JOURNAL OF SOLID STATE CHEMISTRY **68**, 292–299 (1987)

Crystal Structure of $Nd(OH)_2NO_3 \cdot H_2O$ Completely Solved and Refined from X-Ray Powder Diffraction

DANIEL LOUËR AND MICHÈLE LOUËR

Université de Rennes I, Laboratoire de Cristallochimie (U.A. 254), Avenue du Général Leclerc, 35042 Rennes Cedex, France

Received June 19, 1986; in revised form September 9, 1986

The crystal structure of the monoclinic neodymium hydroxynitrate $Nd(OH)_2NO_3 \cdot H_2O$ has been studied using X-ray powder diffraction data. The cell dimensions are $a = 20.996(4)$ Å, $b = 3.875(2)$ Å, $c = 6.282(2)$ Å, and $\beta = 113.73(3)°$. The space group is $C2/m$ with $Z = 4$. Initial positional parameters for the neodymium atom were obtained from the Patterson function derived from 70 unambiguously indexed reflections. The remaining atoms were located by interpretation of Fourier difference maps. The structure refinement was effected by the Rietveld method. The final indicator was $R_F = 0.07$. The structure consists of layers NdX_3 ($X = OH^-$, H_2O, NO_3) linked by hydrogen bonds.

Introduction

Neodymium hydroxynitrates have been identified in the extensive study on the rare-earth hydroxynitrates by Haschke (*1*), who found the hydroxy salt $Nd(OH)_2NO_3$ under hydrothermal conditions. Recently, the powder diffraction data of a hydrated neodymium hydroxynitrate, $Nd(OH)_2NO_3 \cdot H_2O$, were reported (*2*). Single crystals of this material could not be obtained and structural analogies with similar compounds were not detected. As a consequence we decided to analyze the powder diffraction pattern of the microcrystalline solid in order to get information on the crystal structure of this hydroxy salt. In the same way, several works initiated by Werner (see, for example, Ref. (*3, 4*)) have shown that standard Patterson and Fourier methods deduced from powder diffraction data could be employed for the solution of a completely unknown structure and combined with the powerful Rietveld profile refinement (*5*). The implication of these new developments of the powder diffraction method is obviously of great interest in solid state chemistry and materials science. The present paper deals with the procedure used for the *ab initio* determination of the completely unknown crystal structure of $Nd(OH)_2NO_3 \cdot H_2O$ and the discussion on the structural chemistry of this solid.

Experimental Considerations

Microcrystalline powder of the neodymium hydroxynitrate $Nd(OH)_2NO_3 \cdot H_2O$ was obtained by slow hydrolysis of a homogeneous aqueous solution of neodymium nitrate and ammonium nitrate (*2*). The powder diffraction pattern was scanned in steps of 0.04° (2θ) over the angular range 7–85° (2θ) and fixed-time counting (140 sec)

0022-4596/87 $3.00

was employed. Data were obtained by using a Compagnie Générale de Radiologie (C.G.R.) powder diffraction system and the following experimental conditions:

(a) A stabilized Theta 60 generator, operating at 45 kV, 22 mA, with a copper target and 6° take-off angle. $K\alpha_1$ radiation (λ = 1.5405981 Å) was selected by means of an incident-beam, curved-crystal quartz monochromator with asymmetric focusing (short focal distance 90 mm, long focal distance 140 mm). As shown previously (*6*), good discrimination of the $K\alpha_2$ peak is about 1% of the α_1.

(b) A scintillation detector with pulse-height discrimination.

(c) A 250-mm goniometer radius and 0.2 mm receiving-slit aperture.

Throughout the experiment the ambient temperature was maintained at 294 ± 1 K.

The adjustment of the diffractometer was checked by using standard materials ($Pb(NO_3)_2$, ZnO) and the highly oriented layered compound $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ as reference samples. The divergence slits located in the incident beam were adjusted to ensure a complete illumination of the specimen surface at about 12° (2θ). Special care is required in the specimen preparation; a completely random orientation of crystallites is essential in determining the true relative intensities. Consequently the neodymium hydroxynitrate powder was sifted and particles with sizes less than 40 μm were selected. To minimize the orientation effects which occur when powdered samples are packed or pressed, a sample holder designed from that described by McMurdie *et al.* (*7*) was used.

Data Analysis

Indexing

The indexing of the powder pattern is described elsewhere (*2*). It is a crucial stage in the structural analysis, which necessitates high accuracy in the diffraction line positions. In the present study an absolute error less than 0.04° (2θ) was estimated for the peak position measurements. The successive dichotomy method (*8, 9*) was applied to the first 20 lines of the pattern. Only one probable solution was proposed by the program DICVOL. This solution is monoclinic with the refined cell parameters a = 19.381(4) Å, b = 3.884(1) Å, c = 6.291(1) Å, and β = 96.43(2)°. The reliability of the unit cell and indexing is indicated by the figures of merit (*10, 11*) $M_{20} = 34$ and $F_{20} = 48$ (0.0082,51). The average absolute magnitude of the discrepancy between observed and calculated 2θ values $|\overline{\Delta 2\theta}| = 0.0082$ gives an indication of the quality of the data. The calculated density for $Z = 4$ is 3.644 $g \cdot cm^{-3}$, which is in accordance with the measured density (3.60 $g \cdot cm^{-3}$ (2)). The unit cell which was found indexes all the observed lines of the diffraction pattern. From the list of the unambiguous peaks detected in the powder pattern it was seen that all lines could be indexed using the restriction $h + k + l = 2n$. The I-centered monoclinic cell was transformed into a conventional C-centered cell. The cell dimensions, refined from the whole powder pattern, are given in Table I. The possible space groups are $C2$, Cm, and $C2/m$. Since the $C2$ and Cm space groups, involving more variable parameters, did not improve the results, as shown later, the structure was solved in the centrosymmetric $C2/m$ space group.

Structure Solution and Refinement

To extract the constituent Bragg reflections from the complete powder pattern the total pattern decomposition method of Sonneveld and Visser (*12*) recently modified (*13*) was applied. In this procedure, no reference to a structural model is needed. In the present analysis the peak shape was assumed to be represented by a pseudo-Voigt

TABLE I

Details of Rietveld Full-Profile Refinement

a	20.996(4) Å
b	3.875(2) Å
c	6.282(2) Å
β	113.73(3)°
V	467.9(6) Å^3
Space group	$C2/m$
Z	4
2θ range (°)	10–85
Step scan increment (°2θ)	0.04
N° of reflections	212
N° of structural parameters	29
N° of profile parameters	8
N° of atoms	9
$R_F = \Sigma \lvert I_o^{1/2} - I_c^{1/2} \rvert / \Sigma I_o^{1/2}$	0.07
$R_B = \Sigma \lvert I_o - I_c \rvert / \Sigma I_o$	0.11
$R_{\omega p} = \{\Sigma \omega_i [y_i(\text{obs}) - y_i(\text{cal})/c]^2 / \Sigma \omega_i [y_i(\text{obs})]^2\}^{1/2}$	0.19

function. After a careful examination of the output list, 71 integrated intensities with unambiguous index assignments were obtained (the 200 line which occurs at low angle, 9.19° (2θ), was omitted in the calculations). These intensities were used as input data for the Enraf–Nonius's structure determination package (SDP) (*14*). Calculations were performed on a PDP 11/60 computer. From the calculation of a three-dimensional Patterson function, the position of the unique neodymium atom was derived. At the same time, the MULTAN program (*15*) was applied to the data, giving approximate coordinates for neodymium and two oxygen atoms. A least-squares refinement of the Nd position resulted in a conventional R value of 0.30. The strongest peaks from a Fourier difference map could be attributed to the remaining atoms, except for one oxygen atom belonging to a nitrate group. The seven atoms lie on the mirror of the space group $C2/m$. When the geometry of the nitrate group was taken into account, the coordinates of the remaining oxygen atom could be calculated unambiguously; unfortunately they involve a distance between adjacent nitrates that is too short. However, a second Fourier difference map, calculated from seven atom positions, clearly showed a peak located at these coordinates. Another peak in the general position xyz was detected and was also in accordance with the geometry of the nitrate group. These two different sites can be explained by a double orientation of the nitrate plane with respect to an N–O axis. A least-squares refinement of the nine independent atoms, calculated from the 70 integrated intensities, gave an R value of 0.11. For this calculation the simultaneously refined parameters were limited to 10.

At this stage, the least-squares structure refinement was pursued with the Rietveld profile refinement method (*5*), by means of the computer program DBW2.9 (*16*), locally modified for R_B and R_F factors calculations (*17*), which are the most significant indicators of the agreement between the crystal structure model and the actual structure; these figures of merit will be discussed elsewhere (*18*). The intermediate Lorentzian function (IL) defined by Young and Wiles (*19*) was used for the representation of the individual reflection profiles. In order to describe the angular dependence of the peak full-width at half-maximum (ω), the quadratic form in tan θ was used:

$$\omega^2 = U \tan^2\theta + V \tan\theta + W,$$

where U, V, and W are constants whose values were refined in the process. The background was represented by a polynomial of degree 5 (*16*), evaluated from intensities selected in regions where diffraction lines had no contribution. For better accuracy, the evaluation was performed using the Chebyshev series form to represent the polynomial. From the Chebyshev coefficients the usual power-series form of the polynomial was derived. The profile analysis refinement process involved the following parameters: 19 atomic coordinates, 9 isotropic temperature factors, 1 scale factor, 1 zero-point parameter, 4 cell parameters, and 3 half-width and 1 asymmetry parameters. Cell and instrumental parameters were allowed to vary from time to time

TABLE II

Positional and Thermal Parameters for $Nd(OH)_2NO_3 \cdot H_2O$

Atom	*x*	*y*	*z*	*B* (Å²)
Nd	0.2082(1)	0	0.1923(3)	0.30(4)
OH_1	0.2782(7)	0.5	0.384(3)	0.8(4)
OH_2	0.1939(6)	0.5	−0.048(2)	1.0(4)
O_1	0.1428(7)	0.5	0.248(2)	2.8(4)
O_2^*	0.089(1)	0.5	0.512(4)	0.1(7)
O_3^*	0.008(2)	0.5	0.123(4)	2.5(9)
O_4^*	0.058(1)	0.203(6)	0.332(4)	4.5(6)
N	0.080(1)	0.5	0.296(3)	0.5(4)
H_2O	0.0835(7)	0	−0.135(2)	2.4(4)

Note. Atoms marked with * have an occupation number of 0.5.

during the refinement process. Crystallographic details are given in Table I, final atomic parameters in Table II, and selected bond lengths and angles in Table III. Figure 1 shows graphically the fit obtained between calculated and observed patterns. This fit corresponds to satisfactory crystal structure model indicators ($R_F = 0.07$, $R_B = 0.11$). The amplitude of the $R_{\omega p}$ factor (0.19) is typically observed in Rietveld refinements from X-ray diffraction powder data (*20*). It is very sensitive to the reflection profile functions used to describe the observed diffraction line profile (*19*). In the present situation the slight systematic deviation of the difference curve observed for the reflections at low angles (below ~22° (2θ)) is mainly explained by an unsatisfactory representation of the strong asymmetry of lines occurring when no soller slit is used in the diffracted beam. In other respects, in spite of the special experimental attention to ensure a constancy of the incident intensity on the sample throughout the whole angular range, a refinement has been performed with the 10–22° (2θ) range excluded. No significant modification in the atomic positions was observed and a similar structure indicator ($R_F = 0.067$) was obtained; the profile factor ($R_{\omega p} = 0.17$) was obviously slightly better.

Discussion

The crystal structure of $Nd(OH)_2NO_3 \cdot H_2O$ can be described as consisting of layers parallel to the (100) plane, as shown by the ORTEP projection onto the (010) plane in Fig. 2. The hydroxyl groups are clearly differentiated. Indeed, the water molecule is bonded to only one neodymium atom ($d = 2.60$ Å) while the hydroxyl groups are bonded to three neodymium atoms, with bond lengths ranging from 2.40 to 2.56 Å. The Nd–O–Nd angles vary from 105 to 108°, indicating that the probable H position is the fourth vertex of the tetrahedron. All the OH–O distances are greater than 3.1 Å and are not consistent with possible hydrogen bonds. The ninefold coordination of Nd

TABLE III

Selected Interatomic Distances (Å) and Angles (deg)

Nd–O distances			
$Nd–OH_1^{I,II}$	2.44(1) (×2)		
OH_1^{III}	2.56(1) (×1)		
$OH_2^{I,II}$	2.40(1) (×1)		
OH_2^{IV}	2.56(1) (×2)		
$O_1^{I,II}$	2.48(1) (×2)		
H_2O^I	2.60(1) (×1)		
Nitrate group			
Parallel to *ac*			
$N–O_1^I$	1.46(4)	$O_1–N–O_2$	118(1)
O_2^I	1.30(4)	$O_1–N–O_3$	126(1)
O_3^I	1.48(4)	$O_2–N–O_3$	115(1)
Perpendicular to *ac*			
$N–O_1^I$	1.46(4)	$O_1–N–O_4$	117(1) (×2)
$O_4^{I,IV}$	1.30(3) (×2)	$O_4–N–O_4$	125(2)
Possible hydrogen bonds between adjacent layers			
$H_2O–O_3^{VI,VII}$	2.74(3)		
$O_4^{VI,VII}$	2.84(3)		

Symmetry code
I x, y, z; II $x, -y, z$; III $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
IV $\frac{1}{2} - x, \frac{1}{2} - y, -z$; V $x, 1 - y, z$; VI $-x, y, -z$;
VII $-x, -y, -z$

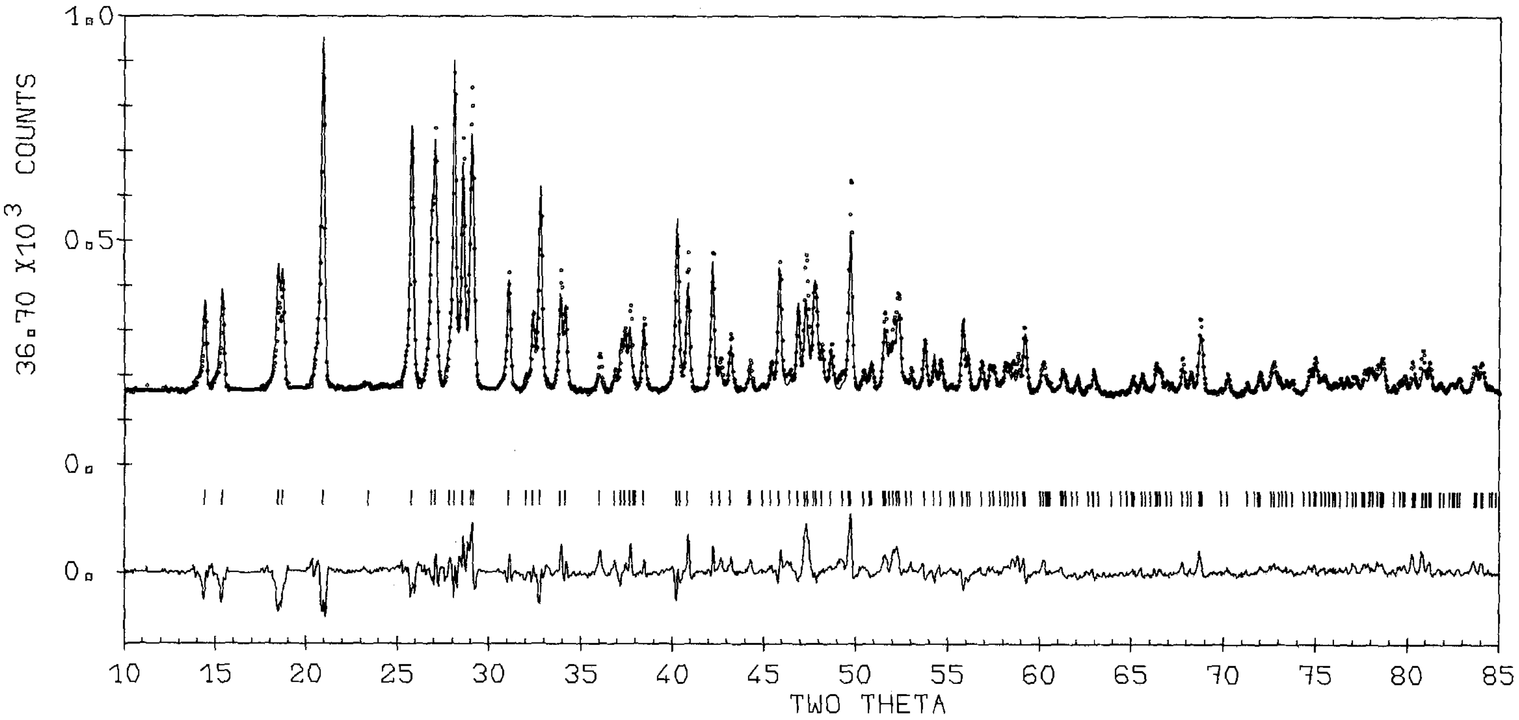

Fig. 1. The final Rietveld difference plot of $Nd(OH)_2NO_3 \cdot H_2O$. In the upper portion, the observed data are shown by the dots; the calculated pattern is shown by the solid line. The lower portion is a plot of the difference, observed minus calculated.

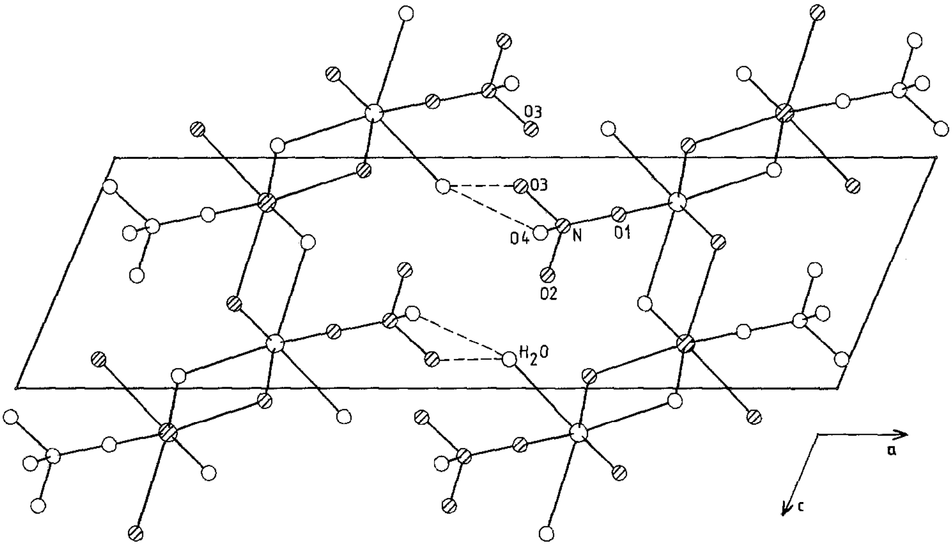

FIG. 2. ORTEP projection onto the (010) plane; all the atoms (except O$_4$) lie on the mirror at $y = 0$ (striped atoms) or $y = \frac{1}{2}$; dashed lines show possible hydrogen bonds.

(Fig. 3) arises from six hydroxyl groups, one water molecule, and two oxygen atoms belonging to two nitrate groups. These latter contribute by giving one oxygen (O$_1$) to the coordination of Nd. The other two oxygen atoms exhibit two different orientations. The atoms N, O$_1$, O$_2$, and O$_3$ (see Fig. 2 and Table III) correspond to the nitrate parallel to the (010) plane and N, O$_1$, and O$_4$ to the group perpendicular to the (010) plane. It has been previously mentioned that the distance between two adjacent nitrates in the [001] direction (O$_3$) was too short. The same problem arises for the two adjacent nitrates in the [010] direction (O$_4$). This situation is not more compatible with the other possible space groups *C*2 or *Cm*, and no improvements were obtained in these noncentrosymmetric space groups. The factors R_F, R_B, and $R_{\omega p}$ were, respectively, 0.08, 0.11, and 0.20 in the *Cm* space group and 0.08, 0.14, and 0.21 in the *C*2 space group. In both cases the distances and angles of the nitrate group were less satisfactory. Consequently, it appears logical to consider a statistical distribution of the two orientations in the *C*2/*m* space group. At the end of the refinement process, the occupation numbers of O$_2$, O$_3$, and O$_4$ were allowed to vary. They did not significantly differ from their initial 0.5 value. It can be noted that the distribution of the two orientations of nitrate groups in the lattice is not really random because the probability of an interaction O$_3$ · · · O$_3$ along [001] and O$_4$ · · · O$_4$ along [010] is practically null. An order at longer distance could be imagined by considering the *b* and *c* axes multiplied by integers. However, it seems that the solution given here consti-

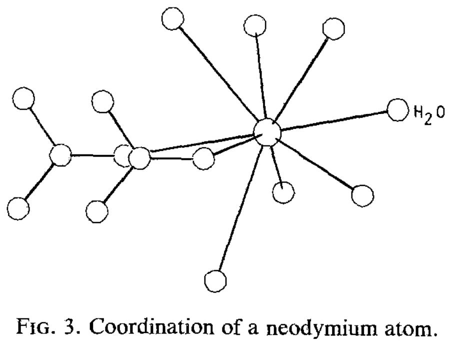

FIG. 3. Coordination of a neodymium atom.

tutes the best possible description with respect to the experimental conditions available for the present powder material.

Disorder of the nitrate groups seems frequent in this kind of solid, in particular in $La(OH)_2NO_3$ (*21*) for which the single crystal study did not allow determination of the atomic coordinates of two oxygen atoms. In $Nd(OH)_2NO_3 \cdot H_2O$, the nitrate group is bonded to two neodymium atoms by only one oxygen; it therefore belongs to the II_1 class of the classification proposed by Leclaire (*22*). The O_3–H_2O or O_4–H_2O distances (see Table III) between two adjacent layers are consistent with the criteria retained for hydrogen bonds (*23*). The exact location of these hydrogen bonds is obviously dependent on the two orientations of the nitrate group.

It is interesting to compare the structure of $Nd(OH)_2NO_3 \cdot H_2O$ with known structures of the related compounds $Ln(OH)_2NO_3$ (Ln = lanthanide). Structures of two polymorphic phases of these anhydrous hydroxynitrates have been described. A recent paper (*24*) reports the crystal structure of $Nd(OH)_2NO_3$ at room temperature (monoclinic $P2_1$). A high-temperature modification of $La(OH)_2NO_3$ (orthorhombic *Cmcm*) (*1, 21*) has also been described. Both of them consist of layers in which *Ln* is surrounded by six hydroxyl ions and three nitrate oxygen atoms. The nitrate groups are linked differently in the crystal structures. In the monoclinic phase of $Nd(OH)_2NO_3$ they form a bidentate ligand, and hydroxyl–oxygen contacts between adjacent layers are consistent with hydrogen bonds. In the orthorhombic phase of $La(OH)_2NO_3$, two oxygen atoms of one nitrate group are bonded to two La belonging to two adjacent layers. In the hydrated compound described in the present paper, the nitrate groups are only linked to Nd by one oxygen atom. Consequently, the original feature of the structure shows similarities with the basic principles of the framework of bivalent metal hydroxynitrates, which have been extensively studied by Louër *et al.* (*25*). As shown in the systematic classification for these hydroxy salts, the structural type I is built from layers $M^{II}X_2$, where X = OH^-, H_2O, or $O(NO_3)$. In the case of $Nd(OH)_2NO_3 \cdot H_2O$ the structure can be described as consisting of NdX_3 layers, where X = OH^-, H_2O, or $O(NO_3)$. In both cases the layers with large interlayer spacing are linked by hydrogen bonds.

Conclusion

The crystal structure of the neodymium hydroxynitrate $Nd(OH)_2NO_3 \cdot H_2O$ has been completely solved from the X-ray diffraction powder data. The solution has been obtained with a reasonable degree of accuracy. This example of moderate complexity, with low symmetry, confirms that, under some favorable circumstances, an *ab initio* structure determination can be performed from high-quality powder data. Examples of structure determination with a similar level of complexity have already been published (see, for example, Refs. (*4, 26, 27*)). In the present case, the position of all atoms were derived from one Patterson function and two Fourier difference maps. In spite of the limited amount of data typically encountered in the powder case, it should be noticed that the structure solution from single crystal data would probably not have been more easily determined. Finally, the structural characteristics of this solid could certainly help in understanding the physicochemical properties of the neodymium hydroxy salts.

Acknowledgments

The authors thank Dr. F. Deneuve, from Rhône Poulenc Recherches, for her cooperation; Professor P.-E. Werner for his many valuable suggestions, Professor R. A. Young for providing the DBW2.9 program, and Professor D. Grandjean for encouragement in this work. Dr. M. Morel and Dr. A. Le Beuze are thanked for their assistance with the computations.

References

1. J. M. Haschke, *Inorg. Chem.* **13,** 1817 (1974).
2. D. Louër, F. Deneuve, C. Herviou, and C. Gourlaouen, *Powder Diffraction,* **1,** 263 (1986).
3. J.-E. Berg and P.-E. Werner, *Zeits. Krist.* **145,** 310 (1977).
4. P.-E. Werner, *Chem. Scrip. A* **26,** 57 (1986).
5. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).
6. D. Louër, J. P. Auffredic, J. I. Langford, D. Ciosmak, and J. C. Niepce, *J. Appl. Crystallogr.* **16,** 183 (1983).
7. H. F. McMurdie, M. C. Morris, E. H. Evans, B. Paretzkin, W. Wong, and C. R. Hubbard, *Powder Diffraction* **1,** 40 (1986).
8. D. Louër and M. Louër, *J. Appl. Crystallogr.* **5,** 271 (1972).
9. D. Louër and R. Vargas, *J. Appl. Crystallogr.* **15,** 542 (1982).
10. P. M. de Wolff, *J. Appl. Crystallogr.* **1,** 108 (1968).
11. G. S. Smith and R. L. Snyder, *J. Appl. Crystallogr.* **12,** 60 (1979).
12. E. J. Sonneveld and J. W. Visser, *J. Appl. Crystallogr.* **8,** 1 (1975).
13. J. J. Langford, D. Louër, E. J. Sonneveld, and J. W. Visser, *Powder Diffraction,* **1,** 211 (1986).
14. "Structure Determination Package" (SDP), Enraf–Nonius, Delft (1981).
15. G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr. A* **27,** 368 (1971).
16. D. B. Wiles and R. A. Young, *J. Appl. Crystallogr.* **14,** 149 (1981).
17. P.-E. Werner, private communication (1986).
18. P.-E. Werner and D. Louër, to be published.
19. R. A. Young and D. B. Wiles, *J. Appl. Crystallogr.* **15,** 430 (1982).
20. R. A. Young, *NBS Spec. Publ. 567,* pp. 143–163 (1980).
21. L. R. Wyles, T. A. Deline, J. M. Haschke, and D. R. Peacore, "The Rare Earth Research Conference, Traverse City, Michigan," Vol. II, p. 550 (1974).
22. A. Leclaire, *J. Solid State Chem.* **28,** 235 (1979).
23. W. H. Baur and A. A. Khan, *Acta Crystallogr. B* **26,** 1584 (1970).
24. D. F. Mullica, E. L. Sappenfield, and D. A. Grossie, *J. Solid State Chem.* **63,** 231 (1986).
25. M. Louër, D. Louër, and D. Grandjean, *Acta Crystallogr. B* **29,** 1696 (1973).
26. A. Clearfield, L. B. McCusker, and P. R. Rudolf, *Inorg. Chem.* **23,** 4679 (1984).
27. H. Behm and Ch. Baerlocher, *Acta Crystallogr. C* **41,** 5 (1985).