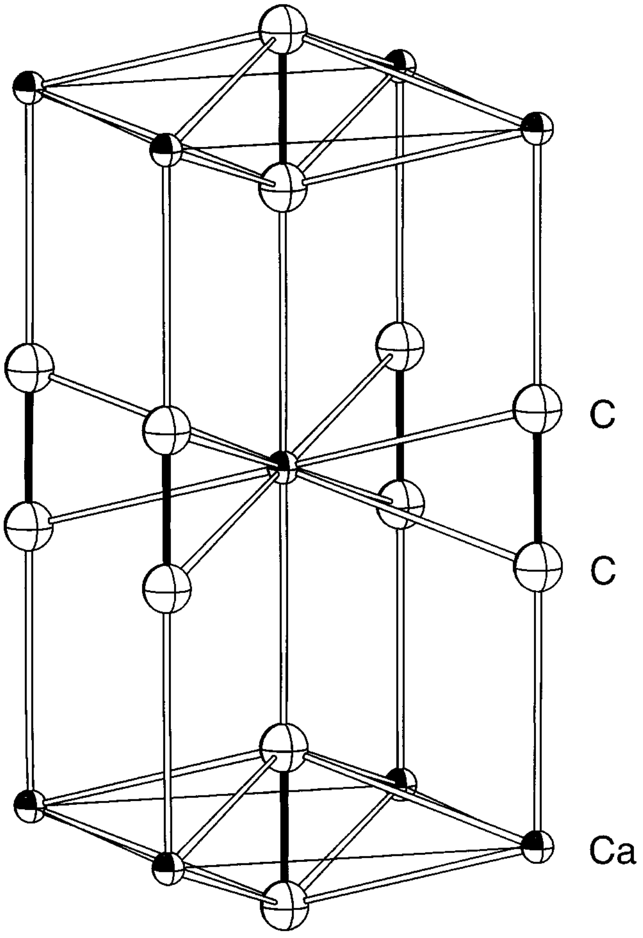

FIG. 1. The calcium carbide structure.

The preparation of near stoichiometric barium and strontium peroxide single crystals followed the same procedure, except that the peroxide powders ("BaO_2" or "SrO_2") were not mixed with the corresponding oxides, but with $KClO_3$ (Merck, reinst.) as on oxidizing reagent. Furthermore, after the reaction was performed in the modified Belt-apparatus, the reaction mixture was cooled down to lower temperatures (400°C for the barium compound and 800°C for the storntium compound) before it was quenched. We emphasise that, for all reactions performed, the mixing of the starting materials, as well as the examination of the products and the selection of the single crystals, was done in a glove box under an argon atmosphere, as the nonstoichiometric peroxide crystals are air and moisture sensitive. Furthermore, the starting materials were stored in the glove box under an argon atmosphere. Powder X-ray diffractometry of a part of some of the reaction products revealed that they were mixtures of the nonstoichiometric peroxides and their corresponding oxides, respectively, of the almost stoichiometric peroxides and KCl. For the single crystal X-ray studies, white single crystals of the peroxides were separated in the glovebox from the surrounding powder and put in Mark-tubes which were sealed afterward.

Single Crystal X-Ray Diffraction

Single crystals suitable for the study were selected from tens of candidates by Weissenberg camera work, since most of the single crystals selected in the glove box had considerable amounts of powder attached to them and since some of the crystals were twinned. Suitable single crystals (in Mark-tubes) were mounted on the Enraf-Nonius CAD-4 four circle single crystal X-ray diffractometer with monochromatized Mo$K\alpha$ radiation (graphite monochromator). Data collection was undertaken at room temperature (296 K) using the ω-2θ scanning method, where three standard reflections were monitored every 200 reflections so as to give no significant intensity deviations. The compounds were confirmed to have the I-centered tetragonal system. Data were collected for five single crystals of barium peroxide and three single crystals of strontium peroxide of varying peroxide composition.

Crystal Structure Refinement

The structures were refined in the space group $I4/mmm$ ($Z = 2$), and the least squares refinement method (on F^2) as implemented in the program SHELXL93 (10) was applied. After the structures were refined, using isotropic temperature factors, numerical absorption corrections were performed using the program package DIFABS (11), and, finally, the structures were refined using anisotropic temperature factors. However, in the case of the two barium peroxide single crystals that show large deviations of the stoichiometric composition, only the barium ions were refined using anisotropic temperature, as the refinements that included anisotropic temperature factors for the oxygen ions became unstable, probably due to poor quality of the crystals. Extinction corrections were applied, details of which can be found in the SHELXL93 manual (10).

Details of the crystal data, data collections, and structure refinements are given in Table 1, while Table 2 shows the atomic parameters, isotropic and anisotropic temperature factors, and site occupancies for the refined structures.

RESULTS AND DISCUSSION

Nonstoichiometry in Barium and Strontium Peroxide

The site occupancies of the O^- ions (of the peroxide molecular ion O^-–$O^- = O_2^{2-}$) in barium and strontium peroxide, which are reported in Table 2, show that these materials are nonstoichiometric: the position 4e in the space group $I4/mmm$ occupied by the O^- ions is not fully occupied for any of the eight crystals of barium or strontium peroxide (for which the standard deviations are small

TABLE 1
Single Crystal Data Collection and Refinement of Nonstoichiometric Barium and Strontium Peroxide Crystals

Crystal data								
Chemical formula[a]	$BaO_{1.97}$	$BaO_{1.94}$	$BaO_{1.86}$	$BaO_{1.79}$	$BaO_{1.72}$	$SrO_{1.98}$	$SrO_{1.96}$	$SrO_{1.90}$
Space group	$I4/mmm$	$I4/mmm$	$I4/mmm$	$I4/mmm$	$I4/mmm$	$I4/mmm$	$I4/mmm$	$I\ 4/mmm$
Z	2	2	2	2	2	2	2	2
a (Å)	3.8059(2)	3.8071(3)	3.8096(2)	3.8085(2)	3.8076(3)	3.5630(2)	3.5619(3)	3.5585(4)
c (Å)	6.837(2)	6.816(1)	6.780(1)	6.6986(6)	6.621(2)	6.616(1)	6.576(1)	6.563(1)
V (Å^3)	99.03(3)	98.80(2)	98.39(2)	97.16(1)	96.00(3)	83.99(2)	83.42(2)	83.10(2)
μ (mm^{-1})	19.62	19.66	19.74	19.98	20.22	31.59	31.80	31.91
Size (μm^3)	$80 \cdot 80 \cdot 10$	$40 \cdot 40 \cdot 40$	$40 \cdot 40 \cdot 40$	$40 \cdot 80 \cdot 120$	$120 \cdot 80 \cdot 40$	$20 \cdot 40 \cdot 60$	$40 \cdot 40 \cdot 40$	$40 \cdot 40 \cdot 40$
Data collection								
Radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
Scan technique	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Scan width $\Delta\omega$(°)	$0.6 + 0.35 \tan\theta$	$0.7 + 0.35 \tan\theta$	$0.6 + 0.35 \tan\theta$	$0.6 + 0.34 \tan\theta$	$0.7 + 0.35 \tan\theta$	$0.9 + 0.35 \tan\theta$	$0.7 + 0.35 \tan\theta$	$0.7 + 0.35 \tan\theta$
$2\theta_{max}$ (°)	130	100	130	130	100	100	60	60
h	$0 \le h \le 9$	$0 \le h \le 8$	$0 \le h \le 9$	$0 \le h \le 9$	$0 \le h \le 8$	$-7 \le h \le 7$	$0 \le h \le 4$	$0 \le h \le 4$
k	$0 \le k \le 9$	$0 \le k \le 8$	$0 \le k \le 9$	$-9 \le k \le 9$	$0 \le k \le 8$	$-7 \le k \le 7$	$0 \le k \le 4$	$0 \le k \le 4$
l	$-17 \le l \le 17$	$-14 \le l \le 14$	$-17 \le l \le 15$	$0 \le l \le 16$	$-14 \le l \le 6$	$-14 \le l \le 14$	$-9 \le l \le 9$	$-9 \le l \le 9$
No. of reflections measured	971	617	960	942	467	1726	157	157
Absorption correction	DIFABS	DIFABS	DIFABS	DIFABS	DIFABS	DIFABS	DIFABS	DIFABS
T_{min}	0.607	0.557	0.684	0.433	0.413	0.689	0.399	0.434
T_{max}	1.250	1.723	1.403	3.392	3.012	1.420	2.310	1.440
$T_{average}$	0.934	0.933	0.941	1.231	1.262	1.010	0.930	0.900
No. of independent reflections	283	181	282	279	175	155	50	50
R_{int}	7.75%	11.22%	8.63%	4.17%	4.53%	9.01%	5.05%	6.42%
Refinement (on F^2)								
No. of parameters refined	8	8	8	9	8	8	8	8
$\Delta_{max} \cdot \sigma^{-1}$	≤ 0.001	≤ 0.001	≤ 0.001	≤ 0.001	≤ 0.001	≤ 0.001	≤ 0.001	≤ 0.001
$\Delta\rho_{max}$ ($e \cdot$ Å^{-3})	6.54	4.04	6.22	3.01	4.28	0.98	0.65	0.82
$\Delta\rho_{max}$ ($e \cdot$ Å^{-3})	-11.07	-6.95	-7.09	-3.75	-7.86	-0.96	-0.58	-0.90
$R1$ [$F_0 > 4 \cdot \sigma(F_0)$]	2.95%	3.50%	3.14%	2.43%	3.91%	2.09%	1.58%	2.61%
w$R2$ [$w = 1/(\sigma^2(F_0^2) + (A \cdot P)^2 + B \cdot P)$; $P = \max(0, F_0^2)/3 + 2/3 \cdot F_c^2$	6.93%	4.50%	4.57%	4.83%	10.21%	2.65%	2.62%	3.48%
Weighting scheme A	0.0249	0.0060	0.0116	0.0192	0.0512	0.0000	0.0000	0.0000
Weighting scheme B	0.0000	0.0000	0.0000	0.0000	0.9085	0.0000	0.0000	0.0000
S	1.248	1.062	1.072	1.226	1.260	1.366	0.952	0.932
Extinction parameter	0.015(1)	0.0021(5)	0.0324(9)	0.013(1)	—	0.0064(7)	0.014(1)	0.009(2)

[a] The oxygen content refers to the total oxygen content. It is calculated from the peroxide site occupancy reported in Table 2 using the condition of charge neutrality.

compared to the peroxide deficiencies). Even the crystals prepared under extremely high oxygen pressure (by oxidation with $KClO_3$) are not fully stoichiometric, but exhibit a small peroxide deficiency in their crystal lattice.

As a consequence of the incomplete occupancy of the peroxide position, oxide ions must be present in the crystal lattice of the nonstiochiometric peroxides, as indeed confirmed by our refined coordinates (Table 2): oxide ions can clearly be seen at the position 2*b* in the space group $I4/mmm$ on those crystals of barium peroxide that show the largest deviation from stoichiometry. We note that the 2*b* position of the oxide ions corresponds to the regular positions of the anions in the rock salt structure. The inability to refine the positions of oxide ions in the other crystals of barium and strontium peroxides is clearly due to the small deviation from the stoichiometric composition in these crystals: a relatively small concentration of oxide ions cannot be detected by single crystal X-ray studies when heavy atoms like barium or strontium are present in the crystal.

We calculate the total oxygen content, $2 - x$, in the nonstoichiometic peroxides MO_{2-x} (M = Ba, Sr) and assume for this purpose that the *peroxide* site occupancies reported in Table 2 are accurate; indeed the standard deviations of all the peroxide site occupancies are considerably smaller than those of the oxide site occupancies. This assumption is necessary since oxide ions could not be refined in every crystal investigated and since the standard deviations of the oxide ions in the two highly nonstoichiometric barium peroxide crystals are also relatively large, as is evident from Table 2.

Simple considerations show us that the oxide content is equal to x and the peroxide content is equal to $2 - 2x$ in MO_{2-x} ($2 - x$ is the total oxygen content), and they enable us to calculate the total oxygen content in the nonstoichiometric peroxides MO_{2-x}: the chemical formulas given in the first rows of Tables 1–3 refer to this total oxygen content and, as noted, are calculated from the assumption that the peroxide content is correctly given by the site

TABLE 2
Refined Atomic Parameters, Isotropic and Anisotropic Temperature Factors, and Site Occupancies

Chemical formula[a]	$BaO_{1.97}$	$BaO_{1.94}$	$BaO_{1.86}$	$BaO_{1.79}$	$BaO_{1.72}$	$SrO_{1.98}$	$SrO_{1.96}$	$SrO_{1.90}$
Position of M (M = Ba or Sr)	2*a*	2*a*	2*a*	2*a*	2*a*	2*a*	2*a*	2*a*
Occupancy of M	1	1	1	1	1	1	1	1
U_{eq} (Å^2)	0.01061(3)	0.01013(4)	0.00978(2)	0.01119(2)	0.01372(5)	0.00875(2)	0.01175(8)	0.0140(1)
$U_{11} = U_{22}$ (Å^2)	0.01052(3)	0.01002(5)	0.00961(3)	0.01093(2)	0.01242(5)	0.00794(2)	0.01147(9)	0.0138(1)
U_{33} (Å^2)	0.01078(5)	0.01035(8)	0.01014(5)	0.01170(4)	0.0163(1)	0.01037(4)	0.0123(2)	0.0146(2)
$U_{12} = U_{13} = U_{23}$ (Å^2)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Position of O^-	4*e*	4*e*	4*e*	4*e*	4*e*	4*e*	4*e*	4*e*
z (O^-)	0.3908(3)	0.3912(3)	0.3908(2)	0.3904(3)	0.3903(9)	0.3879(1)	0.3895(3)	0.3896(4)
Occupancy of O^-	0·9720(80)	0.9416(56)	0.8616(48)	0.7856(64)	0.7192(160)	0.9776(24)	0.9616(40)	0.9008(64)
U_{eq} (Å^2)	0.0142(3)	0.0140(4)	0.0120(3)	0.0157(2)	0.0195(7)	0.0153(1)	0.0208(5)	0.0186(7)
$U_{11} = U_{22}$ (Å^2)	0.0173(4)	0.0170(6)	0.0150(3)	—	—	0.0199(2)	0.0264(7)	0.0240(9)
U_{33} (Å^2)	0.0082(5)	0.0079(8)	0.0060(5)	—	—	0.0063(2)	0.0096(8)	0.008(1)
$U_{12} = U_{13} = U_{23}$ (Å^2)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Position of O^{2-}	—	—	—	2*b*	2*b*	—	—	—
Occupancy of O^{2-}	—	—	—	0.1104(80)	0.3808(352)	—	—	—
U_{eq} (Å^2)	—	—	—	0.015(2)	0.043(5)	—	—	—

[a] The oxygen content refers to the total oxygen content. It is calculated from the peroxide site occupancy (occupancy of O^-) using the condition of charge neutrality.

occupancies of the O^- ions. The formulas show that the deviation from stoichiometry extends from the nearly stoichiometric composition to 1.72 ($1.97 \geq 2 - x \geq 1.72$) in barium peroxide BaO_{2-x} and from the nearly stoichiometric composition to 1.90 ($1.98 \geq 2 - x \geq 1.90$) in strontium peroxide SrO_{2-x}. We recall that the experimental conditions for the preparation of the single crystals were varied in order to prepare single crystals with a very high deviation from the stoichiometric composition, but it was not possible to prepare single crystals of barium or strontium peroxide with a total oxygen composition that was lower than 1.72 or 1.90, respectively. Therefore, it is unlikely that barium and strontium peroxide can show considerably larger deviations from the stoichiometric composition found in $BaO_{1.72}$ and in $SrO_{1.90}$, where, respectively, 28 or 10% of the peroxide ions are replaced by oxide ions in the crystal lattice. It follows from these considerations, first, that the deviation from the stoichiometric composition can be larger in barium than in strontium peroxide and, second, that barium and strontium peroxide do not form a continuous series of solid solutions with the corresponding oxide.

Variation of the Peroxide Bond Length and the c-Axis

We consider now the peroxide bond length in the nonstoichiometric peroxides in more detail: it is obvious from Table 3 that the bond lengths are not constant in the materials, but they decrease with decreasing oxygen content in the crystals; i.e., the peroxide bond length is correlated with the composition of the nonstoichiometric peroxides. This interesting result of the single crystal X-ray studies is confirmed also by Raman spectroscopic measurements which are reported in the Appendix for the nonstoichiometic barium and strontium peroxides. Figure 2 shows for nonstoichiometric barium peroxide that the peroxide bond length is (approximately) a linear function of the total oxygen content in the crystal.

If we turn our attention now to the unit cell axes (Table 1), then we can see that the *a*-axis of all crystals of both barium and strontium peroxide is nearly constant, while the *c*-axis decreases with decreasing peroxide content. This is expected from the crystal structure of the stoichiometric peroxides shown in Fig. 1: the peroxide dumbbells (O_2^{2-}) are aligned along the *c*-axis, and replacing some of them by the smaller,

TABLE 3
Bond Distances (in Å) in the Nonstoichiometric Barium and Strontium Peroxide Crystals

Chemical formula[a]	$BaO_{1.97}$	$BaO_{1.94}$	$BaO_{1.86}$	$BaO_{1.79}$	$BaO_{1.72}$	$SrO_{1.98}$	$SrO_{1.96}$	$SrO_{1.90}$
O^-–O^-	1.493(3)	1.484(4)	1.481(3)	1.468(4)	1.452(12)	1.483(1)	1.453(3)	1.450(5)
M–O^- (M = Ba or Sr) (2x)	2.672(2)	2.666(2)	2.649(2)	2.615(2)	2.584(6)	2.5665(8)	2.561(2)	2.557(2)
M–O^- (M = Ba or Sr) (8x)	2.7928(5)	2.7924(6)	2.7938(4)	2.7913(5)	2.789(2)	2.6263(2)	2.6214(5)	2.6186(7)
M–O^{2-} (M = Ba or Sr)	—	—	—	2.6930(1)	2.6924(2)	—	—	—

[a] The oxygen content refers to the total oxygen content. It is calculted from the peroxide site occupancy reported in Table 2 using the condition of charge neutrality.

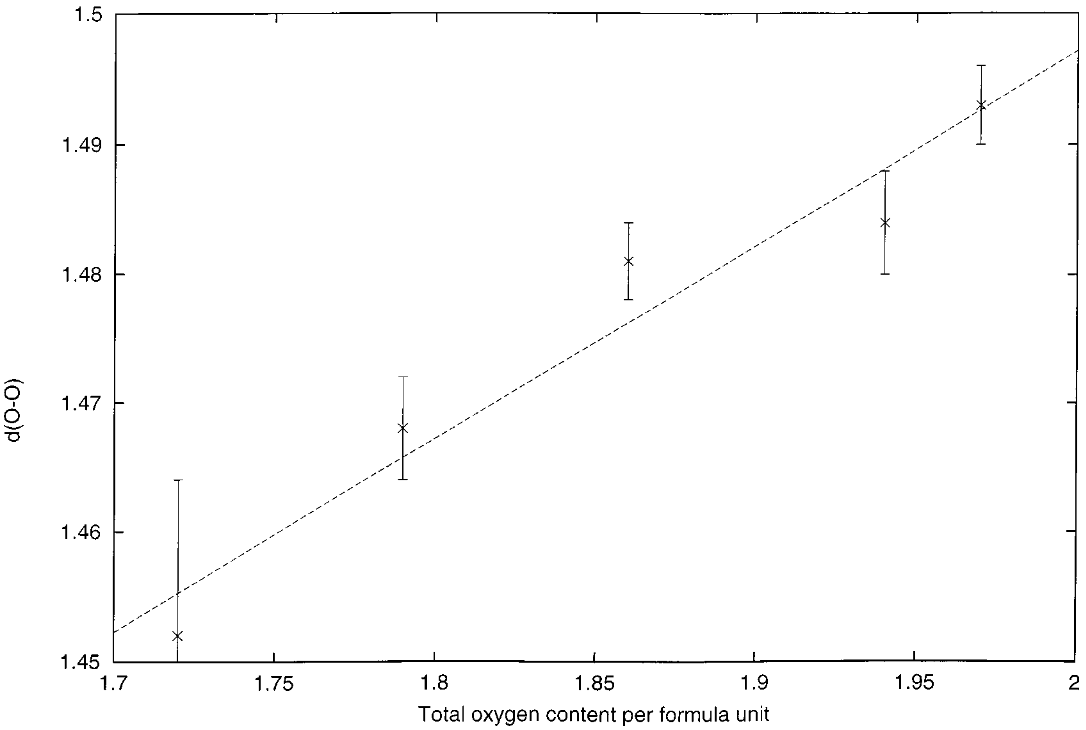

FIG. 2. Variation of the peroxide bond length, *d*(O–O) in anstroms, of nonstoichiometric barium peroxide with the total oxygen content in the crystal. The error bars show the standard deviation of the peroxide bond length.

spherical oxide ions should result in decrease of the *c*-axis, while the *a*-axis should be nearly constant as the diameter of the peroxide ions along the [100] direction is approximately comparable with that of the spherical oxide ions. Figure 3 demonstrates, for the barium compound, that the length of the *c*-axis is approximately a linear function of the total

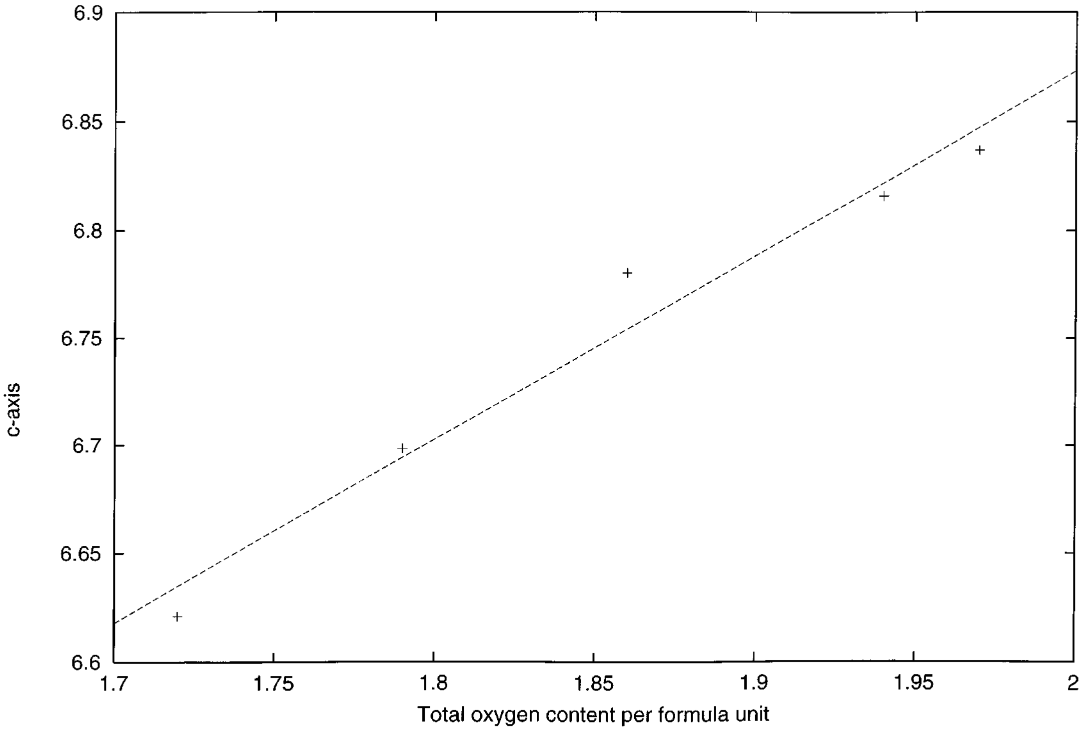

FIG. 3. Variation of the length of the unit cell *c*-axis of nonstoichiometric barium peroxide in anstroms with the total oxygen content in the crystal.

TABLE 4

Summary of the Lattice Parameters *a* and *c*, and Unit Cell Volume *V*, the Peroxide Bond Length *d*(O–O), the Peroxide Content and the Total Oxygen Content per Formula Unit of the Five Crystals of Nonstoichiometric Barium Peroxide BaO_{2-x} Investigated

No.	*a* (Å)	*c* (Å)	*V* (Å^3)	*d*(O–O) (Å)	Peroxide content	Total oxygen content
1	3.8059(2)	6.837(2)	99.03(3)	1.493(3)	1.94(2)	1.97
2	3.8071(3)	6.816(1)	98.80(2)	1.484(4)	1.88(1)	1.94
3	3.8096(2)	6.780(1)	98.39(2)	1.481(3)	1.72(1)	1.86
4	3.8085(2)	6.6986(6)	97.16(1)	1.468(4)	1.57(1)	1.79
5	3.8076(3)	6.621(2)	96.00(3)	1.452(12)	1.44(3)	1.72

oxygen content of the nonstoichiometric barium peroxide, and Table 4 gives, for the five barium peroxide single crystals, a concise summary of some of the most important results of the X-ray investigations and demonstrates also that the *c*-axis and the peroxide bond length decrease with a decreasing peroxide content or a decreasing total oxygen content.

Finally, we compare the results for the nonstoichiometric barium peroxide crystals with those of the single crystal X-ray study of VerNooy (4) and those of Wong-Ng *et al.* (6). The results of VerNooy ($a = 3.8016(4)$ Å, $c = 6.7786(8)$ Å, $Ba(O_2)_{1.76(10)/2}$, $d(O\text{–}O) = 1.482(10)$ Å) are in very good agreement with those reported here: we would expect, according to Fig. 2 and Fig. 3, for a total oxygen content of 1.88 (corresponding to a peroxide content of 1.76), values of the peroxide bond length and of the length of the *c*-axis that are very close to those reported by VerNooy. On the other hand, it is likely that the crystal of Wong-Ng *et al.* ($a = 3.8114(6)$ Å, $c = 6.822(1)$ Å, $BaO_{2.00}$ $d(O\text{–}O) =$ 1.493(2) Å) is probably not stoichiometric $BaO_{2.00}$, because we would expect a *c*-axis of 6.873 Å for the stoichiometric compound (Fig. 3).

CONCLUSIONS

The single crystal X-ray diffraction results clearly indicate that barium and strontium peroxide are nonstoichiometric compounds with a peroxide deficiency and oxide ions present on intersititial sites. The composition range extends from near-stoichiometry to compounds with a total oxygen content of 1.72 in the barium and 1.90 in the strontium peroxide. We find that the oxide ions, present in the lattice for reasons of charge neutrality, occupy a position that is in the middle of the replaced peroxide molecular ion. The decrease of the peroxide content in the crystals results in a decreased *c*-axis of the tetragonal unit, while the *a*-axis is almost constant. Furthermore, the peroxide bond length decreases as well.

A subsequent paper will explore the structures and energetics of these nonstoichiometric peroxides using computational methods, based on density functional theory, which we will show can rationalize many of the experimental observations reported in the present study.

TABLE 5

Variation of the Raman Frequencies, $\tilde{\nu}$, of the O^-–O^- Stretching Vibration with Changing Oxygen Content in Samples of Nonstoichiometric Barium and Strontium Peroxide

Nonstoichiometric peroxide	*c* (Å)	ν (cm^{-1})^d
BaO_{2-x}^{a}	6.85	843
BaO_{2-x}^{b}	6.77	851
SrO_{2-x}^{c}	6.62	865
SrO_{2-x}^{b}	6.58	873

Note. The length of the unit cell *c*-axis of the samples is a measure of their oxygen content.

[a] Barium peroxide from Merck, p.a.

[b] Prepared through high pressure–high temperature synthesis.

[c] Prepared by the oxidizing of strontium nitrate through H_2O_2 (8).

[d] The Raman spectra were recorded using Spex and Dilor XY spectrometers, which have a limit of resolution of 3 cm^{-1}.

APPENDIX

In order to confirm the result of the single crystal X-ray analysis, that the peroxide bond length in nonstoichiometric barium and strontium peroxide is dependent on the oxygen content of the samples, we measured Raman spectra of barium peroxide from Merck (p.a.), of strontium peroxide prepared by oxidising strontium nitrate through H_2O_2, and of one sample of barium and one sample of strontium peroxide prepared through high presure–high temperature

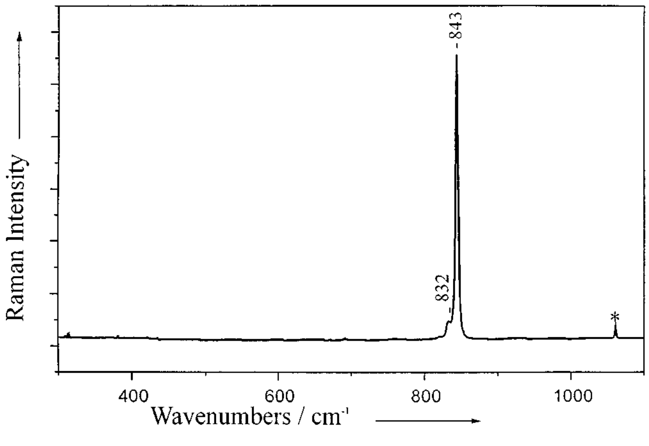

FIG. 4. Raman spectrum of barium peroxide powder from Merck (p.a.). The unit cell *c*-axis of the sample is 6.85 Å and indicates that the sample is almost stoichiometric barium peroxide. The very strong and sharp peak at 843 cm^{-1} corresponds to the O^-–O^- stretching vibration, while the weak shoulder at 832 cm^{-1} is from the O^-–O^- stretching vibration of a small amount of hydrated species present (13). The peak marked with an asterisk is due to carbonate impurities.

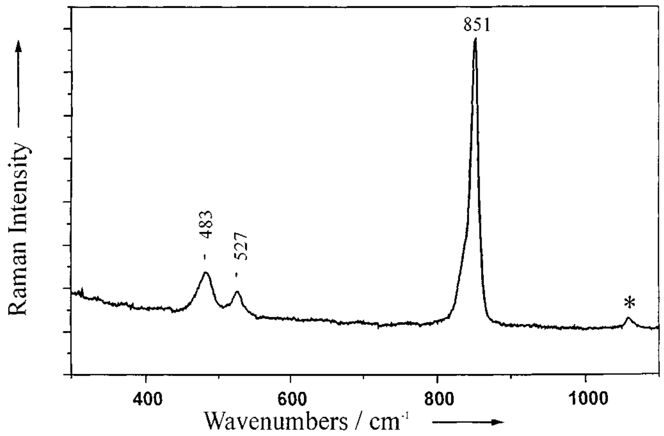

FIG. 5. Raman spectrum of barium peroxide powder prepared through high pressure–high temperature synthesis. The unit cell *c*-axis of the sample is 6.77 Å and indicates that the sample is clearly non-stoichiometric barium peroxide. The very strong and sharp peak at 851 cm^{-1} corresponds to the O^{-}–O^{-} stretching vibration, while the broad and weak peaks at 527 and 483 cm^{-1} are due to BaO (14), which was one of the starting materials of the synthesis. The peak marked with an asterisk is due to carbonate impurities.

synthesis. We recorded also the powder diffraction pattern of each of the four samples in order to determine the lengths of the unit cell *c*-axis of each sample, which is a direct measure of the peroxide content in the sample. The important results of the Raman and X-ray measurements are summarized in Table 5, while the Raman spectra of the two barium peroxide samples can be seen in Figs. 4 and 5; the spectra of the two strontium peroxide samples are similar and are reported elsewhere (12).

The peroxide stretching frequency of the sample of non-stoichiometric barium (strontium) peroxide, that was prepared through high pressure–high temperature synthesis, is 8 cm^{-1} higher than that of the other sample of barium (strontium) peroxide, which indicates clearly a change in the peroxide bond lengths and therefore confirms nicely the single crystal X-ray results that predict a shorter peroxide bond length for the samples of peroxide that have a smaller oxygen content compared to samples with a higher oxygen content.

ACKNOWLEDGMENTS

The author would like to thank Prof. K.-J. Range very much for his constant interest in this work, for many useful and helpful discussions, and for the possibility of performing all the experiments and measurements at his institute at the University of Regensburg. Mrs. D. De Waal is thanked for measuring the Raman spectra, and Prof. C. R. A. Catlow is gratefully acknowledged for advice regarding the text of the paper.

REFERENCES

1. J. D. Bernal, E. Diatlova, I. A. Kazarnovskii, and S. Reichstein, *Z. Kristallogr. A* **92,** 344 (1935).
2. A. F. Mayorova *et al.*, *Thermochim. Acta* **217,** 241 (1993).
3. R. S. Roth, C. J. Rawn, and M. D. Hill, NIST Special Publication 804, p. 225, 1991.
4. P. D. VerNooy, *Acta Crystallogr. C* **49,** 433 (1993).
5. K.-J. Range, F. Rau, U. Schiessl, and U. Klement, *Z. Anorg. Allg. Chem.* **620,** 879 (1994).
6. W. Wong-Ng and R. S. Roth, *Physica C* **233,** 97 (1994).
7. G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Band 2, p. 925. Ferdinand Enke Verlag, Stuttgart, 1978.
8. M. Centnerszwer, M. Blumenthal, *Bull. Int. Acad. Pol. Sci. Lett. Cl. Sci. Math. Nat. Ser. A*, 540 (1935).
9. K.-J. Range and R. Leeb, *Z. Naturforsch. B* **30,** 889 (1975).
10. G. M. Sheldrick, "Program for the Refinement of Crystal Structures," Göttingen, 1993.
11. N. Walker and D. Stuart, *Acta Crystallogr. A* **39,** 158 (1983).
12. M. Königstein, Dissertation, Universität Regensburg, 1996.
13. H. H. Eysel and S. Thym, *Z. Anorg. Allg. Chem.* **411,** 97 (1975).
14. K. H. Rieder, B. A. Weinstein, M. Cardona, and H. Bilz, *Phys. Rev. B* **8,** 4780 (1973).