JOURNAL OF SOLID STATE CHEMISTRY 109, 406–409 (1994)

BRIEF COMMUNICATION

On the Alkali-Earth Mercurates, MHgO$_2$

S. N. Putilin,* S. M. Kazakov,* and M. Marezio†

*Chemical Department, Moscow State University, 119899 Moscow, Russia; and †Laboratoire de Cristallographie, CNRS-UJF, BP 166, 38042 Grenoble Cedex, France

Received June 3, 1993; accepted July 22, 1993

During the investigation of the BaO–HgO–CuO system, a new polymorph of BaHgO$_2$ was obtained. This phase was characterized by X-ray powder diffraction, scanning electron microscopy, and EDS analysis. As the SrHgO$_2$ and CaHgO$_2$ counterparts, it crystallizes with the 3R delafossite structure with cell parameters a = 4.097(1), c = 19.348(2), space group $R\bar{3}m$, and Z = 3. It is also shown that the distortion from the 3R delafossite structure, reported for SrHgO$_2$, might be the effect of a merohedral twinning due to stacking faults.

INTRODUCTION

Following the discovery of superconductivity at 94 K in HgBa$_2$CuO$_{4+\delta}$ (1), the phases in the systems MO–HgO–CuO (where M is an alkali-earth element) have gained specific interest. In the MO–HgO binary system, only the mercurates of alkali-earth elements with composition MHgO$_2$ have been reported. In these compounds the alkali-earth cations are surrounded by six oxygen atoms, and the mercury cations are two coordinated.

Soll and Müller-Buschbaum published the synthesis and the structure of BaHgO$_2$ (2) and HgBa$_{0.75}$Sr$_{0.25}$O$_2$ (3). They showed that these phases crystallize in the hexagonal symmetry with a = 6.904, c = 11.970, and space group $P6_322$. In these structures the alkali-earth cations have a trigonal MO_6 prismatic coordination and the Hg cations have a twofold dumbbell coordination. Later, Putilin *et al.* reported the synthesis of CaHgO$_2$ and SrHgO$_2$ compounds (4), and by X-ray powder diffraction data they showed that these compounds crystallize with the delafossite structure (space group $R\bar{3}m$) in which the alkali-earth cations have an octahedral coordination and the Hg cations have a twofold one. Subsequently, Soll and Müller-Buschbaum (5) found that the structure of SrHgO$_2$ should be described in space group $P3_221$. These findings, based on single crystal data, proved that the structure of SrHgO$_2$ is a distorted delafossite.

We report herein the synthesis of BaHgO$_2$ with the delafossite structure. This represents a new polymorph for BaHgO$_2$. We also demonstrate that the discrepancy between single crystal and powder data for SrHgO$_2$ might be due to the presence in the crystals of twinning by merohedry due to stacking faults.

EXPERIMENTAL

The starting materials for the synthesis were BaO$_2$ (95%, Aldrich), HgO (98%, Aldrich), and CuO (Norma-Pur, Prolabo). The first step consisted in preparing precursors consisting only of barium and copper oxides. They were prepared by annealing weighed mixtures of the starting materials at 930°C for 30 hr in an atmosphere of dry oxygen in a tube furnace. Then these precursors were mixed with HgO in a dry box using an agate mortar, placed in silica tubes, and sealed after evacuation. The tubes were heated to 800°C over 5 hr and then cooled to room temperature in the furnace. Usually, these samples contained different proportions of HgBa$_2$CuO$_{4+\delta}$, BaHgO$_2$, and Ba$_2$Cu$_3$O$_{5+\delta}$. Pure samples were obtained by heat-treating, under the same conditions, pressed pellets containing BaO$_2$ and HgO.

After the tubes were opened the samples were investigated by X-ray powder diffraction using a Guinier–Hägg focusing camera. Finely powdered silicon (a = 5.43088 Å at 25°C) was used as internal standard. The indexing of the powder pattern corresponding to one of the pure samples is given in Table 1. All reflections could be indexed on a rhombohedral cell. The parameters quoted in Table 1 were refined from Guinier data. The intensities were evaluated from a diffractogram obtained with a position-sensitive detector (up to θ = 40°). The choice of such a detector was due to the instability of BaHgO$_2$ after grinding in air. The compound decomposes completely after 20 hr.

The space group symmetry ($R\bar{3}m$), unit cell parameters,

0022-4596/94 $6.00

TABLE 1
X-Ray Powder Data for $BaHgO_2$[1]

h	k	l	d(obs)	d(exp)	Intensity
0	0	3	6.4587	6.4493	6
1	0	1	3.4917	3.4899	10
0	1	2	3.3332	3.3311	100
0	0	6	3.2269	3.2247	54
1	0	4	2.8618	2.8609	55
1	0	7	2.1809	2.1805	1
0	0	9	2.1497	2.1498	2
1	1	0	2.0488	2.0485	25
0	1	8	2.0019	1.9994	29
1	1	3	1.9533	2.8829	2
0	2	1	1.7665	1.7666	2
2	0	2	1.7453	1.7450	14
1	1	6	1.7293	1.7291	21
1	0	10	1.6989	1.6987	19
0	2	4	1.6655	1.6656	10
0	0	12	1.6125	1.6123	7
0	1	11	1.5760	1.5759	2
1	1	9	1.4829	1.4830	2
2	0	8	1.4305	1.4305	7
1	2	2	1.3285	1.3284	9
0	2	10	1.3075	1.3075	4
2	1	4	1.2921	1.2923	6
0	1	14	1.2877	1.2878	6
1	1	12	1.2670	1.2670	8

[1] The refined parameters are a = 4.097(1) and c = 19.348(2) Å.

and intensity distribution in the powder pattern strongly indicated that the new phase was $BaHgO_2$ with the delafossite structure, namely the Ba member of the series $MHgO_2$. Powder intensities calculated for $BaHgO_2$ using the structural model of $SrHgO_2$ (4) yielded a good fit with observed intensities ($R(I) < 15\%$). Figure 1 shows the lattice parameter variation with the ionic radius of the M alkali-earth for the $MHgO_2$ series. The smoothness of the curve shows that our assumption is indeed correct.

To corroborate these findings the composition of the new phase was determined by using a scanning electron microscope JEOL 840A equipped with an EDS attachment (Kevex Quantum). The EDS analysis of the samples prepared with CuO as starting material revealed that the new phase contained mainly Hg and Ba; in some cases, traces of Cu were also detected. Grains of other barium cuprates were also detected with the SEM.

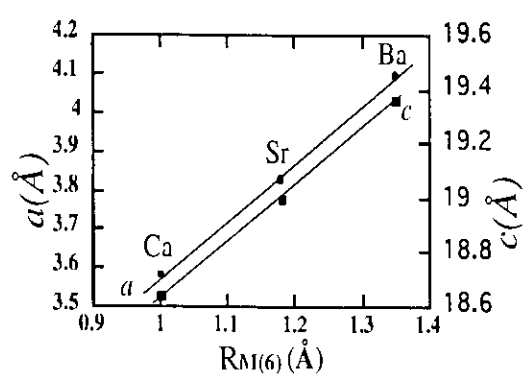

FIG. 1. Lattice parameters of $BaHgO_2$ vs ionic radius.

Since the formula of the new compound is $BaHgO_2$, it was produced by the solid state reaction

$$Ba_2CuO_{3+\delta} + HgO = BaHgO_2 + BaCuO_2 + \frac{\delta}{2}O_2.$$

During the various syntheses carried out to prepare $HgBa_2CuO_{4+\delta}$, $BaHgO_2$ was obtained only as a small impurity. When the starting composition was very close to Ba : Hg : Cu = 50 : 25 : 25, the formation of $HgBa_2CuO_{4+\delta}$ was not observed, and the sample contained only $BaHgO_2$ as the major component with $BaCuO_2$ and $Ba_2Cu_3O_{5+\delta}$ as impurities.

TWINNING IN THE DELAFOSSITE STRUCTURE

As stated above, the alkali-earth mercurates with the delafossite structure were described in the space group $R\bar{3}m$ (4). Subsequently, Soll and Müller-Buschbaum (5) reported that the structure of $SrHgO_2$ should be described in the primitive trigonal space group $P3_221$ with the same unit cell. Their assumption was based on single crystal X-ray diffraction data. The atom coordinates of both models are approximately the same, but in the primitive space group the atoms are slightly displaced from the special positions of the R space group. The choice of the primitive space group was based on the presence of reflections not allowed by the R lattice. The structural refinement carried out by Soll *et al.* yielded a relatively high R value (14%) for single crystal data, even if one takes into account that only an empirical absorption correction was applied. This uncertainty led us to carefully analyze again the X-ray powder pattern of $SrHgO_2$. We did not observe any reflections which would deny the R condition, even though the powder pattern calculated from the data of Soll and Müller-Buschbaum (5) indicated that reflections such as 010, 112, 114, 020 should have an intensity of about 2% of that of the strongest reflection. Reflections with comparable intensities are clearly visible in our X-ray data.

On the other hand, the presence of other reflections, such as the 011 (forbidden by the R lattice), cannot be determined from a powder pattern because they overlap precisely onto the $01\bar{1}$ (allowed in the R lattice). On the contrary, these two reflections can be easily distinguished by the single-crystal diffractometer technique. Possibly, Soll *et al.* found that some of these reflections had a nonzero intensity, and the choice of the primitive space group was based on this experimental fact. However, the

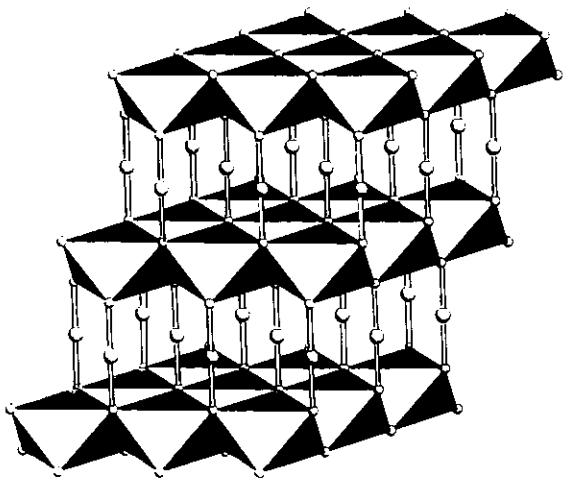

FIG. 2. The 3R Delafossite structure showing the way the octahedral layers are linked together by the O–Hg–O bonds.

presence in the single crystal data of reflections forbidden by the R lattice might be due to twinning.

The structure of 3R delafossite ($CuAlO_2$) (6, 7, 8) contains infinite one-octahedron-thick layers of close-packed AlO_6 octahedra. The layers are linked together by the Cu cations, forming linear O–Cu–O bonds which are appropriate for Cu^{+1} cations. The relationship between a given layer and those above and below is such that a cubic close-packed array is obtained if the layers collapse on top of each other. This arrangement is referred to as the 3R delafossite (6) (see Fig. 2). Another polymorph can exist for this type of compound, namely the 2H delafossite (7). The only difference between the two structures is in the way the MO_6 octahedron layers are stacked. If the layers collapse in the 2H structure, a hexagonal close-packed array is obtained. Figure 3 shows a schematic representation of the two structures. Only the top triangle of each coordination octahedron is drawn. The numbers refer to the layers in the unit cell. In the 3R delafossite structure there are 3 layers per unit cell and the fourth layer coincides with the first one. In this case the space group is $R\bar{3}m$ and the c-parameter is about 18 Å. In the 2H delafossite structure there are 2 layers per unit cell and the third layer is placed exactly as the first one. This leads to the space group $P6_3/mmc$ with a c-parameter of about 11 Å.

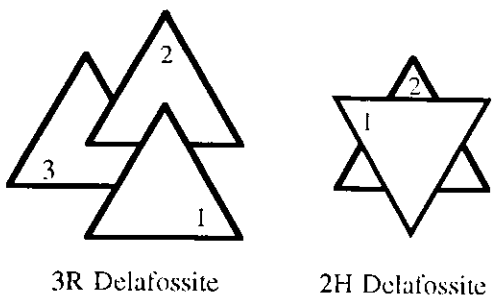

FIG. 3. Schematic representation of 3R and 2H delafossite structures. Each MO_6 octahedron is represented by the top triangle. Numbers correspond to the different layers.

Due to the similarity of the two structures, stacking faults can occur during the crystal growth, especially under limit conditions. One could have, for example, the following sequence: 1′2′3′1′2′3′1′2″3″1″2″3″. This would be the sequence of a delafossite structure in which a stacking fault occurs between the 1′ and the 2″ layers. The sequence of these two layers is that of a 2H structure. The crystal would contain two individuals, both with the 3R delafossite structure, which are not coherent, but are rotated 60° with respect to each other. The diffraction pattern of such a crystal would contain the diffraction effects coming from the two individuals. These diffraction effects form two identical rhombohedral lattices related to each other by a 60° rotation. For example, the forbidden $01\bar{1}$ reflection observed by Soll *et al.* would be the allowed $01\bar{1}$ of the second individual. The same result can also be obtained by the symmetry operations which exist in the trigonal lattice, but not in the rhombohedral structure. These are the $A_{6[60°]}$ and the (001) mirror plane operations. In other words, the crystal contains twinning by merohedry. This twinning will affect the single crystal data, but not the powder data.

Usually, the presence of twinning leads to a higher symmetry. In the present case it might seem that twinning leads to a lower symmetry. This is not so, because by merohedrism the threefold axis of the rhombohedral structure becomes sixfold. The difference in intensity between $01\bar{1}$ and 011 (which is actually the $01\bar{1}$ of the other individual), which leads to the choice of a primitive trigonal space group, is due to the inequality in volume of the two individuals.

Twinning in $CuAlO_2$ crystals with the 3R delafossite structure has been studied in detail by Ishiguro *et al.* (6). They found that twinning in these crystals occurs by a 60° rotation around the c-axis. The single crystals have octahedral or rhombohedral habit, while the twin crystals have triangular or hexagonal prismatic habit with concave angles or triangular laminar habit without apparent concave angles. This latter habit may reveal the wrong space group because it would hide the presence of twinning.

CONCLUSIONS

A new polymorph of $BaHgO_2$ has been synthesized. It has the 3R delafossite structure with cell parameters a = 4.097(1), c = 19.348(2), space group $R\bar{3}m$, and Z = 3. The discrepancy between single crystal and powder data

for $SrHgO_2$, which also has the 3R delafossite structure, is probably due to the presence in the single crystals of merohedral twinning due to stacking faults.

ACKNOWLEDGMENT

SNP thanks for its support the "Poisk" Project of the Russian Scientific Council for Superconductivity.

REFERENCES

1. S. N. Putilin, E. V. Antipov, O. Chmaissem, and M. Marezio, *Nature* **362,** 226 (1993).
2. M. Soll and Hk. Müller-Buschbaum, *J. Less-Common Met.* **162,** 169 (1990).
3. M. Soll and Hk. Müller-Buschbaum, *Monatsh. Chem.* **121,** 787 (1990).
4. S. N. Putilin, M. G. Rozova, D. A. Kashporov, E. V. Antipov, and L. M. Kovba, *Zh. Neorg. Khim.* **36,** 1645 (1991); *Russ. J. Inorg. Chem. (Engl. Transl.)* **36** (7), 928 (1991).
5. M. Soll and Hk. Müller-Buschbaum, *J. Less-Common Met.* **175,** 295 (1991).
6. T. Ishiguro, A. Kitazawa, N. Mizutani, and M. Kato, *J. Solid State Chem.* **40,** 170 (1981).
7. B. U. Köhler and M. Jansen, *Z. Kristallogr.* **165,** 313 (1983).
8. B. U. Köhler and M. Jansen, *Z. Anorg. Allg. Chem.* **543,** 73 (1986).