On the Space Group of Cesium Perbromate, $CsBrO_4$

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Cesium Perbromate, Space Group, Crystal Structure

The correct space group of cesium perbromate, $CsBrO_4$, is $I4_1/amd$ and not $I4_1/a$ as previously reported. The compound is isostructural with α-$CsReO_4$, the high-temperature modification of cesium perrhenate. By analogy with $CsReO_4$ and $CsIO_4$, a phase transformation to a low-temperature modification is predicted for $CsBrO_4$.

Gebert, Peterson, Reiss and Appelman [1] reported the crystal structure of cesium perbromate as determined from single-crystal X-ray data. These authors found a tetragonal unit cell with $c/a = 2.577$ and $Z = 4$. They observed the extinction conditions $h+k+l \neq 2n$ for hkl, $h(k) \neq 2n$ for $hk0$ and $l \neq 4n$ for $00l$ and therefore refined the structure in space group $I4_1/a$, obviously assuming that $4/m$ was the correct Laue class.

We determined recently the crystal structure of α-$CsReO_4$, the high-temperature modification of cesium perrhenate [2]. For this compound a tetragonal unit cell was found as well with $c/a = 2.423$ and $Z = 4$, *i.e.* very similar to that of $CsBrO_4$. The space group of α-$CsReO_4$, however, was unambiguously confirmed to be $I4_1/amd$ from Laue class ($4/mmm$) and extinction conditions ($h+k+l \neq 2n$ for hkl, $h(k) \neq 2n$ for $hk0$ and $2h+l \neq 4n$ for hhl). The reported crystal structures of $CsBrO_4$ and α-$CsReO_4$ are almost identical. We suspected therefore that space group $I4_1/amd$ might be the correct one for $CsBrO_4$ as well.

An inspection of the positional parameters published by Gebert *et al.* [1] shows indeed that the x parameter for oxygen in the general position 16f of space group $I4_1/a$ is equal to zero within less than one standard deviation. This parameter is constrained to $x = 0$ for the 16h position in $I4_1/amd$.

We repeated the structure refinement for $CsBrO_4$ in space group $I4_1/amd$, using the F_{obs} values given in Table 3 of ref. [1]. The results can be summarized as follows:

i) The differences between the F_{obs} values for hkl- and khl-reflections are small (generally less than 5%) in accordance with Laue class $4/mmm$.

ii) hhl-reflections violating the extinction rule $2h+l \neq 4n$ have generally the lowest F_{obs} values in the structure factor list given in [1], pointing towards space group $I4_1/amd$. Unfortunately, Gebert *et al.* gave no standard deviations for the measured F values so that no evaluation statistics can be made. It should be noted, however, that the F_{calc} values for all hhl reflections with $2h+l \neq 4n$ are calculated as zero or almost zero by Gebert *et al.*

iii) The results of the least-squares refinement in $I4_1/a$ and $I4_1/amd$ are virtually identical (Table I).

Table I. Comparison of the structure refinements for $CsBrO_4$ in space groups $I4_1/a$ and $I4_1/amd$.

Tetragonal, $a = 5.751(4)$ Å, $c = 14.821(12)$ Å, $c/a = 2.577$, $Z = 4$

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}*
Space group $I4_1/a$ [1]										
Cs	4a	0	0	0	0.031(1)	U_{11}	0.027(1)	0	0	0
Br	4b	0	0	1/2	0.029(1)	U_{11}	0.027(1)	0	0	0
O	16f	0.0002(13)	0.2307(11)	0.4385(5)	0.053(4)	0.058(4)	0.079(4)	0.003(3)	0.004(2)	0.040(4)
Space group $I4_1/amd$**										
Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs	4a	0	0	0	0.030	U_{11}	0.029	0	0	0
Br	4b	0	0	1/2	0.029	U_{11}	0.028	0	0	0
O	16h	0	0.2304	0.4391	0.048	0.054	0.085	0	0	0.046

* Calculated from the β values given in ref. [1];
** because no standard deviations for F_{obs} are reported in ref. [1], no standard deviations for the atomic positions and anisotropic dispacement factors can be given.

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No coordinate and no anisotropic displacement parameter in $I4_1/a$ needed to be adjusted by more than two standard deviations in order to satisfy the symmetry requirements of $I4_1$/amd.

This leads us to the conclusion that space group $I4_1$/amd is the correct one for $CsBrO_4$. Since the coordinates are essentially unchanged, the crystallochemical features of the structure remain unaltered, so that the description given in [1] is still valid.

As mentioned above, $CsBrO_4$ is isostructural with α-$CsReO_4$, the high-temperature modification of cesium perrhenate. The phase transformation from the room temperature modification β-$CsReO_4$ (space group Pnma [3]) to α-$CsReO_4$ is of first order [2, 4]. Similar observations have been made in the case of cesium periodate, $CsIO_4$, where a phase transformation of the ferroelastic-paraelastic type takes place at about 150 °C [5–8]. For this compound the exact structural data could not yet be determined due to the limited stability of $CsIO_4$ crystals when exposed to X-rays. We could confirm, however, the diffraction symbol $Pn \cdot a$ for the room temperature modification (which agrees with the space group Pnma for β-$CsReO_4$), as well as a tetragonal unit cell with c/a = 2.393 (a = 6.030(5), c = 14.43(1) Å) for the high-temperature modification, again showing the close similarity to $CsReO_4$. By analogy with $CsReO_4$ and $CsIO_4$, a phase transformation to a low-temperature modification is therefore predicted for $CsBrO_4$. In this respect it might be of importance that the true space group of $CsBrO_4$ is $I4_1$/amd and not $I4_1/a$ because Pnma, the space group expected for the low-temperature modification, is a subgroup (not a maximal one, however) of $I4_1$/amd. In contrast, there are no orthorhombic subgroups of $I4_1/a$.

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