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The Crystal Structures of $BaZnO_2$, $BaCoO_2$ and $BaMnO_2$

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Earth-alkali oxides and bivalent transition-metal oxides will form compounds $AB\mathrm{O}_2$ when the earth-alkali ion is large and the transition-metal ion is small.

In the investigation of the systems Ba–M–O, in which M represents Mn, Co, Ni, Zn and Be, a similarity between the powder diagrams of the compounds $BaCoO_2$, $BaMnO_2$ and the compound $BaZnO_2$ was found.

A crystallographic analysis has been made on a powder diagram of $BaZnO_2$, which results in a model in which the Zn and O ions are arranged in a distorted high (β-) quartz structure, while the Ba ions fill up the widened holes between the O tetrahedra.

This behaviour of the earth alkali metal in $BaZnO_2$ can be compared with that of the alkali metal in $KFeO_2$.

Experimental

Mixtures of $BaCO_3$ and $M^{\mathrm{II}}\mathrm{O}$ or $M^{\mathrm{II}}\mathrm{CO}_3$ weighed in the ratio 1:1 were fired in high vacuum or in a flow of a suitable gas in a resistance furnace at temperatures up to 1100 °C. Completion of the reaction could be checked by loss of weight. MgO was chosen as refractory material to avoid chemical attack by BaO. Crucibles ground from a non-porous single crystal of MgO were used.

The reaction products were obtained under the following conditions:

Mixture 1:1	Atmosphere	Temp. (°C.)	Product	Appearance
$BaCo_3$, $MnCO_3$	H_2	980	$BaMnO_2$	black
$BaCO_3$, $CoCO_3$ or CoO	high vacuum	1010	$BaCoO_2$	black
$BaCO_3$, NiO	high vacuum	1000	$BaNiO_2$	black
$BaCO_3$ or $Ba(NO_3)_2$, ZnO*	N_2	1000	$BaZnO_2$	yellow-white
$BaCO_3$, $BeCO_3$	H_2	1100	$BaBeO_2$	pink-white

* The powder diagram of the reaction product of $Ba(NO_3)_2$ and ZnO giving the clearest, sharpest lines was used in the crystallographic analysis of $BaZnO_2$.

The existence of these compounds was reported by Scholder (1954).

A similarity was found in the powder diagrams of $BaZnO_2$, $BaCoO_2$ and $BaMnO_2$. $BaNiO_2$ gave a different pattern, which showed a good agreement with the results of Lander (1951). A third pattern was found in the case of $BaBeO_2$.

$BaZnO_2$

By Hull's graphical method a satisfying hexagonal indexing could be given to a powder diagram from a Guinier focusing camera. The cell dimensions were $a = 5{\cdot}927 \pm 0{\cdot}005$ and $c = 6{\cdot}707 \pm 0{\cdot}006$ Å. The measured density 5·50 g.cm.$^{-3}$ corresponds with three molecules of $BaZnO_2$ per unit cell.

The lines 110 and 102 were very strong, while 001, 002, 111, 103, 203, 004, 301, 213, 221, 005 and 400 were absent or very weak. The absence of $00l$ with $l \neq 3$ suggested a threefold screw axis. This, together with the correspondence of volume of the unit cell, ratio a/c and number of molecules per unit cell between $BaZnO_2$ and the low (α-)quartz structure made a trial of the space group D_3^4–$P3_121$ (low quartz) worth while.

The threefold positions are:

$$\begin{array}{llll} a & x, 0, \tfrac{1}{3}; & 0, x, \tfrac{2}{3}; & \bar{x}, \bar{x}, 0. \\ b & x, 0, \tfrac{5}{6}; & 0, x, \tfrac{1}{6}; & \bar{x}, \bar{x}, \tfrac{1}{2}. \end{array}$$

The sixfold positions are:

$$\begin{array}{llll} c & x, y, z; & \bar{y}, x-y, \tfrac{1}{3}+z; & y-x, \bar{x}, \tfrac{2}{3}+z; \\ & y, x, \bar{z}; & \bar{x}, y-x, \tfrac{1}{3}-z; & x-y, \bar{y}, \tfrac{2}{3}-z. \end{array}$$

A first trial was made with the Zn ions situated in the a-positions and the Ba ions in the b-positions, scattering effect of the O ions being omitted. The absence or weakness of the lines mentioned above could be accounted for by giving the Ba ions the parameter $x = \tfrac{2}{3}$. A good agreement between observed and calculated intensities could be achieved by giving the metal ions the parameters $x_{\mathrm{Zn}} = 0{\cdot}50$ and $x_{\mathrm{Ba}} = 0{\cdot}65$.

The parameters x, y, z, of the O ions, which occupy the c-positions of the space group $P3_121$ cannot easily be analyzed from a powder diagram. However, an investigation can be made into whether a plausible O-arrangement exists which is compatible with the Zn and Ba parameters already found. When space

Table 1. *X-ray data for* $BaZnO_2$

$10^3 \sin^2\theta$ (obs.)	$10^3 \sin^2\theta$ (calc.)	*hkl*	*I* (obs.)	*I* (calc.)
—	13·6	001	—	0
22·9	23·0	100	3	5
36·1	36·2	101	12	20
—	52·7	002	—	0
69·0	68·9	110	22	25
75·7	75·7	102	30	30
81·9	82·1	111	1	1
91·9	91·8	200	3	5
104·9	105·0	201	8	11
118·7	118·6	003	2	1
121·5	121·6	112	2	4
—	141·6	103	—	0
144·6	144·5	202	11	7
160·9	160·8	210	1	0
174·3	174·0	211	4	14
187·4	187·5	113	3	7
206·5	206·7	300	3	2
210·0	210·4	203	1	1
—	210·9	004	—	0
213·9	213·5	212	6	6
219·3	219·9	301	1	1
233·6	233·9	104	4	5
259·9	259·4	302	1	1
275·3	275·6	220	4	2
279·3	279·4	213	1	1
	279·8	114		1
—	288·8	221	—	0
298·6	298·6	310	2	1
303·0	302·7	204	3	2
311·5	311·8	311	2	7
324·9	325·3	303	2	5
—	328·3	222	—	0
—	329·5	005	—	0
352·2	351·3	312	2	2
	352·5	105		1
—	367·5	400	—	0
371·9	371·7	214	1	3
379·9	380·7	401	2	2

and symmetry rules were taken into account, a suitable O-arrangement was found starting from the high (β-)quartz structure. A model resulted with the O parameters

$$x=0{\cdot}41,\ y=0{\cdot}19,\ z=0{\cdot}15\,,$$

in which the Zn ions are situated in the centre of four O ions.

In this model the Ba ions are surrounded by ten O ions, six of them in a ring at approximately the same height. The distances between the Ba and the O ions vary from 2·64 to 4·36 Å. The Zn ions are surrounded by four O ions in a distorted tetrahedral arrangement. The distance between the Zn and O ions is 1·92 Å. The distances between the O ions vary from 3·02 to 3·19 Å.

Though these O parameters have little quantitative value, they are included in the final intensity calculation. The usual geometrical factors were applied, but absorption and temperature factors were omitted. The results are shown in Table 1.

$BaCoO_2$, $BaMnO_2$

The powder diagram of the compound $BaCoO_2$ could be indexed in the same way as $BaZnO_2$, giving $a=5{\cdot}85$ and $c=6{\cdot}73$ Å. The stronger lines of $BaZnO_2$ appear with the same intensity pattern, so that a similar structure can be assumed.

The X-ray analysis of $BaMnO_2$ was disturbed by the ready decomposition (and probably oxidation) of the product. In most cases BaO reflections could be detected. However, a weak powder diagram could be obtained which showed a resemblance to the $BaZnO_2$ pattern without disturbing lines.

The lines could be given the indices of the strongest $BaZnO_2$ reflections. The possibility that $BaMnO_2$ has a similar structure is not excluded; however, methods should be found to improve the powder diagram of this unstable product.

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