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Crystal Structure of Triclinic CeP_5O_{14}: A New Type of Ultraphosphate

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The new form of cerium(III) ultraphosphate, CeP_5O_{14} described here is triclinic with $a = 9.227(5)$, $b = 8.890(5)$, $c = 7.219(4)$ Å, $\alpha = 110.12(5)°$, $\beta = 102.68(5)°$, $\gamma = 82.13(5)°$. Space group is $P1$. $Z = 2$. $D_x = 3.186$ mg/m^3. Crystal structure of this salt has been solved by using 4587 independent reflections with a final R value 0.029. The atomic arrangement can be described as $[P_{10}O_{28}]$ sheets spreading in (110) planes. The internal structure of these sheets is mainly a linkage of $(P_{12}O_{36})$ rings in which 40% of the phosphorus atoms are branching phosphorus.

Introduction

The chemistry of rare earth phosphates has developed rapidly in the last few years. Such rapid development may be attributed, mainly, to the use of neodynium ultraphosphate as a suitable material for miniature solid-state lasers (*1–4*). Rare earth ultraphosphates LnP_5O_{14}, sometimes erroneously called pentaphosphates, crystallize with three different types of structure (*5, 6*). The rare earths, from La to Tb, form monoclinic crystals with space group $P2_1/a$ (type I). The elements Tb–Dy, Y form a second monoclinic variety (type II) of ultraphosphates with space group $C2/c$. The lanthanide group Dy–Er and Y form a third LnP_5O_{14} type (III) which is orthorhombic with space group $Pcmn$.

Cerium ultraphosphate is known to crys-

TABLE I

MEASUREMENT PARAMETERS USED FOR THE X-RAY DIFFRACTION DATA COLLECTION

Apparatus	Philips PW 1100	Total background measurement time	10 sec
Wavelength	Ag$K\bar{\alpha}$ (0.5608 Å)	Scan width	1.20°
Monochromator	Graphite plate	Reference reflections (every 2 hr)	4 6 $\bar{2}$ and $\bar{4}$ $\bar{6}$ 2
Scan mode	ω	Number of measured reflections	4822 (±H, ±K, L)
Scan speed	0.03° sec^{-1}	Crystal size	0.25 × 0.19 × 0.13 mm^3
Theta range	3–30°(θ)		

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tallize with the monoclinic form (I) with a = 13.113, b = 9.063, c = 8.790 Å, β = 90.45°, Z = 2, $P2_1/a$.

In the present study we describe for this salt a new crystallographic form, triclinic $P1$, not yet observed.

Chemical preparation and crystal chemistry of this new phase have been already described elsewhere (*7*).

Experimental

Parameters used for the X-ray diffraction data collection are reported in Table I.

TABLE II

ANISOTROPIC THERMAL PARAMETERS

Atoms	$\beta(1,1)(\sigma)$	$\beta(2,2)(\sigma)$	$\beta(3,3)(\sigma)$	$\beta(1,2)(\sigma)$	$\beta(1,3)(\sigma)$	$\beta(2,3)(\sigma)$
Ce(1)	0.00131(2)	0.00191(2)	0.00380(5)	−0.00041(3)	0.00057(5)	0.00135(5)
Ce(2)	0.00137(2)	0.00187(2)	0.00308(5)	−0.00062(3)	0.00031(5)	0.00112(5)
P(1)	0.0018(1)	0.0031(1)	0.0039(3)	−0.0008(2)	0.0004(3)	0.0017(3)
P(2)	0.0017(1)	0.0024(1)	0.0047(3)	−0.0002(2)	0.0013(3)	0.0016(3)
P(22)	0.0023(1)	0.0026(1)	0.0036(3)	−0.0003(2)	0.0002(3)	0.0015(3)
P(3)	0.0016(1)	0.0022(1)	0.0042(3)	−0.0006(2)	0.0004(3)	0.0006(3)
P(4)	0.0018(1)	0.0027(1)	0.0043(3)	0.0003(2)	0.0006(3)	0.0015(3)
P(5)	0.0016(1)	0.0020(1)	0.0047(3)	−0.0005(2)	0.0002(3)	0.0018(3)
P(6)	0.0016(1)	0.0022(1)	0.0043(3)	−0.0007(2)	0.0011(3)	0.0014(3)
P(66)	0.0015(1)	0.0024(1)	0.0044(3)	−0.0004(2)	0.0001(3)	0.0012(3)
P(7)	0.0014(1)	0.0024(1)	0.0043(3)	0.0000(2)	0.0002(3)	0.0017(3)
P(8)	0.0017(1)	0.0020(1)	0.0036(3)	−0.0004(2)	0.0018(3)	0.0008(3)
O(L12)	0.0058(5)	0.0023(4)	0.0055(9)	−0.0011(7)	0.0021(10)	0.0024(9)
O(E11)	0.0043(4)	0.0040(4)	0.0091(10)	−0.0024(7)	0.0033(10)	0.0043(9)
O(E12)	0.0029(4)	0.0063(6)	0.0058(10)	−0.0010(8)	0.0002(10)	0.0020(12)
O(L222)	0.0020(4)	0.0063(6)	0.0078(11)	−0.0017(8)	0.0013(10)	−0.0031(13)
O(L23)	0.0035(4)	0.0068(5)	0.0092(10)	0.0032(8)	0.0019(10)	0.0089(10)
O(E21)	0.0033(4)	0.0073(6)	0.0108(11)	−0.0031(8)	0.0056(10)	0.0045(12)
O(L224)	0.0014(3)	0.0074(5)	0.0075(9)	0.0006(7)	0.0010(9)	0.0083(10)
O(E221)	0.0055(5)	0.0036(5)	0.0166(14)	−0.0014(9)	−0.0053(15)	0.0083(12)
O(E222)	0.0024(4)	0.0082(6)	0.0078(10)	0.0013(8)	0.0011(10)	0.0091(12)
O(L34)	0.0046(4)	0.0051(5)	0.0052(10)	−0.0032(8)	0.0015(10)	0.0018(10)
O(E31)	0.0103(7)	0.0035(5)	0.0062(11)	−0.0059(9)	0.0074(13)	−0.0042(11)
O(E32)	0.0022(4)	0.0092(6)	0.0114(11)	−0.0023(7)	0.0005(10)	0.0109(12)
O(L45)	0.0023(3)	0.0040(4)	0.0067(9)	−0.0007(6)	0.0003(9)	0.0032(9)
O(E41)	0.0046(5)	0.0027(4)	0.0102(12)	0.0036(8)	−0.0002(12)	0.0008(11)
O(L56)	0.0031(4)	0.0020(4)	0.0177(14)	−0.0005(7)	0.0004(12)	0.0059(11)
O(E51)	0.0055(5)	0.0048(5)	0.0042(10)	0.0017(9)	−0.0020(11)	0.0015(11)
O(E52)	0.0035(4)	0.0068(6)	0.0103(10)	−0.0001(8)	0.0055(10)	0.0070(11)
O(L67)	0.0025(3)	0.0044(5)	0.0075(10)	−0.0027(7)	0.0038(9)	−0.0029(12)
O(L666)	0.0015(3)	0.0042(4)	0.0083(100	−0.0005(6)	0.0019(9)	0.0050(9)
O(E61)	0.0027(4)	0.0073(5)	0.0095(10)	−0.0009(7)	0.0047(9)	0.0066(11)
O(L668)	0.0026(3)	0.0027(4)	0.0056(9)	−0.0007(6)	0.0012(9)	−0.0001(9)
O(E661)	0.0016(3)	0.0074(6)	0.0115(11)	−0.0003(7)	0.0008(10)	0.0087(12)
O(E662)	0.0061(5)	0.0036(5)	0.0054(10)	−0.0031(8)	0.0003(12)	−0.0020(11)
O(L78)	0.0023(3)	0.0041(4)	0.0073(9)	−0.0007(6)	0.0042(8)	0.0022(10)
O(E71)	0.0028(4)	0.0042(5)	0.0061(10)	−0.0007(7)	−0.0009(10)	.0028(10)
O(E72)	0.0051(5)	0.0033(4)	0.0105(11)	0.0024(8)	0.0020(12)	0.0052(10)
O(L81)	0.0016(3)	0.0053(5)	0.0062(9)	0.0004(6)	0.0012(8)	0.0052(9)
O(E81)	0.0043(4)	0.0025(4)	0.0092(10)	−0.0015(7)	0.0034(10)	0.0025(9)

Crystal structure has been solved by using classical methods: study of the three-dimensional Patterson function, followed by successive Fourier syntheses.

After some refinement cycles the final R value is 0.029 with anisotropic thermal parameters (Table II). The final atomic coordinates and the equivalent temperature factors are reported in Table III. Being given the wavelength used and the size of the

TABLE III

FINAL ATOMIC COORDINATES AND THERMAL FACTORS

CALCULATED FROM $B_{eq.} = \frac{4}{3} \sum_i \sum_j a_i \cdot a_j \cdot \beta_{ij}$

Ce(1)	0.00000(0)	0.00000(0)	0.00000(0)	0.559(03)
Ce(2)	0.46469(3)	0.50580(4)	0.53310(6)	0.516(03)
P(1)	0.1272(2)	0.0521(2)	0.5675(3)	0.726(17)
P(2)	0.1553(2)	0.3997(2)	0.7406(3)	0.691(17)
P(22)	0.1486(2)	0.6200(2)	0.1518(3)	0.723(17)
P(3)	0.8759(2)	0.5883(2)	0.6283(3)	0.685(17)
P(4)	0.9082(2)	0.4669(2)	0.2013(3)	0.747(17)
P(5)	0.6009(2)	0.6054(2)	0.1177(3)	0.665(16)
P(6)	0.6779(2)	0.9402(2)	0.2111(3)	0.634(16)
P(66)	0.4024(2)	0.1177(2)	0.1051(3)	0.690(17)
P(7)	0.6733(2)	0.1195(2)	0.6374(3)	0.674(17)
P(8)	0.4346(2)	0.9568(2)	0.6850(3)	0.600(16)
O(L12)	0.1473(6)	0.2268(5)	0.7409(8)	1.127(60)
O(E11)	0.0848(6)	0.9525(6)	0.6696(8)	1.284(59)
O(E12)	0.0446(6)	0.0703(7)	0.3798(8)	1.518(67)
O(L222)	0.2097(5)	0.4864(7)	0.9679(9)	1.515(60)
O(L23)	−0.0117(6)	0.4504(7)	0.6890(9)	1.423(64)
O(E21)	0.2503(6)	0.4162(7)	0.6122(9)	1.618(66)
O(L224)	0.9792(5)	0.5666(6)	0.1091(8)	1.201(59)
O(E221)	0.1369(7)	0.7762(6)	0.1202(11)	2.033(73)
O(E222)	0.2308(6)	0.5920(7)	0.3360(9)	1.453(65)
O(L34)	0.9232(6)	0.5777(6)	0.4234(8)	1.256(62)
O(E31)	0.9117(8)	0.7459(6)	0.7710(9)	1.851(76)
O(E32)	0.7277(5)	0.5302(7)	0.5897(9)	1.612(66)
O(L45)	0.7409(5)	0.4730(6)	0.1053(8)	1.011(53)
O(E41)	0.9720(6)	0.3034(6)	0.1727(9)	1.576(63)
O(L56)	0.6958(6)	0.7651(5)	0.2128(10)	1.658(62)
O(E51)	0.5237(6)	0.5896(6)	0.9132(8)	1.498(69)
O(E52)	0.5215(6)	0.6036(7)	0.2718(9)	1.586(67)
O(L67)	0.7365(5)	0.0445(6)	0.4316(8)	1.295(56)
O(L666)	0.5048(5)	0.9756(6)	0.1699(8)	0.978(52)
O(E61)	0.7567(5)	0.9696(7)	0.0738(8)	1.393(62)
O(L668)	0.4448(5)	0.0954(5)	0.8914(8)	0.912(51)
O(E661)	0.2491(5)	0.0800(7)	0.0811(9)	1.510(63)
O(E662)	0.4564(7)	0.2738(6)	0.2381(9)	1.447(65)
O(L78)	0.5730(5)	0.9725(6)	0.6064(8)	1.045(52)
O(E71)	0.8017(5)	0.1232(6)	0.7991(8)	1.186(58)
O(E72)	0.5736(6)	0.2628(6)	0.6339(9)	1.489(64)
O(L81)	0.3008(5)	0.0081(6)	0.5413(8)	0.997(53)
O(E81)	0.4320(6)	0.7973(6)	0.6974(9)	1.251(59)

Note. P_i ($i = 1, 2, 3 \ldots n$). Bonding oxygen atoms connecting two phosphorus atoms P_i and P_j are denoted O(Lij), while the two external oxygen atoms of a given P_i phosphorus are noted O(Ei1) and O(Ei2).

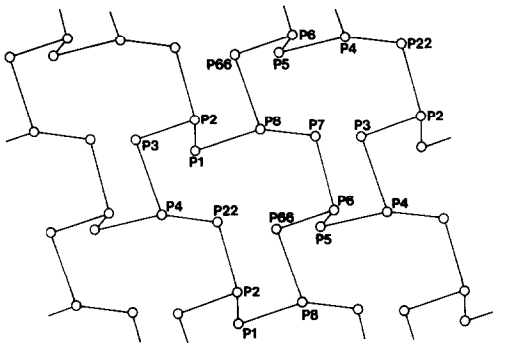

FIG. 1. Schematic representation of the phosphorus atoms inside the $[P_{10}O_{28}]$ sheets, projected on the $(\vec{a},\vec{c})$ plane. Oxygene atoms are not represented. We can see 12-membered conjugate corrugated rings.

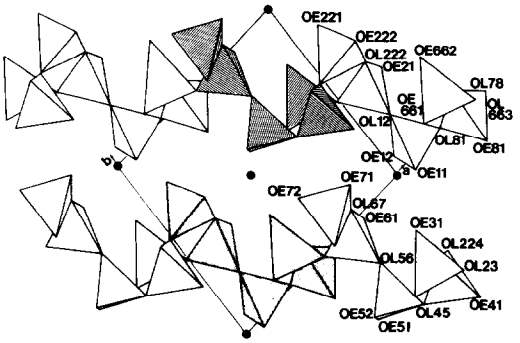

FIG. 2. Atomic arrangement of CeP_5O_{14} (triclinic form) in projection along the c axis. $[P_{10}O_{28}]$ sheets spreading in (110) are obvious. The 10 independent PO_4 tetrahedra are distinguished by dotted shading.

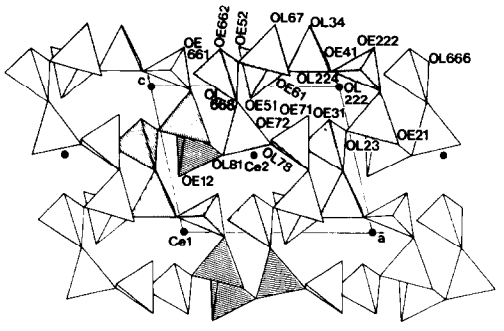

FIG. 3. Projection of structure of CeP_5O_{14} (triclinic) on the $(\vec{a},\vec{c})$ plane. The internal structure of the sheets is mainly a linkage of $(P_{12}O_{36})$ rings. Dotted shading indicates these rings.

crystal no absorption corrections have been made. A unitary weighting scheme has been used. Space group $P\bar{1}$ suggested by the strong piezoelectric effect observed during the characterization of this compound is confirmed by the crystal structure determination. Final atomic coordinates reported in Table II correspond to a final set of 4587 reflections such that $F_0 > \sqrt{3}\sigma_F$.

TABLE IV

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN THE ($P_{10}O_{28}$) SHEETS

P(1)O_4 TETRAHEDRON

P(1)	O(L12)	O(E11)	O(E12)	O(L81)
O(L12)	1.629(4)	2.438(5)	2.533(7)	2.468(6)
O(E11)	103.80(26)	1.467(5)	2.585(7)	2.545(6)
O(E12)	110.26(26)	124.34(28)	1.457(5)	2.489(6)
O(L81)	98.21(23)	110.09(25)	107.05(27)	1.636(4)

P(2)O_4 TETRAHEDRON

P(2)	O(L12)	O(L222)	O(L23)	O(E21)
O(L12)	1.552(4)	2.383(6)	2.395(6)	2.550(6)
O(L222)	100.16(29)	1.556(5)	2.504(7)	2.529(8)
O(L23)	101.28(26)	107.67(28)	1.546(4)	2.549(6)
O(E21)	115.78(28)	114.00(28)	116.07(31)	1.458(5)

P(22)O_4 TETRAHEDRON

P(22)	O(L222)	O(L224)	O(E221)	O(E222)
O(L222)	1.598(5)	2.471(6)	2.492(7)	2.466(8)
O(L224)	99.89(25)	1.631(4)	2.484(7)	2.522(6)
O(E221)	108.81(35)	106.56(26)	1.455(5)	2.569(7)
O(E222)	107.32(29)	109.16(36)	122.73(31)	1.462(5)

P(3)O_4 TETRAHEDRON

P(3)	O(L23)	O(L34)	O(E31)	O(E32)
O(L23)	1.607(5)	2.470(7)	2.516(7)	2.433(6)
O(L34)	100.86(27)	1.597(5)	2.453(7)	2.524(7)
O(E31)	110.35(32)	106.81(28)	1.457(4)	2.545(7)
O(E32)	104.69(28)	111.02(29)	121.24(32)	1.464(4)

P(4)O_4 TETRAHEDRON

P(4)	O(L224)	O(L34)	O(L45)	O(E41)
O(L224)	1.556(5)	2.408(7)	2.447(6)	2.548(6)
O(L34)	101.31(26)	1.558(5)	2.500(7)	2.544(6)
O(L45)	104.01(28)	107.14(30)	1.550(6)	2.495(6)
O(E41)	115.65(28)	115.23(29)	112.29(28)	1.454(4)

TABLE IV—*Continued*

P(5)O_4 TETRAHEDRON

P(5)	O(L45)	O(L56)	O(E51)	O(E52)
O(L45)	1.623(5)	2.453(6)	2.494(7)	2.524(7)
O(L56)	97.76(24)	1.633(4)	2.540(7)	2.485(6)
O(E51)	108.10(30)	110.53(29)	1.456(5)	2.557(7)
O(E52)	109.40(31)	106.38(29)	121.97(30)	1.468(5)

P(6)O_4 TETRAHEDRON

P(6)	O(L56)	O(L67)	O(L666)	O(E61)
O(L56)	1.543(4)	2.463(7)	2.438(6)	2.529(7)
O(L67)	105.37(33)	1.554(6)	2.505(8)	2.473(9)
O(L666)	103.23(23)	106.79(28)	1.567(4)	2.555(6)
O(E61)	114.90(29)	110.38(30)	115.33(27)	1.457(5)

P(66)O_4 TETRAHEDRON

P(66)	O(L666)	O(L668)	O(E661)	O(E662)
O(L666)	1.612(4)	2.511(7)	2.449(5)	2.516(6)
O(L668)	102.42(24)	1.610(5)	2.538(6)	2.444(6)
O(E661)	105.56(25)	111.34(27)	1.462(4)	2.557(6)
O(E662)	109.43(26)	105.01(26)	121.52(29)	1.469(4)

P(7)O_4 TETRAHEDRON

P(7)	O(L67)	O(L78)	O(E71)	O(E72)
O(L67)	1.613(6)	2.438(7)	2.458(8)	2.529(7)
O(L78)	97.49(26)	1.630(4)	2.530(6)	2.521(6)
O(E71)	106.00(29)	109.65(26)	1.463(4)	2.565(6)
O(E72)	110.18(34)	108.74(24)	121.99(27)	1.469(4)

P(8)O_4 TETRAHEDRON

P(8)	O(L668)	O(L78)	O(L81)	O(E81)
O(L668)	1.570(4)	2.454(6)	2.493(7)	2.543(5)
O(L78)	103.93(23)	1.547(4)	2.445(5)	2.489(6)
O(L81)	105.95(24)	104.14(26)	1.553(5)	2.548(6)
O(E82)	114.25(28)	111.86(24)	115.59(25)	1.458(4)

OTHER INTERESTING DISTANCES AND BOND ANGLES

P(1)–P(2)	2.932(2)	P(1)–O(L12)–P(2)	134.40(33)
P(1)–P(8)	2.875(2)	P(1)–O(L18)–P(8)	128.76(34)
P(2)–P(22)	2.950(2)	P(2)–O(L222)–P(22)	138.60(34)
P(2)–P(3)	2.991(2)	P(2)–O(L23)–P(3)	143.06(37)
P(3)–P(4)	2.962(2)	P(3)–O(L34)–P(4)	139.79(31)
P(4)–P(22)	2.901(2)	P(4)–O(L422)–P(22)	131.12(29)
P(4)–P(5)	2.955(2)	P(4)–O(L45)–P(5)	137.29(36)
P(5)–P(6)	2.968(2)	P(5)–O(L56)–P(6)	138.24(30)
P(6)–P(66)	2.902(2)	P(6)–O(L666)–P(66)	131.90(27)
P(6)–P(7)	2.946(2)	P(6)–O(L67)–P(7)	136.97(36)
P(7)–P(8)	2.933(2)	P(7)–O(L78)–P(8)	134.88(27)
P(8)–P(66)	2.938(2)	P(8)–O(L866)–P(66)	135.08(28)

Description of the Structure

In this atomic arrangement the linkage of the PO_4 tetrahedra is a bidimensional one, which can be roughly described as built of $[P_{10}O_{28}]$ sheets spreading in (110) planes. Sheets themselves can be depicted as a linkage of $(P_{12}O_{36})$ rings. Figure 1 gives a schematic representation of the phosphorus atoms inside these sheets while Figs. 2 and 3 are a projection of the arrangement along the *c* and *b* axis, respectively. As shown in Fig. 1 the same phosphorus atom can occur twice in the same $(P_{12}O_{36})$ ring (P6, P4, P2, P8). This fact explains the apparent inconsistency in the nomenclature of the phosphorus atoms. Phosphorus atoms P2, P4, P6, and P8 are branching phosphorus, that is to say, phosphorus connected to three other phosphorus or, in other words, sharing three of their oxygen atoms with neighboring phosphorus. The percentage of such "branching phosphorus" is 40% as in all other types of LnP_5O_{14} ultraphosphates. Main interatomic distances and bond angles in these $P_{10}O_{28}$ sheets are reported in Table IV.

Interatomic distances P–O and $\widehat{O\text{–}P\text{–}O}$ angles (Table IV) observed for the 10 independent PO_4 tetrahedra show they are distorted. For instance, $\widehat{O\text{–}P\text{–}O}$ angles deviate strongly of their theoretical value (109.28°) when the oxygen atoms involved in these angles belong to the rare earth coordination.

As commonly observed in condensed phosphates the neighbors of the cerium atoms are all external oxygen atoms (OE*ij*). Around each cerium atom one finds an eightfold coordination with Ce–O distances ranging from 2.38 to 2.55 Å (Table V). These distances are larger than those already observed in other ultraphosphates (*8, 9*). The two CeO_8 polyhedra have no common oxygen atom. A careful examination of these polyhedra shows no pseudosymmetry. The shortest Ce–Ce distance is 6.288 Å, larger than the Nd–Nd distance observed in NdP_5O_{14} (5.19 Å) (*10*).

The remarkably long distance between CeO_8 polyhedra and their lack of symmetry can be used to construct new interesting materials (*11*) mainly fast luminophors.[1]

TABLE V

CERIUM–OXYGEN DISTANCES IN THE CeO_8 POLYHEDRA

	$Ce(1)O_8$ Polyhedron		
Ce(1)–O(E11)	2.554(6)	Ce(1)–O(E41)	2.556(4)
Ce(1)–O(E12)	2.546(6)	Ce(1)–O(E61)	2.490(4)
Ce(1)–O(E221)	2.517(5)	Ce(1)–O(E661)	2.383(4)
Ce(1)–O(E31)	2.416(4)	Ce(1)–O(E71)	2.458(4)
	$Ce(2)O_8$ Polyhedron		
Ce(2)–O(E21)	2.476(4)	Ce(2)–O(E52)	2.502(5)
Ce(2)–O(E222)	2.494(4)	Ce(2)–O(E662)	2.397(4)
Ce(2)–O(E32)	2.398(4)	Ce(2)–O(E72)	2.525(4)
Ce(2)–O(E51)	2.540(5)	Ce(2)–O(E81)	2.457(4)

References

1. H. G. DANIELMEYER AND H. P. WEBER, *J. Quantum Electronics*, **8,** 805 (1972).
2. C. BERCHER, *J. Chem. Phys.* **61,** 2297 (1974).
3. T. C. DAMEN, H. P. WEBER, AND B. C. TOFIELD, *Appl. Phys. Lett.* **23,** 519 (1973).
4. K. R. ALBRAND, R. ATTIG, J. FENNER, J. P. JESER, AND D. MOOTZ, *Mater. Res. Bull.* **9,** 129 (1974).
5. M. BAGIEU-BEUCHER, AND D. TRANQUI, *Bull. Soc. Fr. Minér. Cristallogr.* **93,** 505 (1970).
6. A. DURIF, *Bull. Soc. Fr. Minér. Cristallogr.* **94,** 314 (1971).
7. M. RZAIGUI AND N. KBIR ARIGUIB, in press.
8. D. TRANQUI, M. BAGIEU, AND A. DURIF, *Acta Crystallogr. B* **30,** 1751 (1974).
9. D. TRANQUI, M. BAGIEU-BEUCHER, AND A. DURIF, *Bull. Soc. Fr. Minér. Cristallogr.* **95,** 437 (1972).
10. H. Y. P. HONG, *Acta Crystallogr. B* **30,** 468 (1974).
11. P. MAESTRO AND P. DOUGIER, *Acta Chim.* (juin-juillet), 15 (1982).

[1] The structure factor table is available on request from the authors.