

Knowledge of the crystal structure of methoxysilane has also assisted the interpretation and analysis of its solid-state vibrational spectra (Cradock, 1987).

MD thanks the Fond der Chemischen Industrie for financial support.

#### References

- ALMENNINGEN, A., BASTIANSEN, O., EWING, V., HEDBERG, K. & TRÄTTEBERG, M. (1963). *Acta Chem. Scand.* **17**, 2455–2460.  
 ANDRÉ, D., FOURME, R. & ZECHMEISTER, K. (1972). *Acta Cryst.* **B28**, 2389–2395.  
 BARROW, M. J., EBSWORTH, E. A. V. & HARDING, M. M. (1979). *Acta Cryst.* **B35**, 2093–2099.  
 BLAKE, A. J., CRADOCK, S., EBSWORTH, E. A. V., RANKIN, D. W. H. & WELCH, A. J. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2029–2033.

- BLAKE, A. J., EBSWORTH, E. A. V., HENDERSON, S. G. D. & WELCH, A. J. (1985). *Acta Cryst.* **C41**, 1141–1144.  
 BLAKE, A. J., EBSWORTH, E. A. V. & WELCH, A. J. (1984). *Acta Cryst.* **B40**, 895–897.  
 CRADOCK, S. (1987). Personal communication.  
 GLIDEWELL, C., RANKIN, D. W. H., ROBIETTE, A. G., SHELDRIK, G. M., BEAGLEY, B. & FREEMAN, J. M. (1970). *J. Mol. Struct.* **5**, 417–422.  
 GOULD, R. O. & TAYLOR, P. (1985). *CALC*. Program for molecular geometry calculations. Univ. of Edinburgh, Scotland.  
 KIMURA, K. & KUBO, M. (1959). *J. Chem. Phys.* **30**, 151–158.  
 MALLINSON, P. D. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.  
 MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting crystal and molecular structures. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SHELDRIK, G. M. (1984). *SHELX84*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

*Acta Cryst.* (1988). **C44**, 3–6

## Structure of $Y_2BaCuO_5$

BY S. F. WATKINS AND F. R. FRONCZEK

*Louisiana State University, Baton Rouge, LA 70803, USA*

AND K. S. WHELOCK, R. G. GOODRICH, W. O. HAMILTON AND W. W. JOHNSON

*Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803, USA*

(Received 6 July 1987; accepted 4 September 1987)

**Abstract.** Dyttrium barium copper(II) pentoxide,  $M_r = 458.7$ , orthorhombic,  $Pnma$ ,  $a = 12.176$  (2),  $b = 5.655$  (2),  $c = 7.130$  (1) Å,  $V = 491.0$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 6.205$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 357.0$  cm<sup>-1</sup>,  $F(000) = 812$ ,  $T = 295$  (1) K. A total of 1167 unique reflections was measured with a final  $R$  of 0.039 over 907 intensities  $> 2.5\sigma(I)$ . The lattice contains  $Ba^{2+}$ ,  $Y^{3+}$ , and  $CuO_5^{8-}$  ions. Each Ba ion is closely associated with at least nine O atoms, and each Y ion is surrounded by seven O atoms. The covalently bonded anion is a distorted square pyramid, with Cu 0.22 Å above the basal plane. The Cu–O(apex) vector is tilted 9.6° from the perpendicular and is significantly longer [2.196 (7) Å] than the Cu–O(basal) distances [1.971 (6), 2.010 (6) Å]. The powder X-ray diffraction pattern for this structure has been calculated.

**Introduction.** The discovery that certain ternary oxides of copper exhibit the phenomenon of high-temperature superconductivity (Bednorz & Mueller, 1986; Wu, Ashburn, Torng, Hor, Meng, Gao, Huang, Wang & Chu, 1987) has resulted in intense activity to understand the physical origin of the superconductive

phenomenon, and to characterize the principles of structural chemistry responsible for the electrical properties of these materials. The initial discovery of Bednorz & Mueller (1986) involved a substitution compound of  $La_2CuO_4$  ( $K_2NiF_4$  phase-type) in which some of the lanthanum had been substituted by an alkaline-earth ion. Further observation of increases in the superconducting transition temperature under pressure led to the eventual preparation of the 1:2:3 phase,  $YBa_2Cu_3O_{7-x}$ , which exhibits superconductivity above 90 K (Hor, Gao, Huang, Wang, Forster, Vassiliou, Chu, Wu, Ashburn & Torng, 1987). The preparation has been generalized to include most of the lanthanides (Engler, Lee, Nazzari, Beyers, Lim, Grant, Parkin, Ramirez, Vazquez & Savoy, 1987) with the apparent requirement that the compound contain Cu; this stimulated the investigation of the ternary phase diagram of  $CuO + BaO + Ln_2O_3$  ( $Ln = Y$ , lanthanide), with most of the effort concentrated on yttrium.

Most of the preparative techniques involve the sintering of oxides, carbonates, or other easily decomposed oxygen-containing precursors, and the product characterization techniques most frequently relied upon

have been powder X-ray diffraction and electron microprobe analysis. Single-crystal structure determinations of the pure phases in the ternary phase diagram have tended to be the exception rather than the rule, since these materials usually do not melt congruently (Wold, 1987).

In the preparation of the 1:2:3 phase, two groups (Hinks, Soderholm, Capone, Jorgensen, Schuller, Segre, Zhang & Grace, 1987; Sun, Webb, Naito, Char, Hahn, Hsu, Kent, Mitzi, Oh, Beasley, Beballe, Hammond & Kapitulnik, 1987) report the initial appearance of a dark green insulating phase which, upon subsequent grinding and reheating, produced a material containing the desired superconducting phase. The dark green phase was identified as Y<sub>2</sub>BaCuO<sub>5</sub>, the approximate structure of which has been deduced from X-ray powder diffraction (Michel & Raveau, 1980). We report here the determination of the structure of Y<sub>2</sub>BaCuO<sub>5</sub> by single-crystal methods with an accompanying sevenfold improvement in the precision of the structural parameters.

**Experimental.** Preparation of the crystalline 2:1:1 phase, Y<sub>2</sub>BaCuO<sub>5</sub>, resulted from an attempt to prepare an oxygen-deficient non-superconducting phase with the same metal-ion stoichiometry as the superconducting 1:2:3 phase. Quantities of Y<sub>2</sub>O<sub>3</sub> (0.889 g, Aldrich Gold Label, 99.99%), BaCO<sub>3</sub> (3.030 g, Fischer Certified ACS precipitated) and CuO (1.847 g, Johnson–Matthey Puratronic) were weighed out as received and ground together in a corundum mortar and pestle. The mixture was placed in an Alundum combustion boat and heated to 1250 K for approximately 15 h in air. This is in contrast to the conditions we typically use when the superconducting phase is sought, *i.e.* flowing oxygen in place of air. Upon cooling, the preparation exhibited a mass of dark green, almost black crystals which had sintered together. This mass of crystals was removed from the combustion boat intact, leaving several pale purple masses on the floor of the Alundum boat. Previous attempts to synthesize the superconducting phase have been successful when flowing oxygen was used, and no reaction between the Alundum boat and the starting materials was observed in those cases.

A very dark green prismatic crystal was selected for study (see Tables 1 and 2). Cell constants were derived from least-squares refinement of 25 reflections having  $29 < 2\theta < 33^\circ$ . The structure was solved by direct methods and refined by weighted full-matrix least squares. Refinement in centrosymmetric space group *Pnma* and in noncentrosymmetric space group *Pn2<sub>1</sub>a* produced equivalent structural models and residuals, but the correlation coefficients and estimated standard deviations of all parameters in *Pn2<sub>1</sub>a* were significantly larger. Therefore, the centrosymmetric space group was deemed correct. Systematic absences are  $0kl$  with  $k + l$

Table 1. *Experimental details*

Crystal size (mm)	0.08 × 0.08 × 0.24
Instrument	Enraf–Nonius CAD-4
Monochromator	Incident beam, graphite
Attenuator	Zr foil, factor 17.5
Scan type	$\omega$ - $2\theta$
Data collected	$0 < h < 19, 0 < k < 9, 0 < l < 11$
Scan rate ( $^\circ \text{ min}^{-1}$ )	0.87 to 3.30
Scan width ( $^\circ$ )	$0.7 + 0.350 \tan \theta$
Maximum $2\theta$ ( $^\circ$ )	70
Reflections	1289 total 1167 unique
Corrections	Lorentz–polarization Anisotropic decay (0.976–1.827 on <i>l</i> ) Standard reflections 600,020,004 Empirical absorption (0.58–0.99 on <i>l</i> ) Extinction $[7.21(13) \times 10^{-7}]$

Table 2. *Structure solution and refinement*

Solution	Direct methods
Refinement	Full-matrix least squares
Function minimized	$\sum_w ( F_o  -  F_c )^2$
Weights	$4F_o^2/\sigma^2(F_o^2)$
Reflections included	907 with $I > 2.5\sigma(I)$
Parameters refined	50
Unweighted residual	0.039
Weighted residual	0.046
Goodness of fit	1.82
Maximum shift/e.s.d.	0.10
Maximum, final $\Delta F$ map	$+3.27 \text{ e } \text{ \AA}^{-3}$
Minimum, final $\Delta F$ map	$-3.20 \text{ e } \text{ \AA}^{-3}$

odd and  $hk0$  with  $h$  odd. Scattering factors, including anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The highest peaks in the final difference Fourier map were associated with the barium ion with values approximately 5% of the barium peak. Computer programs used: *MULTAN80* (Main *et al.*, 1980); *Enraf–Nonius SDP* (Frenz, 1978); *PLUTO78* (Motherwell & Clegg, 1978).

**Discussion.** Final positional and anisotropic thermal parameters are shown in Table 3,\* and selected internuclear distances are listed in Table 4. Fig. 1 is a stereoscopic view of the unit cell. Table 5 lists the 20 strongest powder diffraction lines calculated using *POWD10* (Smith & Holomany, 1980). The crystallographically independent unit was correctly described by Michel & Raveau (1980). It consists of O atoms O1 and O2 in general positions  $[8(d)]$ , while the four metal atoms and the remaining O atom lie on mirror planes  $[4(c)]$ .

To guide our discussion of the coordination chemistry of the metal ions, we shall use the following approximate radii (Huheey, 1972): Ba<sup>2+</sup> = 1.45, Y<sup>3+</sup> = 0.95, Cu<sup>II</sup> = 0.65, O<sup>2-</sup> = 1.40 Å. Comparing these values with Table 4, we infer that Cu is covalently bonded to atoms O1 and O2 which, together with their

\* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44349 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Atomic positional and thermal parameters ( $\text{\AA}^2$ )

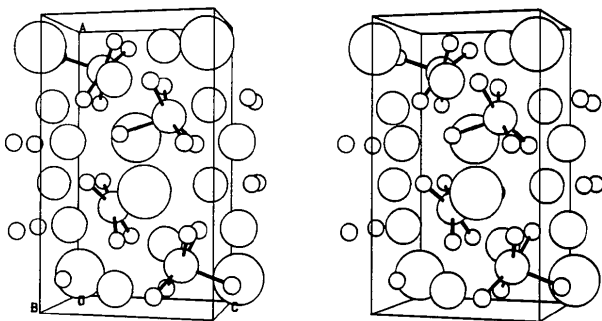
	<i>x</i>	<i>y</i>	<i>z</i>	$U_{xx}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ba	0.09520 (5)	0.250	0.06985 (9)	0.0041 (1)	0.0029 (2)	0.0037 (2)	0.0056 (2)	0	-0.0009 (2)	0
Y1	0.07382 (8)	0.750	0.3959 (1)	0.0013 (1)	0.0003 (3)	0.0022 (4)	0.0012 (3)	0	0.0001 (3)	0
Y2	0.28827 (8)	0.750	0.1163 (1)	0.0013 (1)	0.0001 (3)	0.0016 (5)	0.0020 (3)	0	0.0001 (3)	0
Cu	0.6595 (1)	0.750	0.7126 (2)	0.0022 (3)	0.0019 (5)	0.0020 (6)	0.0025 (4)	0	0.0013 (4)	0
O1	0.5681 (4)	0.507 (1)	0.8345 (7)	0.005 (1)	0.002 (2)	0.007 (3)	0.005 (2)	-0.002 (2)	0.000 (2)	0.001 (2)
O2	0.7712 (4)	0.503 (1)	0.6432 (7)	0.005 (1)	0.003 (2)	0.005 (3)	0.007 (2)	0.002 (2)	0.002 (2)	0.004 (2)
O3	0.6000 (6)	0.750	0.422 (1)	0.005 (1)	0.008 (3)	0.006 (4)	0.003 (3)	0	-0.002 (3)	0

Table 4. Selected interatomic distances ( $\text{\AA}$ )

Ba—O1	3.245 (5)	Ba—O2'	2.992 (5)
Ba—O1'	3.067 (5)	Ba—O3	2.600 (8)
Ba—O2	2.963 (5)	Ba—O3'	2.829 (8)
Cu—O1	1.971 (6)	Cu—O3	2.196 (7)
Cu—O2	2.010 (6)		
Y1—O1	2.300 (6)	Y1—O2	2.386 (5)
Y1—O1'	2.364 (5)	Y1—O3	2.289 (7)
Y2—O1	2.300 (6)	Y2—O2'	2.349 (5)
Y2—O2	2.327 (5)	Y2—O3	2.309 (8)

Table 5. Powder pattern (relative intensities)

<i>d</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i>	<i>d</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i>
2.993	3	1	1	100	1.651	1	3	2	10
2.927	1	1	2	66	2.421	3	1	2	9
2.827	0	2	0	32	1.562	4	2	3	9
1.989	4	2	1	26	1.507	7	1	2	9
2.702	2	1	2	19	2.304	5	0	1	8
2.800	4	0	1	16	1.873	4	0	3	8
2.214	2	0	3	16	1.944	3	2	2	7
1.662	3	3	1	14	1.414	0	4	0	7
2.509	4	1	1	11	1.309	3	1	5	7
1.743	2	2	3	11	2.180	1	2	2	6

Fig. 1. Stereoview of the unit cell of  $\text{Y}_2\text{BaCuO}_5$ . The Cu—O bonds are shown. The largest circles are  $\text{Ba}^{2+}$ .

mirror-equivalent counterparts, form the base of the square-pyramidal anion. The metal atom is 0.22  $\text{\AA}$  above the base toward the apex. The apical O atom, O3, is much less tightly bound to the metal; furthermore, the Cu—O3 vector is tilted 9.6° from the perpendicular toward the O2...O2' base edge.

Each Y cation is surrounded by seven O atoms: six are arranged as a trigonal prism with the seventh (O3) capping one rectangular face. Face- and edge-sharing of

these polyhedra leads to a three-dimensional network as previously described (Michel & Raveau, 1980). All Y—O distances are within the expected range.

Characterization of the Ba coordination polyhedron is somewhat arbitrary; the sum of radii suggests that 2.85  $\text{\AA}$  is the expected Ba—O contact distance, but the observed distances cover a broad range. Atom O3 is very closely associated with Ba which undoubtedly causes the observed anion distortion. A total of nine O atoms are within 3.07  $\text{\AA}$  while the tenth and eleventh O atoms are at 3.25  $\text{\AA}$ . No other atoms are closer to Ba than 4  $\text{\AA}$ . This suggests that the cavity in which  $\text{Ba}^{2+}$  resides is irregularly shaped and generally larger than the ion. The observed thermal parameters for Ba are consistent with this hypothesis.

If thermal parameters derived from diffraction data are a physically meaningful measure of the anisotropic restoring forces acting on an atom in a crystal, then contact distances will be correlated with orientation and size of the vibrational displacement tensor. In this work, such correlations are indeed found for Ba (0.93) and Cu (0.99), and to a lesser extent for Y (0.61). However, no such correlation can be assigned to oxygen since each of these atoms contributes only 1% to the total scattered intensity, with consequent loss of precision in the measured parameters.

It is interesting to note that the thermal parameters for both Y atoms are small. The model of Michel & Raveau (1980) also included a small thermal parameter for one Y atom. Anomalously low thermal parameters would be produced during model refinement if the  $\text{Y}^{3+}$  sites were partially occupied by lanthanide ions. However, analysis of the 99.99% yttrium oxide starting material revealed lanthanide oxides to be present at under 50 p.p.m. each. Thus, we believe that partial occupation by heavier cations is a minor effect; primarily, it is the cavity size and shape which severely restricts thermal vibration at the  $\text{Y}^{3+}$  sites.

As this work was being prepared for publication another single-crystal study appeared (Hazen, Finger, Angel, Prewitt, Ross, Mao, Hadidiacos, Hor, Meng & Chu, 1987).

#### References

- BEDNORZ, J. G. & MUELLER, K. A. (1986). *Z. Phys. B*, **64**, 189–193.

- ENGLER, E. M., LEE, V. Y., NAZZAL, A. I., BEYERS, R. B., LIM, G., GRANT, P. M., PARKIN, S. S. P., RAMIREZ, M. L., VAZQUEZ, J. W. & SAVOY, R. J. (1987). *J. Am. Chem. Soc.* **109**, 2848–2849.
- FRENZ, B. A. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.
- HAZEN, R. M., FINGER, L. W., ANGEL, R. J., PREWITT, C. T., ROSS, N. L., MAO, H. K., HADIDIACOS, C. G., HOR, P. H., MENG, R. L. & CHU, C. W. (1987). *Phys. Rev. B*, pp. 7238–7241.
- HINKS, D. G., SODERHOLM, L., CAPONE, D. W. II, JORGENSEN, J. D., SCHULLER, I. K., SEGRE, C. U., ZHANG, K. & GRACE, J. D. (1987). *Appl. Phys. Lett.* Submitted.
- HOR, P. H., GAO, L., HUANG, Z. J., WANG, Y. Q., FORSTER, K., VASSILOUS, J., CHU, C. W., WU, M. K., ASHBURN, J. R. & TORNG, C. J. (1987). *Phys. Rev. Lett.* **58**, 911–912.
- HUHEEY, J. E. (1972). *Inorganic Chemistry: Principles of Structure and Reactivity*. New York: Harper & Row.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MICHEL, C. & RAVEAU, B. (1980). *J. Solid State Chem.* **43**, 73–80.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78*. A program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SMITH, K. D. & HOLOMANY, M. (1980). *A FORTRAN IV Program for Calculating X-ray Powder Diffraction Patterns*. Pennsylvania State Univ., USA.
- SUN, J. Z., WEBB, D. J., NAITO, N., CHAR, K., HAHN, M. R., HSU, J. W. P., KENT, A. D., MITZI, D. B., OH, B., BEASLEY, M. R., BEBALLE, T. H., HAMMOND, R. H. & KAPITULNIK, A. (1987). *Phys. Rev. Lett.* **58**, 1574–1576.
- WOLD, A. (1987). Private communication to K. S. WHEELOCK.
- WU, M. K., ASHBURN, J. R., TORNG, C. J., HOR, P. H., MENG, R. L., GAO, L., HUANG, Z. J., WANG, H. Q. & CHU, C. W. (1987). *Phys. Rev. Lett.* **58**, 908–910.

*Acta Cryst.* (1988). **C44**, 6–8

## Structure de NdH(PO<sub>3</sub>H)<sub>2</sub>·2H<sub>2</sub>O

PAR M. LOUKILI

*Ecole Normale Supérieure, Département Chimie, BP, 34A, Fès, Maroc*

J. DURAND ET L. COT

*Laboratoire de Physicochimie des Matériaux (UA 407), ENSCM, 8 rue de l'Ecole Normale, 34075 Montpellier CEDEX, France*

ET M. RAFIQ

*Laboratoire de Chimie Minérale, Faculté des Sciences, Fès, Maroc*

(Reçu le 16 février 1987, accepté le 8 septembre 1987)

**Abstract.**  $M_r = 341.2$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.6840$  (9),  $b = 16.503$  (4),  $c = 7.053$  (3) Å,  $V = 778.0$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 2.88$  (1),  $D_x = 2.906$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 7.14$  mm<sup>-1</sup>,  $F(000) = 644$ ,  $T = 293$  K,  $R = 0.031$  for 362 independent reflexions. The structure contains two phosphite anions connected by a weak hydrogen bond. The Nd<sup>3+</sup> cation is eight-coordinated by seven phosphite anion O atoms and one water O atom.

**Introduction.** Le phosphite de néodyme NdH(PO<sub>3</sub>H)<sub>2</sub>·2H<sub>2</sub>O appartient à une nouvelle famille de composés dans laquelle le néodyme peut être substitué par La, Ce, Pr, Sm, Eu ou Gd. Toutes ces phases sont isostructurales.

Quelques phosphites alcalins: Na<sub>2</sub>PO<sub>3</sub>H·5H<sub>2</sub>O (Colton & Henn, 1971), (NH<sub>4</sub>)<sub>2</sub>PO<sub>3</sub>H·H<sub>2</sub>O (Rafiq, Durand & Cot, 1982), alcalino-terreux: MgPO<sub>3</sub>H·6H<sub>2</sub>O (Corbridge, 1956), Ca(HPO<sub>3</sub>H)<sub>2</sub>·H<sub>2</sub>O (Larbot, Durand & Cot, 1984), et de métaux de transition divalents:

CuPO<sub>3</sub>H·2H<sub>2</sub>O (Handlovic, 1969) et Cd(H<sub>2</sub>PO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (Loub, Podlahova & Jecny, 1978) ont fait l'objet de déterminations structurales.

Les seules études concernant les métaux trivalents sont relatives à la préparation et l'analyse par spectroscopie d'absorption infra-rouge (Muck & Petru, 1971; Ebert & Kavan, 1978) ou la caractérisation cristallographique (Larbot, Battou, Durand & Cot, 1982) des phases mises en évidence.

L'étude structurale du composé NdH(PO<sub>3</sub>H)<sub>2</sub>·2H<sub>2</sub>O a pour but de mieux connaître l'arrangement type de la famille des phosphites des éléments de terre rare de formule générale MH(PO<sub>3</sub>H)<sub>2</sub>·2H<sub>2</sub>O.

**Partie expérimentale.** Les cristaux en forme de fines aiguilles sont obtenus par évaporation lente d'une solution obtenue par dissolution de Ln<sub>2</sub>O<sub>3</sub> dans un excès d'acide phosphoreux H<sub>2</sub>PO<sub>3</sub>H (Loukili, Rafiq, Durand & Cot, 1987). Les premiers cristaux qui apparaissent correspondent à la phase monoclinique