Journal of Solid State Chemistry **148,** 242–249 (1999)
Article ID jssc.1999.8443, available online at http://www.idealibrary.com on IDEAL®

Crystal Structure of New Palladium Fluorides A_2PdF_6 and $AA'PdF_6$ ($A^{2+} = Ba^{2+}, Sr^{2+}, Pb^{2+}$)

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Received January 4, 1999; in revised form June 22, 1999; accepted July 2, 1999

A new series of palladium (II) fluorides has been prepared. The A_2PdF_6 compounds crystallize in the orthorhombic space group *Cmca*. The structure of Ba_2PdF_6 ($a = 17.09(2)$ Å, $b = 6.163(2)$ Å, $c = 6.158(1)$ Å, $Z = 4$) has been refined from single crystal data to conventional $R_1 = 0.0325$ ($wR_2 = 0.0948$) for 661 independent reflections. A Rietveld analysis of $BaSrPdF_6$ and refinement of the lattice parameters of Pb_2PdF_6 have confirmed the same cationic distribution. Pd^{II} ions are fourfold-coordinated to fluorine. The isolated $[PdF_4]^{2-}$ square-planes form layers, perpendicular to the *a*-axis, interleaved by bilayers of $[AF_8]^{6-}$ antiprisms. © 1999 Academic Press

INTRODUCTION

A wide range of A_2MF_6 ternary fluorides have been reported in the literature (1). When A is a divalent cation as Ba^{2+}, Pb^{2+}, and Sr^{2+}, these compounds mainly crystallize in two structural types.

The Ba_2MF_6 (M = Mg and Mn (10 kbar) (2); M = Fe, Co, Ni, Zn, and Ag (3)) phases adopt the Aurivillius-type structure of Bi_2NbO_5F which exhibits a tetragonal symmetry (space group $I422$, $Z = 2$) (4). The homologous Pb_2MF_6 (M = Mg, Mn, Fe, Co, Ni, Zn) compounds have superstructures induced by deviation from bridge linearity (space group $P4_2/nbc$, $Z = 8$) (5, 6). When M is a Jahn–Teller cation (Cr^{2+}, Cu^{2+}), the distortion of the MF_6 octahedra leads to a symmetry lowering which becomes orthorhombic (space group *Bbcm*, $Z = 4$ (standard group *Cmca*)) (7). This structure is based on sequences of $[Ba_2F_2]^{2+}$ layers interleaved with perovskite slabs (8).

Another structure, related to the $KBrF_4$ type, has been found for Sr_2CuF_6 which exhibits also an orthorhombic symmetry (space group *Bbcm*, $Z = 4$) (9). This structure can be described as an intergrowth between a $SrCuF_4$ half-block and a SrF_2 half-block of the fluorite-type. Such arrangement results in a stacking of two layers of $[SrF_8]^{6-}$ polyhedra and of one layer of $[CuF_4]^{2-}$ square-planes, perpendicular to the c-axis.

Compounds with general formula A_2PdF_6 (A = divalent element) have never been pointed out up to now. Moreover, as for copper and silver, two types of environments can be found for divalent palladium: either an octahedral or a square-planar surrounding, depending on its d^8 electronic configuration. These two coordination numbers are even simultaneously present in $CsPd_2F_5$ (10, 11). Moreover the Ba(Sr, Pb)PdF_4 (12) and Ba(Sr)AgF_4 (13) compounds crystallize with the same structure as $SrCuF_4$. On the contrary in Ba_2CuF_6, the Cu^{2+} cation is located in a distorted octahedral environment (7, 14, 15), while Ba_2AgF_6 might adopt the Ba_2ZnF_6 type (13).

On the basis of these previous works and taking into account the competition between the steric and electronic effects, it seemed worthwhile to determine if the A_2PdF_6 compounds belonged to the Aurivillius type or to the Sr_2CuF_6 type, considering the respective ionic radii of Cu^{2+}, Pd^{2+}, and Ag^{2+}. The structural study of Ba_2PdF_6 was therefore undertaken and extended to the $BaSrPdF_6$ and Pb_2PdF_6 compounds.

EXPERIMENTAL

Sample Preparation

Polycrystalline samples were synthesized by solid state reactions from stoichiometric mixtures of the binary fluorides. The starting materials were mixed under a dry argon atmosphere in a glove box due to oxygen and moisture sensitivity. The reactions were carried out in sealed platinum tubes for 15 h at 650°C. The mixture was annealed several times in the same conditions with intermediate grindings in order to get pure powders. All reactions were followed by a temperature quenching.

Single crystals of Ba_2PdF_6 were obtained by melting about 3 g of polycrystalline sample at 850°C followed by cooling to 455°C at a rate of 0.7°C/h and then to room temperature at a rate of 7°C/h. The melting point was previously determined by differential thermal analysis. An orange single crystal of $(0.10 \times 0.17 \times 0.38)\ mm^3$ size was selected for the structural determination.

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X-Ray Diffraction Analysis

Weissenberg and precession photographs of a single crystal showed an orthorhombic symmetry belonging to the Laue class *mmm* with systematic extinctions consistent with space group *Cmca*.

Intensity data were collected on an Enraf Nonius CAD4 four-circle automatic diffractometer using graphite-monochromated Mo$K\alpha$ radiation over the half reciprocal space group. In order to check the intensities' stability during the data collection, three reference reflections were systematically measured every two hours. An unusual loss of 40% intensity was thus observed. A correction was then made by linear interpolation from the intensities of the reference reflections.

Corrections were applied for Lorentz and polarization effects, followed by an empirical absorption correction using psi-scan technique leading to a R_{int} factor equal to 0.077. For extinction corrections an empirical coefficient ε was used in the expression $F_c(\text{corr}) = F_c(1 + 10^{-3}\varepsilon F_c^2\lambda^3/\sin 2\theta)$. The unit-cell parameters were refined from 25 reflections over $5.5° \leq \theta \leq 20.2°$.

Intensity treatment and refinement calculations were performed using the SHELXL93 program (16). The atomic scattering factors and anomalous dispersion parameters were taken from the International Tables for X-ray Crystallography (17). The crystal data and experimental conditions are listed in Table 1. The quality of the acquisition and refinement was based on the conventional reliability factors R_{int} and R_1, wR_2, respectively.

TABLE 1
Crystal Data and Experimental Conditions for Data Collection

Formula	Ba_2PdF_6
Symmetry	orthorhombic
Reflection conditions	$hkl: h + k = 2n$; $h0l: l = 2n$; $hk0: h = 2n\ (k = 2n)$
Space group	*Cmca* (no. 64)
Unit-cell parameters (Å)	$a = 17.09(2)$ $b = 6.163(2)$ $c = 6.158(1)$
Volume (Å^3)	648.8(5)
Z	4
Dc (g.cm^{-3})	5.07
Dm (g.cm^{-3})	5.04
Crystal size (mm^3)	$0.10 \times 0.17 \times 0.38$
Radiation	Mo$K\alpha$ ($\lambda = 0.71073$ Å), graphite monochromator
Adsorption coefficient (mm^{-1})	$\mu = 14.8$
$F(000)$	848
Measuring range (°)	$\theta\text{max} = 40$
Scan type	ω–2θ
Index ranges	$0 \leq h \leq 30$; $-11 \leq k \leq 11$; $-11 \leq l \leq 11$
Reflections collected	2859
Independent reflections	990 [661 $Fo^2 > 2\sigma(Fo^2)$]
Extinction coefficient	$\varepsilon = 0.004376$
R_{int}	0.077
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0325$; w$R_2 = 0.0948$
Goodness of fit, S	1.222
Final Fourier residuals (e.Å^{-3})	-6.91 and 4.82

TABLE 2
Rietveld Data and Experimental Conditions for Data Collection

Formula	$BaSrPdF_6$
Symmetry	orthorhombic
Reflection conditions	$hkl: h + k = 2n$; $h0l: l = 2n$; $hk0: h = 2n\ (k = 2n)$
Space group	*Cmca* (no. 64)
Unit-cell parameters (Å)	$a = 16.872(2)$ $b = 6.007(2)$ $c = 6.014(2)$
Volume (Å^3)	609.5(5)
Z	4
Dc (g.cm^{-3})	4.41
Radiation	Cu$K\alpha$, ($\lambda = 1.5418$ Å), graphite monochromator
Peak shape function PV = ηL + (1 − η)G	$\eta = 0.56(3)$
FWHM function	$H^2 = U\text{tg}^2\theta + V\text{tg}\theta + W$. $U = 0.24(4)$, $V = -0.09(4)$, $W = 0.039(7)$
Measuring range (°)	$10 < 2\theta < 120$
Reflections collected	482
Parameters used in refinement	38
cR_p	0.072
cR_{wp}	0.091
R_I	0.038
$R_I(SrF_2)$	0.035
$R_I(PdO)$	0.070
$R_I(Pd)$	0.064

A complementary study of the $BaSrPdF_6$ phase was carried out by the Rietveld method (18). Powder X-ray diffraction (XRD) profiles were recorded on a Philips PW 1050 diffractometer in Bragg–Brentano geometry, using graphite-monochromated Cu$K\alpha$ radiation. The sample was set into an air-tight cell, filled in a dry atmosphere, by dusting the powder through a 20 μm sieve in order to minimize orientation effects. Owing to the Bragg–Brentano geometry of the equipment, the mylar windows of the cylindrical cell are crossed by the X-ray beam over a quasi-constant thickness. Data were collected over $10 \leq 2\theta \leq 120°$, in 0.02° steps, with integration times of 20 s.

The refinements were performed with the FULLPROF program package (19). The background level was optimized with a polynomial function and the peak shape was fitted by a pseudo-Voigt function. The change in the peak full-width at half-maximum (FWHM) across the diffraction pattern was defined by the function determined by Caglioti *et al.* (20). The reliability factors were the usual ones in Rietveld method (R_I, R_p, and R_{wp}) (21). The powder data and experimental conditions are given in Table 2.

TABLE 3
Atomic Coordinates and Displacements (Å^2) in Ba_2PdF_6 (e.s.d. in parentheses)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}(Å^2)
Ba	8*d*	0.16019(2)	0	0	0.00808(13)	0.00931(15)	0.01071(15)	0.00019(5)	0	0	0.00937(11)
Pd	4*b*	1/2	0	0	0.0051(2)	0.0106(2)	0.0117(2)	0.00086(10)	0	0	0.00916(11)
F1	8*e*	1/4	0.2553(3)	1/4	0.0124(11)	0.0146(10)	0.0139(9)	0	− 0.0007(9)	0	0.0136(5)
F2	16*g*	0.08144(12)	0.6587(3)	0.1597(3)	0.0237(10)	0.0259(10)	0.0303(10)	0.0096(9)	− 0.0121(9)	− 0.0135(9)	0.0266(5)

STRUCTURE DETERMINATION

Ba_2PdF_6

The *Cmca* space group determined from photographic study was compatible with the two structural models obtained for Ba_2CuF_6 (7) and Sr_2CuF_6 (9).

At first calculations were made by using the atomic coordinates given by the first model (Ba_2CuF_6) as initial parameters. The isotropic atomic displacements found for fluorine atoms were not suitable and the reliability factors were rather high. The study was subsequently continued considering the Sr_2CuF_6 model, in which only two sites are occupied by fluorine atoms instead of three for the former hypothesis. The refinement rapidly converged to $R_1 = 0.0325$ and $wR_2 = 0.0948$ values for 661 reflections considering anisotropic atomic displacements. An important electronic residue close to the barium site has nevertheless not been interpreted; it probably results from the difficult acquisition conditions due to the hygroscopicity of these fluorides.

The four independent positions and the corresponding anisotropic atomic displacements are reported in Table 3. The interatomic distances and angles are listed in Table 4 and will be discussed in connection with the structure description.

$BaSrPdF_6$

This study was performed in order to verify whether the same structure was obtained when the barium atom was substituted by a smaller alkaline-earth cation, or on the contrary a cationic ordering could occur in this eightfold-coordinated site owing to the difference between the ionic radii.

The structure of $BaSrPdF_6$ was refined by the Rietveld method. The previous structural results of Ba_2PdF_6 were used as a starting model. The analysis of the X-ray diffraction pattern profile in the space group *Cmca* pointed out the presence of parasitic phases: PdO, Pd, and SrF_2. Other preparations were carried out, but it was impossible to hinder the presence of these phases in small quantities. The structural determination was then undertaken by refining simultaneously the structural parameters of $BaSrPdF_6$ and of the minor impurities.

At first, the isotropic displacements of $BaSrPdF_6$ were refined separately. The obtained values seemed coherent;

TABLE 4
Interatomic Distances (Å) and Angles (°) in Ba_2PdF_6 (e.s.d. in parentheses)

Pd	F(2)	F(2)	F(2)	F(2)
F(2)	1.965(2)	3.930(2)	2.784(2)	2.774(2)
F(2)	180	1.965(2)	2.774(2)	2.784(2)
F(2)	90.2(1)	89.8(1)	1.965(2)	3.930(2)
F(2)	89.8(1)	90.2(1)	180	1.965(2)

Ba	F(1)	F(1)	F(2)	F(2)	F(1)	F(1)	F(2)	F(2)
F(1)	2.646(1)	4.310(1)	3.846(2)	4.6682)	3.080(1)	3.082(1)	2.994(2)	5.264(2)
F(1)	109.08(4)	2.646(1)	4.668(2)	3.846(2)	3.082(1)	3.080(1)	5.264(2)	2.994(2)
F(2)	92.55(5)	122.63(5)	2.676(2)	4.625(2)	5.294(2)	2.994(2)	3.276(2)	3.278(2)
F(2)	122.63(5)	92.55(5)	119.60(9)	2.676(2)	2.994(2)	5.294(2)	3.278(2)	3.276(2)
F(1)	70.60(1)	70.65(1)	162.05(5)	67.92(4)	2.684(1)	4.403(1)	3.866(2)	4.704(2)
F(1)	70.65(1)	70.60(1)	67.92(4)	162.05(5)	110.23(4)	2.684(1)	4.704(2)	3.866(2)
F(2)	68.34(4)	161.96(5)	75.36(5)	75.42(5)	92.15(6)	122.42(5)	2.684(1)	4.644(2)
F(2)	161.96(5)	68.34(4)	75.42(5)	75.36(5)	122.42(5)	92.15(6)	119.8(1)	2.684(1)

nevertheless they appeared very inaccurate for fluorine atoms. Consequently, an average atomic displacement for all the fluorine atoms was taken into account. The final reliability factor R_I relative to the $BaSrPdF_6$ phase is equal to 0.038. Figure 1 shows the good agreement between the experimental and calculated X-ray diffraction patterns.

The atomic coordinates and the isotropic atomic displacements are presented in Table 5; the main interatomic distances are reported in Table 6. They will be discussed in connection with the structure description.

The persistance of parasitic phases in the final product can probably be explained by the presence of small amounts of oxide in the starting palladium fluoride, but can also be due to a slight hydrolysis. In addition, the presence of metallic palladium is extremely difficult to avoid during the synthesis of PdF_2. Consequently, an excess of SrF_2 is always observed in so far as it probably reacts on PdF_2 less strongly than BaF_2. In the $BaSrPdF_6$ phase, a substoichiometry of strontium could therefore be considered, thus giving rise to a $Ba_{1-x}Sr_xPdF_6$ formulation.

Nevertheless, the good reliability factors ($cR_p = 0.072$, $cR_{wp} = 0.091$, and $R_I = 0.038$), and the normal evolution of B_{iso} atomic displacements (Table 5), led us not to take into account such eventual substoichiometry of strontium in the 8*d* site. Moreover the standard deviations, relatively large because of the high Berar factor, did not allow us to go further in the refinement on the basis of such a hypothesis.

To conclude, the obtained positions are close to the atomic coordinates found on the single crystal for Ba_2PdF_6 and the atomic displacements are relatively similar. The $BaSrPdF_6$ phase adopts the same structure as Ba_2PdF_6 with a statistical occupation of the 8*d* site both by barium and strontium atoms.

Pb_2PdF_6

The X-ray diffraction pattern of Pb_2PdF_6 is similar to that of Ba_2PdF_6. It has been indexed in the space group *Cmca* by analogy with the reflections observed for the Ba_2PdF_6 single crystal. The unit-cell parameters have been determined from a slow powder diffraction pattern, using a silicon standard, followed by least-squares refinement on the basis of 25 reflections. They are $a = 16.738(3)$ Å, $b = 5.913(2)$ Å, $c = 5.918(1)$ Å. A gradual decrease of the unit-cell volume is observed as a function of A^{2+} cation size

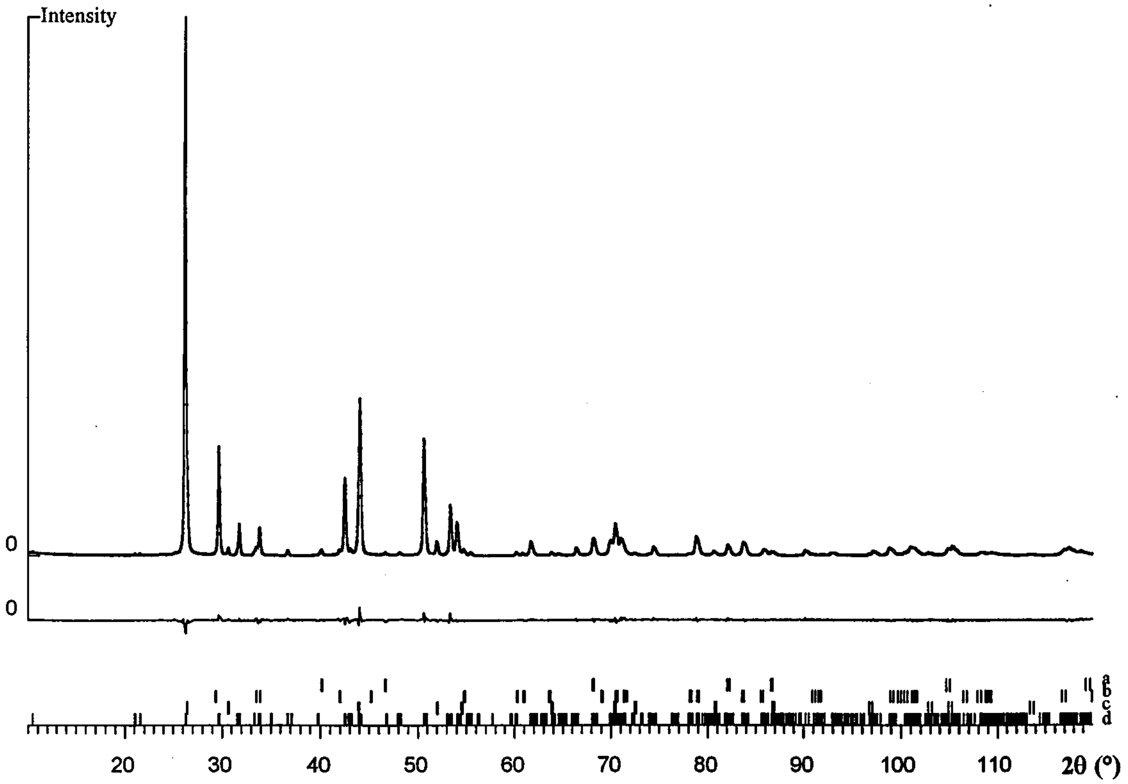


FIG. 1. Observed (dots) and calculated (full line) X-ray diffraction patterns of $BaSrPdF_6$ and difference curve. Tick marks indicate the positions of allowed Bragg reflections for (a) Pd, (b) PdO, (c) PdF_2, (d) $BaSrPdF_6$.

TABLE 5
Atomic Coordinates and Isotropic Atomic Displacements in $BaSrPdF_6$; the Atomic Displacements Obtained for Ba_2PdF_6 are Reported for Comparison (e.s.d. in parentheses are multiplied by Berar's factor)

Atom	Site	x	y	z	B_{iso} (Å^2)	Occupancy	Ba_2PdF_6 crystal B_{eq} (Å^2) $= U_{eq} \times 8\pi^2$
Ba	8*d*	0.1612(4)	0	0	0.5(1)	0.50	0.74
Sr	8*d*	0.1612(4)	0	0	0.5(1)	0.50	0.74
Pd	4*b*	1/2	0	0	0.9(2)	1.00	0.72
F1	8*e*	1/4	0.244(8)	1/4	2.0(6)	1.00	1.08
F2	16*g*	0.0828(16)	0.674(7)	0.156(7)	2.0(6)	1.00	2.10

($r_{Ba^{2+}}$(1,42 Å) > $r_{Pb^{2+}}$(1,29 Å) > $r_{Sr^{2+}}$(1,26 Å) in eightfold coordination) (23).

STRUCTURE DESCRIPTION AND DISCUSSION

The structure of the A_2PdF_6 and $AA'PdF_6$ fluorides is related to that of Sr_2CuF_6 (space group *Bbcm* (standard group: *Cmca* no. 64), where $a = 5.708$ Å, $b = 5.708$ Å, and $c = 16.446$ Å, $Z = 4$) (9).

Only two independent fluorine atoms are involved in the structure. The palladium atom is only connected to F(2) and this arrangement leads to isolated square-planes formulated as $[PdF(2)_4]^{2-}$. The four Pd–F distances (1.965 Å in Ba_2PdF_6 and 1.98 Å in $BaSrPdF_6$) are on the same order of magnitude as those encountered in $SrPdF_4$ and $BaPdF_4$ (1.96 Å) (12). These distances are not so affected by the variation of alkaline-earth cation size.

The F(1) atom is only connected to barium and forms $[F(1)–Ba_4]$ tetrahedra, connected together by edges like in the fluorite type. These tetrahedra form infinite layers perpendicular to the *a*-axis which can be formulated as $[Ba_2F_2]^{2+}$. Therefore, the structure can be described as the stacking of two layers perpendicular to the *a*-axis: the first is constituted by the $[PdF_4]^{2-}$ square-planes and the second by the $[F(1)–Ba_4]$ tetrahedra (Fig. 2). Table 7 gives the F(1) environment in the tetrahedra, which are nearly regular (bond lengths and angles).

It is also possible to emphasize other features: the whole cations form a fcc network in which a layer of $[PdF_4]^{2-}$ polyhedra is isolated by two layers of $[AF_8]^{6-}$ polyhedra. The layers stacking, perpendicular to the *a*-axis, is represented in Fig. 3. It presents similarities with that observed in the $NaRECu_2F_8$ compounds described in a previous work (22).

TABLE 6
Interatomic Distances (Å) in $BaSrPdF_6$ (e.s.d. in parentheses are multiplied by Berar's factor)

Pd–F2:	4 × 1.98(4)	Ba(Sr)–F1:	2 × 2.58(3)
			2 × 2.62(3)
		Ba(Sr)–F2:	2 × 2.55(4)
			2 × 2.67(4)

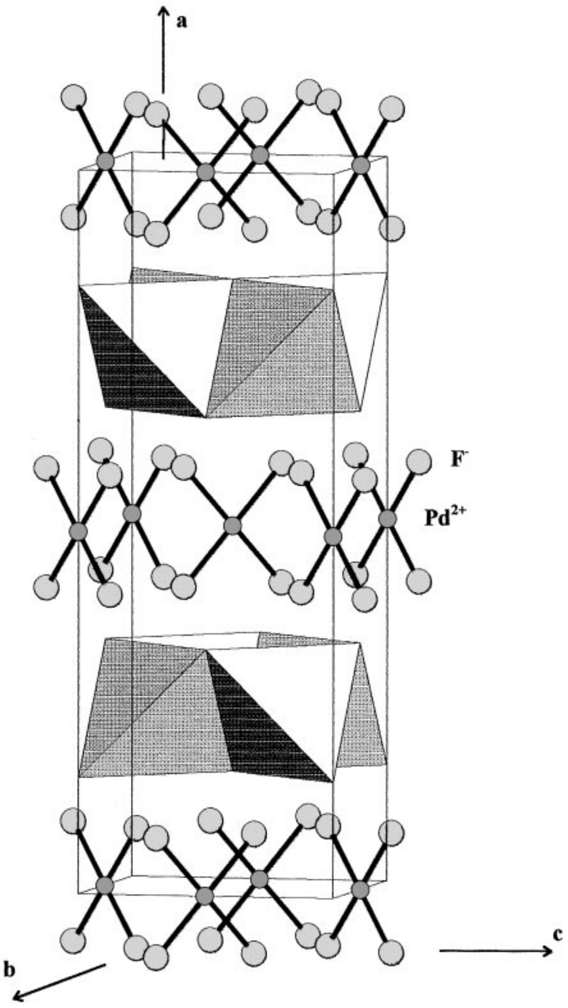


FIG. 2. Perspective view of the structure of Ba_2PdF_6.

TABLE 7
Interatomic Distances (Å) and Angles (°) in the [F(1)–Ba_4] Tetrahedra in Ba_2PdF_6 (e.s.d. in parentheses)

F(1)	Ba	Ba	Ba	Ba
Ba	2.646(1)	4.348(1)	4.350(1)	4.356(1)
Ba	110.50(7)	2.646(1)	4.356(1)	4.350(1)
Ba	109.40(1)	109.65(1)	2.684(1)	4.348(1)
Ba	109.65(1)	109.40(1)	108.20(7)	2.684(1)

The large A^{2+} cations are located in the center of distorted antiprisms. Each layer of $[AF_8]^{6-}$ polyhedra is shifted by a (1/2 1/2 1/2) vector with respect to the adjacent one; every polyhedron is therefore surrounded by eight other ones (four in the (b, c) plane and four above (or below)), with which it is connected by eight of its edges. The so-constituted bilayers are separated one from each other by layers of $[PdF_4]^{2-}$ square-planes in which the isolated $[PdF_4]^{2-}$ units are oriented at 90° from each adjacent one. Each fluorine atom, located at their tops, is shared with two AF_8 polyhedra of the adjacent layer (Fig. 4). Finally, the layer of square-planes at $x = 1/2$ level is shifted by a 1/2**b** vector from that at the $x = 0$ level (Fig. 3).

The Ba(Sr)–F distances in $BaSrPdF_6$ (from 2.55 to 2.67 Å) are shorter than in Ba_2PdF_6 (from 2.646 to 2.684 Å), in agreement with the respective size of the large cations occupying the same site. All the bond lengths are slightly smaller than the sum of Shannon's radii (23). Similar differences had already been observed in Sr_2CuF_6 ($d_{Sr-F} = 2.469$ to 2.491 Å and $d_{Shannon} = 2.59$ Å) (9).

Finally, the (2 + 2 + 4) distribution of Ba–F bonds found on single crystal is changed into (2 + 2 + 2 + 2) in $BaSrPdF_6$. The size difference between alkaline-earth cations induces an additional distortion of AF_8 antiprisms.

If the structure of Ba_2PdF_6 is described in the space group *Bbcm* (no. 64, instead of standard group *Cmca*) in order to obtain the larger unit-cell parameter in the **c** direction, a direct correlation appears between the unit-cells of BaF_2 (fluorite), $BaPdF_4$ ($KBrF_4$ type), and Ba_2PdF_6 compounds as shown in Fig. 5. The last two phases are deduced from the first one by a quasi-doubling and a quasi-tripling of the c parameter. Such a feature had already been established between SrF_2, $SrCuF_4$, and Sr_2CuF_6 (24).

STRUCTURAL RELATIONSHIP: Ba_2PdF_6/Ba_2CuF_6

According to the two structural hypotheses considered at the beginning of this study and to the similarity of the space groups, it seemed worthwhile to compare these two structural types on the basis of this work and Reinen *et al.*'s study (14).

The Ba_2CuF_6 structure, represented in Fig. 6 in the space group *Cmca*, can be compared to the Ba_2PdF_6 one (Fig. 2). The A^{2+}, M^{2+} cations and a type of F^- ion occupy the same sites (8d, 4b, and 8e, respectively) in both structural models. In Ba_2PdF_6 the sixteen remaining fluorine atoms are located in the (x, y, z) general position (16g site with $x = 0.08$), whereas in the Ba_2CuF_6 structural type, eight of them occupy the (0, y, z) position (8f site with y and z close

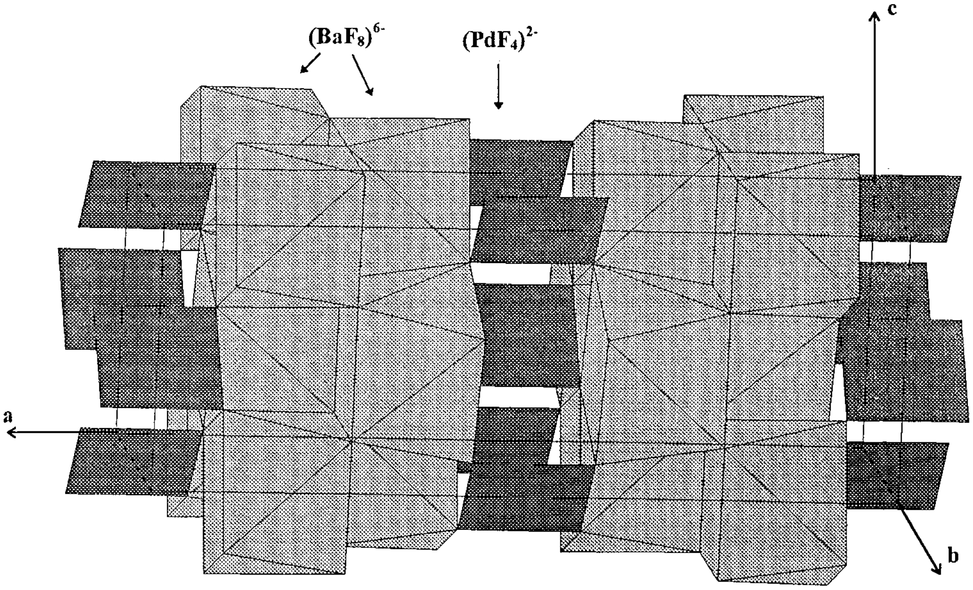


FIG. 3. Polyhedra layers stacking along the [100] direction.

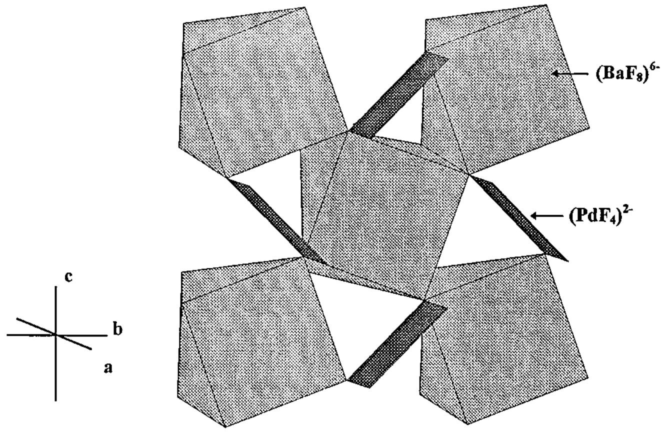


FIG. 4. Polyhedra connection along the [011] and [0$\bar{1}$1] directions.

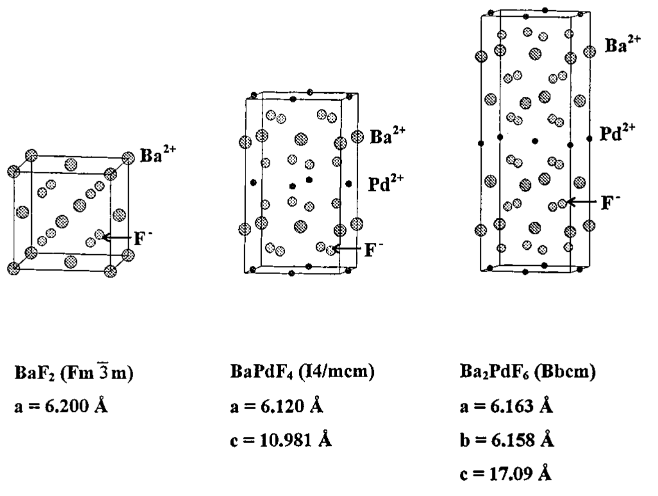
to the previous ones), while eight others are situated in the 8*d* site (*x*, 0, 0).

The change from the Ba_2PdF_6 structure to the Ba_2CuF_6 one can thus be described as resulting from a splitting of the 16*g* site in two 8*f* and 8*d* sites. Consequently, the barium coordination increases from eight to twelve fluorine atoms and the $[PdF_4]^{2-}$ square-planar environment evolves to $[CuF_6]^{4-}$ distorted octahedra.

CONCLUSION

The A_2PdF_6 compounds crystallize in the orthorhombic space group *Cmca*. Their structure is related to that of Sr_2CuF_6.

The comparison between Sr_2CuF_6 and Ba_2CuF_6 crystal structures shows that the larger Ba^{2+} cations which are twelvefold-coordinated to fluorine constrain the Cu^{2+} cations to be located in a distorted octahedra. On the other hand in Ba_2PdF_6, the stronger crystal field of Pd^{2+} ($3d^8$, LS) ions compared to Cu^{2+} ($3d^9$) imposed on Ba^{2+} cations to be eightfold-coordinated to fluorine. Thus, Sr_2PdF_6 will probably adopt the same structure.



BaF_2 (Fm$\bar{3}$m)
a = 6.200 Å

$BaPdF_4$ (I4/mcm)
a = 6.120 Å
c = 10.981 Å

Ba_2PdF_6 (Bbcm)
a = 6.163 Å
b = 6.158 Å
c = 17.09 Å

FIG. 5. Structural correlations between BaF_2, $BaPdF_4$, and Ba_2PdF_6 compounds.

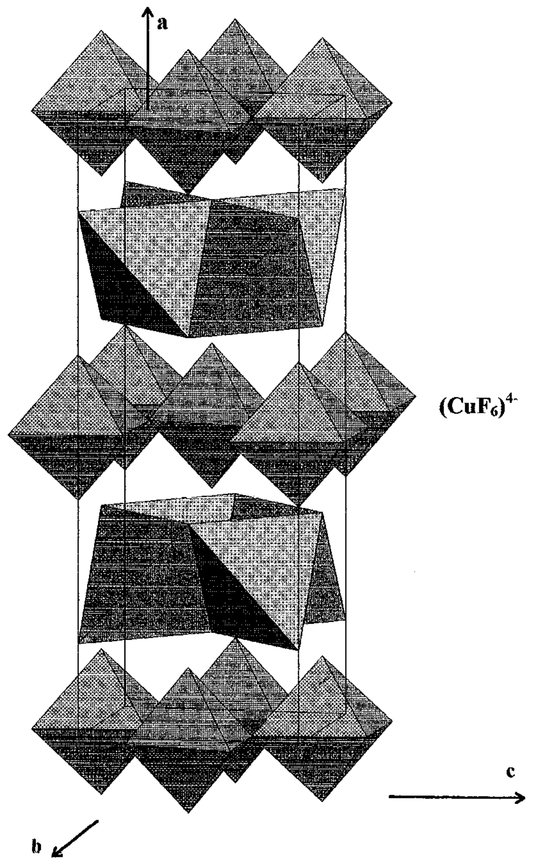


FIG. 6. Perspective view of the structure of Ba_2CuF_6 (space group *Cmca*).

ACKNOWLEDGMENTS

The authors are indebted to L. Lozano for the preparation of single crystals and to E. Lebraud for his contribution to the X-ray analysis.

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