

## Synthesis and structural characterization of CsNiP crystal

G S GOPALAKRISHNA\*, B H DORESWAMY<sup>†</sup>, M J MAHESH, M MAHENDRA<sup>†</sup>,  
M A SRIDHAR<sup>†</sup>, J SHASHIDHARA PRASAD<sup>†</sup> and K G ASHAMANJARI

Department of Studies in Geology, <sup>†</sup>Department of Studies in Physics, University of Mysore, Manasagangothri,  
Mysore 570 006, India

MS received 21 August 2003

**Abstract.** CsNiP crystals were synthesized by hydrothermal technique and characterized by the X-ray diffraction method. This alkaline transition metal phosphide crystallizes in the hexagonal system with space group  $P6_3/mmc$  and cell parameters,  $a = 7.173(2)$  Å,  $c = 5.944(9)$  Å,  $V = 264.87(7)$  Å<sup>3</sup> and  $Z = 2$ . The final residual factor is  $R1 = 0.0362$  for 206 reflections with  $I > 2s(I)$ .

**Keywords.** Phosphides; hydrothermal; crystal structure; FTIR; DTA.

### 1. Introduction

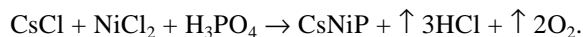
Synthetic alkaline metal phosphide derivatives were reported for the first time in the later part of fifties and early part of sixties (Issleib and Tzschach *et al* 1959; Fluck and Issleib 1965). However, studies of these alkaline metal phosphides gained momentum since last three decades (Johnson and Jeitschlo 1972; Barz *et al* 1983; Muller *et al* 1983; Schnering *et al* 1999). In recent years, structural data of phosphides also were reported (Shannon 1976; Jeitschlo and Braun 1977; Braun and Jeitschlo 1980a, b; Nakotte *et al* 1999; Sekine *et al* 1999; Rabe *et al* 2000). The alkaline metal phosphides are good diamagnetic semiconductors (Ackermann and Wold 1977; Danebrock *et al* 1996; Shirotani *et al* 1996; Kuriyama *et al* 1998) and also show superconductivity at low temperature (Sakon *et al* 1999; Shirotani *et al* 2000). Here, we report a new material of mono CsNiP derivative in the form of a single crystal exhibiting paramagnetic properties.

### 2. Experimental

CsNiP crystals were synthesized by the hydrothermal method. The growth of phosphides by the hydrothermal technique is relatively new and the use of hydrothermal method is quite complicated for these compounds because of the highly corrosive and volatile nature of phosphorus at higher temperature. The present experiments were carried out in Morey type autoclaves provided with Teflon liners, at the temperature and pressure of 260°C and 100 bars (Byrappa *et al* 1985). The crystallization was carried out by spontaneous nucleation controlled through a slow and programmed rate of heating. The starting mate-

rial such as chloride or nickel was taken in a Teflon liner and 85% H<sub>3</sub>PO<sub>4</sub> was poured into it. The alkaline component of the starting material was taken in the form of molar solutions having a definite molarity. CsNiP crystals were synthesized under the following conditions: Molar ratio = Cs<sub>2</sub>O : Ni<sub>2</sub>O<sub>3</sub> : P<sub>2</sub>O<sub>5</sub>, 3–4 : 1–1.5 : 10–12,  $T = 260^\circ\text{C}$ ;  $P = 100$  bars; duration = 8–10 days.

The following reaction could explain the formation of CsNiP



The crystals obtained by this method were of good quality exhibiting translucent luster having well developed morphology. The size of crystals ranged from 0.5–2 mm with pinkish yellow colour.

A single crystal of CsNiP of dimension 0.3 × 0.2 × 0.25 mm was used for X-ray diffraction study. The measurements were made on a DIPLabo Imaging Plate system with graphite monochromated radiation (MoK<sub>α</sub>). Thirty six frames of data were collected by oscillation method. Successive frames were scanned in steps of 5°/min with an oscillation range of 5°. Image processing and data reduction were done using Denzo (Otwinowski and Minor 1997; Mackay *et al* 1999). All frames could be indexed with a hexagonal primitive lattice. The phase set with the highest combined figure of merit gave the positions of all the non-hydrogen atoms. Least-squares refinement using SHELXL-97 (Sheldrick 1997) with isotropic temperature factors for all the non-hydrogen atoms converged the residual  $R1$  to 0.0923. Anisotropic refinement was started at this stage and  $R1$  finally converged to 0.0362. The details of crystal data and refinement are given in table 1.

### 3. Results and discussion

The study of morphology of a crystal is important due to its application in device potential. Generally the crystals

\*Author for correspondence

obtained by the hydrothermal method are of good quality and exhibit well developed morphology with smooth surface and translucent luster. The SEM studies of CsNiP crystal show fibrous nature; rod shaped habit with relatively smooth surface (figure 1).

The final positional coordinates with equivalent isotropic temperature factors and anisotropic thermal parameters ( $U_{ij}$ ) of all the atoms are listed in tables 2 and 3, respectively. Selected bond distances and angles are given in table 3. The bond distances and angles are in good agree-

ment with the standard values. Figure 2 represents the ORTEP (Johnson 1976) of the molecules with thermal ellipsoids at 50% probability. All the three atoms are at special positions. Ni atom lies on six-fold axis with six phosphorous atoms at their symmetry equivalent positions. The molecular packing along the axes exhibit channel type framework structure having Cs atoms inside it (figures 3 and 4). This helps for tunnelling of Cs atoms through the channels (Mahendra et al 2003).

FTIR-spectrum was recorded using a high resolution Perkin Elmer Infrared Spectrophotometer in the range 4000–400  $\text{cm}^{-1}$  (figure 5). The spectrum exhibits prominent multiple absorption bands, especially in the range 2922–1377.1  $\text{cm}^{-1}$ . The broadness at the 1635 and 651.9  $\text{cm}^{-1}$

**Table 1.** X-ray crystallographic details.

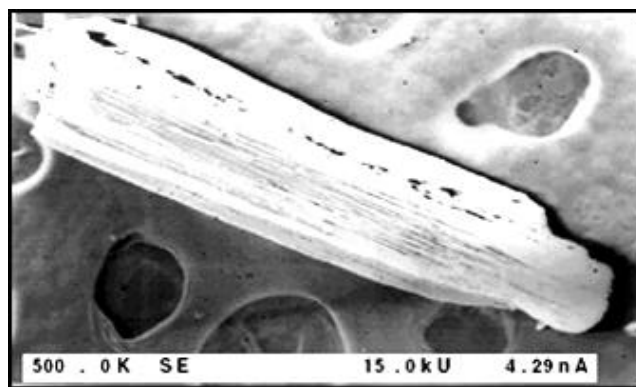
Empirical formula	Cs Ni P
Formula weight	222.59
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal colour, habit	Transparent, rectangular
Crystal system	Hexagonal
Space group	$P6_3/mmc$
Cell dimensions	$a = 7.173(2)$ Å, $c = 5.944(9)$ Å
Volume	$264.87(7)$ Å <sup>3</sup>
Z	2
Density(calculated)	$2.791 \text{ mg/m}^3$
Absorption coefficient	$10.541 \text{ mm}^{-1}$
$F_{000}$	196
Crystal size	$0.3 \times 0.2 \times 0.25 \text{ mm}$
Theta range for data collection	$3.28^\circ$ to $32.31^\circ$
Index ranges	$0 \leq h \leq 9$ $0 \leq k \leq 9$ $-8 \leq l \leq 8$
Reflections collected	764
Independent reflections	206 [ $R(\text{int}) = 0.1089$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	206/0/10
Goodness-of-fit on $F^2$	1.298
Final $R$ indices [ $I > 2S(I)$ ]	$R1 = 0.0362$ , $wR2 = 0.1079$
$R$ indices (all data)	$R1 = 0.0366$ , $wR2 = 0.1084$
Extinction coefficient	$0.096(13)$
(Shift/e.s.d.) <sub>max</sub>	0.000
Largest diff. peak and hole	$1.129$ and $-1.799 \text{ e.Å}^{-3}$

**Table 2.** Atomic coordinates and equivalent thermal parameters.

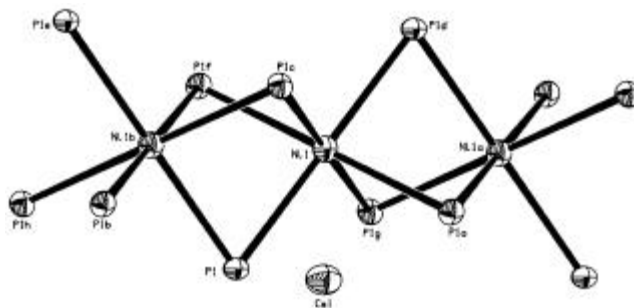
Atom	x	y	z	$U_{\text{eq}}$
Cs1	0.3333	0.6667	0.2500	0.0273(4)
Ni1	0.0000	1.0000	0.0000	0.0172(4)
P1	0.15337(13)	0.84663(13)	-0.2500	0.0160(4)

**Table 3.** Anisotropic thermal parameters.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cs1	0.0228(4)	0.0228(4)	0.0364(6)	0.0114(2)	0.000	0.000
Ni1	0.0176(5)	0.0176(5)	0.0162(7)	0.0088(3)	0.000	0.000
P1	0.0172(6)	0.0172(6)	0.0170(8)	0.0113(6)	0.000	0.000



**Figure 1.** SEM photograph.



**Figure 2.** Perspective diagram of the molecule with thermal ellipsoids at 50% probability [Symmetry codes:  $a = (x - y, x, -1/2 + z)$ ,  $b = (x - y, x, 1/2 + z)$ ,  $c = (-y, x - y, z)$ ,  $d = (-x, -y, -1/2 + z)$ ,  $e = (-x, -y, 1/2 + z)$ ,  $f = (-x + y, -x, z)$ ,  $g = (y, -x + y, -1/2 + z)$  and  $h = (y, -x + y, 1/2 + z)$ ].

indicate the phosphide nature of the compound unlike pyrophosphates (Gopalakrishna *et al* 2001).

The DTA curve was recorded using DTA/ETA Model 021 from room temperature to 500°C. CsNiP shows multiple phase transitions at 150, 283 and 384°C, respectively (figure 6), indicating that this compound has relatively low thermal stability compared to the phosphates (Mahendra *et al* 2003).

Magnetic measurements were done using Gouy's balance method for the determination of magnetic susceptibility in the magnetic field strength ranging from 0.5–2.5 K

gauss at 300°K. Magnetic moments of nickel compounds fall into two broad classes. First, those having essentially temperature independent magnetic moments due to mono-nuclear complexes having interaction between the unpaired electrons on different nickel ions in the range 2.9–3.9 BM. Second, moments are below the spin only value and temperature dependent. The present compound exhibits magnetic moments in the range 2.17–2.60 BM at magnetic field strength 0.5–2.5 K gauss indicating that this CsNiP compound is temperature dependent. Detailed investigations are discussed elsewhere (Martin *et al* 1996; Shirovani *et al* 1996; Sakon *et al* 1999).

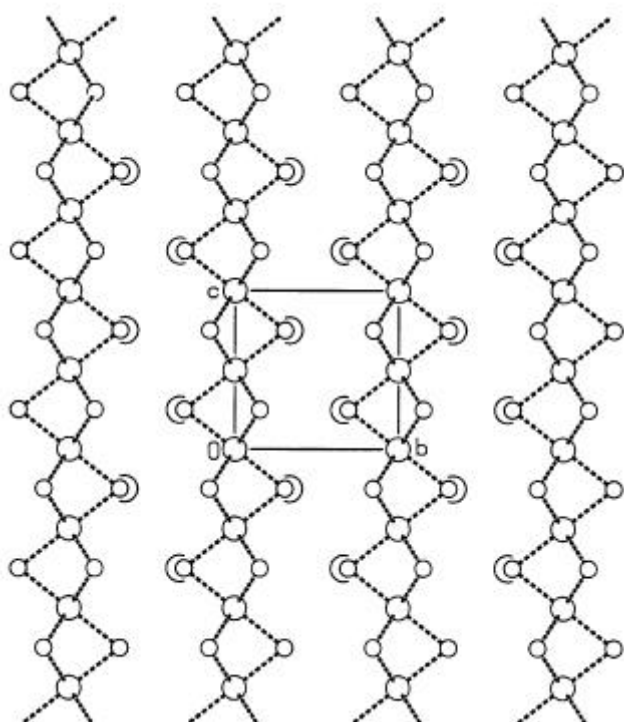


Figure 3. Packing of the molecule down *a* axis.

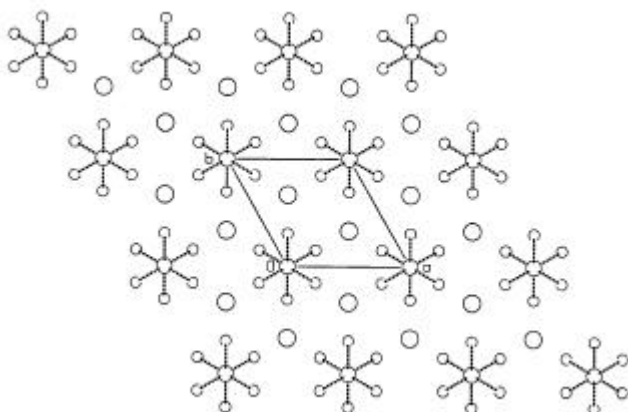


Figure 4. Packing of the molecule down *c* axis.

#### 4. Conclusions

Mono cesium nickel-phosphide compound was synthesized by hydrothermal method in the form of single crystal. X-ray studies revealed that this compound crystallized in hexagonal system with space group  $P6_3/mmc$  and exhibits

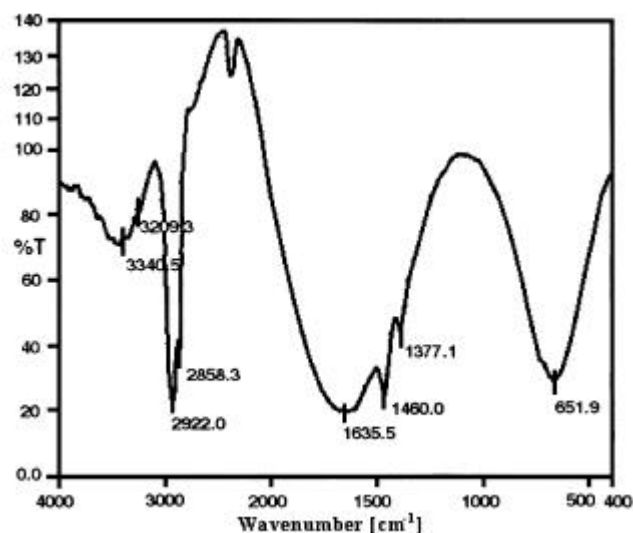


Figure 5. FTIR spectrum.

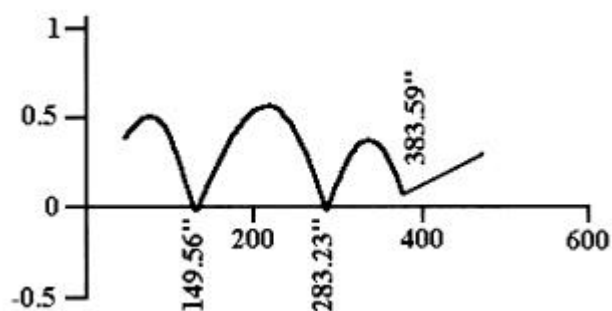


Figure 6. DTA curve.

**Table 4.** Bond lengths (Å) and angles (°).

Atoms	Length	Atoms	Length
Cs(1)-P(1)#1	3.5904(4)	Ni(1)-Ni(1)#4	2.9719(5)
Cs(1)-P(1)#4	3.5905(8)	P(1)-Cs(1)#1	3.5904(5)
Cs(1)-P(1)#9	3.7191(1)	P(1)-Cs(1)#6	3.5905(4)
Ni(1)-P(1)#2	2.4164(1)		
Atoms	Angle	Atoms	Angle
P(1)#2-Cs(1)-P(1)#3	120.00(2)	P(1)#4-Cs(1)-P(1)#10	120.42(1)
P(1)#3-Cs(1)-P(1)#4	174.73(5)	P(1)#7-Cs(1)-P(1)#11	145.01(2)
P(1)#5-Cs(1)-P(1)#7	120.42(7)	P(1)#2-Ni(1)-P(1)	93.85(4)
P(1)#6-Cs(1)-P(1)#7	91.59(2)	P(1)#4-Ni(1)-Ni(1)#12	127.95(2)
P(1)#3-Cs(1)-P(1)#8	91.58(2)	Ni(1)-P(1)-Cs(1)#1	92.08(2)
P(1)#7-Cs(1)-P(1)#8	145.01(2)	Cs(1)#1-P(1)-Cs(1)#6	174.73(5)
P(1)#8-Cs(1)-P(1)#9	106.09(4)	Ni(1)-P(1)-Cs(1)#13	164.90(4)
P(1)#2-Cs(1)-P(1)#10	91.58(2)		

[Symmetry transformations used to generate equivalent atoms: #1 ( $-x + 1, -y + 2, -z$ ), #2 ( $x - y + 1, x + 1, -z$ ), #3 ( $y, -x + y, z + 1/2$ ), #4 ( $y - 1, -x + y, z + 1/2$ ), #5 ( $x - y + 1, x, -z$ ), #6 ( $-x, -y + 1, -z$ ), #7 ( $x, y, z + 1$ ), #8 ( $-y + 1, x - y + 1, -z - 1/2$ ), #9 ( $-y + 1, x - y + 1, -z + 1/2$ ), #10 ( $-x + y, -x + 1, z + 1$ ), #11 ( $-x + y, -x + 1, z$ ), #12 ( $y - 1, -x + y, z - 1/2$ ) and #13 ( $x, y, z - 1$ )].

channel type structures. Magnetic measurements indicated that it is a temperature dependent mononuclear compound.

### Acknowledgements

The authors would like to express their thanks to DST, New Delhi, for financial assistance under the projects SP/S2/M-44/96-97 and SP/I2/FOO/93.

### References

- Ackermann J and Wold A 1977 *J. Phys. Chem. Solids* **38** 1013  
 Barz H, Ku H C, Meisner G P, Fisk Z and Matias B T 1983 *Proc. Nat. Acad. Sci. USA* **77**  
 Braun D J and Jeitschlo W J 1980a *Solid State Chem.* **32** 357  
 Braun D J and Jeitschlo W J 1980b *Less Common Metals* **72** 147  
 Byrappa K, Gopalakrishna G S, Venkatachalapathy V and Puttaraju B 1985 *J. Mater. Sci.* **20** 1419  
 Danebrock M E, Evers C B H and Jeitschko W 1996 *J. Phys. Chem. Solids* **57** 381  
 Fluck E, Issleib K and Tell B 1965 *Naturforsch. Z.* **20** 1123  
 Gopalakrishna G S, Prasad J S and Lokanath N K 2001 *Proc. joint 4th and 6th ICSTR* (eds) Yanagisawa and Qi Feng (Kochi, Japan)  
 Gopalakrishna G S, Prasad J S, Ashamanjari K G, Mahesh M J and Madhu S P 2003 *Ind. Miner.* **37** 57  
 Issleib K and Tzschach A 1959 *Chem. Ber.* **92** 1118  
 Jeitschlo W and Braun D J 1977 *Acta Crystallogr.* **B33** 3401  
 Johnson C K 1976 ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program. Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA  
 Johnson V and Jeitschlo W 1972 *J. Solid State Chem.* **4** 123  
 Kuriyama K, Kushida K and Taguchi R 1988 *Solid State Commun.* **108** 429  
 Mackay S, Gilmore C J, Edwards C, Stewart N and Shankland K 1999 *maXus computer program for the solution and refinement of crystal structures* (The Netherlands: Bruker Nonius, Japan: MacScience and The University of Glasgow)  
 Mahendra M, Madhu S P, Doreswamy B H, Gopalakrishna G S, Sridhar M A and Prasad J S 2003 *Mater. Res. Bull.* **33** 1309  
 Muller R, Shelton R N, Richardson H W and Jacobson R A 1983 *J. Less Common Metals* **92** 177  
 Nakotte H et al 1999 *Physica* **B259–261** 280  
 Otwinowski Z and Minor W 1997 in *Methods in enzymology*, 276 (eds) C W Carter Jr. and R M Sweet (New York: Academic Press) pp 307–326  
 Rabe G W, Heise H, Liable-Sands L M, Guzei I A and Rheingold A L 2000 *J. Chem. Soc. Dalton Trans.* 1863  
 Sakon T et al 1999 *Physica* **B259–261** 300  
 Schnering H G, Liable-Sands W, Incarvito C D, Lam K C and Rheingold A L 1999 *Inorg. Chem.* **38** 4342  
 Sekine C, Saito H, Sakai A and Shiroani I 1999 *Solid State Commun.* **109** 449  
 Shannon R D 1976 *Acta Crystallogr.* **A32** 751  
 Sheldrick G M 1997 *SHELXL-97. Program for the refinement of crystal structures* (Germany: University of Göttingen)  
 Shiroani I, Adachi Takafumi, Todo Kenji, Sakae, Nozawa Kiyokazu, Yagi Takehiko and Kinoshita Minoru 1996 *J. Phys. Chem. Solids* **57** 211  
 Shiroani I, Takaya M, Kaneko I, Sekine C and Yagi T 2000 *Solid State Commun.* **116** 683