J MATER SCI **41** (2006) 1423–1427

Hydrothermal synthesis and characterization of CsNiP and 2($LiZnHP_2O_7$) crystals

G. S. GOPALAKRSHNA*, M. J. MAHESH, S. P. MADHU, K. G. ASHAMANJARI
Department of Studies in Geology, University of Mysore, Manasagangotri, Mysore, 570 006, INDIA
E-mail: gopalakrish2004@yahoo.com

M. A. SHRIDHARA, S. PRASAD
Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, 570 006, INDIA

CsNiP and 2($LiZnHP_2O_7$) crystals were synthesized by hydrothermal technique at moderate P-T conditions. Solubility results of both the compound shown positive thermal coefficient and single crystal X-ray studies revealed, CsNiP crystallized in hexagonal system with cell parameters; $a = 7.173(2)$, $c = 5.944(9)$ Å, $V = 264.87(7)$ Å^3 and space group P63/mmc and 2($LiZnHP_2O_7$) crystallized in orthorhombic system with cell parameters; $a = 12.3636$ Å, $b = 27.5330$ Å, $c = 6.8647$ Åand space group, Pca21 exhibiting ring type of cavities with open aperture in the structure. CsNiP is a frequency dependent paramagnetic and 2($LiZnHP_2O_7$) is a diamagnetic. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Phosphates and phosphides have been extensively studied owing to their wide application as prospective materials in technology, viz phosphates in electronic devices, as solid electrolytes, sensors, laser materials, piezoelectric, luminescence, opto-electronics, ceramics and as magnetic materials [1–5]. Synthetic alkaline metal phosphide derivatives were reported for the first time in the later part of 1950s [6,7]. However, the study of phosphides gained momentum since last three decades [14]. These phosphides have exhibited remarkable mechanical, electrical and magnetic properties [8]. The alkaline metal phosphides have shown superconductivity at low temperature [12, 13] and also good diamagnetic semiconductors [9–11]. Here, we report a new type of phosphide and Phosphate derivatives in the form of single crystals.

2. Experimental procedure

2.1. Crystal growth

CsNiP and 2($LiZnHP_2O_7$) crystals were synthesized by a hydrothermal technique at moderate temperature and pressure conditions by following earlier reported procedure [15]. The reagents used are of analar grade of M^+OH (M^+ = Cs and Li) (99.99%), H_3PO_4 (98%), $M^{+2}Cl_2$ (M^{+2} = Ni and Zn) (99%) and HNO_3 (69–72%), from S.D.Fine chemicals without further purification. Initially, known quantity of M^+OH and H_3PO_4 were taken in a Teflon lined Morey type autoclave with capacity of 50 ml. Later a known quantity of $M^{+2}Cl_2$ was added to it and thoroughly stirred well till homogeneity attained with pH in the range of 4.12–4.28. The experiments were carried out at temperature of 250–265° C and pressure range of 60–80 bars. The crystallization was carried out by spontaneous nucleation and the rate of nucleation was controlled through slow rate of heating. These crystals were obtained under the following molar ratios:

Molar ratio = $M^+{}_2O$:: $M^{+2}{}_2O$ :: P_2O_5 (M^+ = Li and Cs M^{+2} = Ni and Zn) 3–4 :: 1–1.5 :: 10–12

The synthesis experiments were carried out continuously for 8–10 days and followed by sudden arrest of the crystallization process by quenching the experiments to the ambient conditions. The measured pH of the resultant product was in the range of 3.51- 3.59 The resultant product was washed with the distilled water using ultra sonic cleaner. In the present experiments H_3PO_4 solution has been used as the solvent and alkali and transitional elements were as solutes. Based on the acid-bases used,

---

*Author to whom all correspondence should be addressed.

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-7443-5

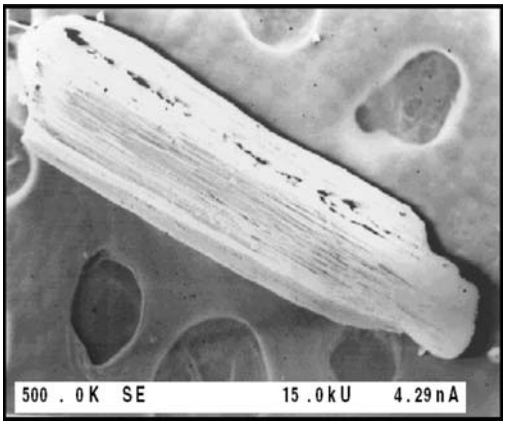

Figure 1 SEM photograph of CsNiP.

arbitrary reactions have been predicted as follows:

CsNiP:/>

$$CsCl + H_3PO_4 \rightarrow H_2CsP + HCl + \uparrow 2O_2 \quad (1)$$

$$NiCl_2 + H_3PO_4 \rightarrow HNiPO_4 + 2HCl \quad (2)$$

$$H_2CsP + HNiPO_4 \rightarrow CsNiP + H_3PO_4 \quad (3)$$

2(Li ZnHP$_2$O$_7$):

$$2LiOH + 2H_3PO_4 \rightarrow H_4Li_2(PO_4)_2 + 2H_2O \quad (1)$$

$$2ZnCl_2 + 2H_3PO_4 \rightarrow Zn_2H_2(PO_4)_2 + 2HCl \quad (2)$$

$$H_4Li_2(PO_4)_2 + Zn_2H_2(PO_4)_2 \rightarrow 2(LiZnHP_2O_7) + 2H_2O \quad (3)$$

The crystals obtained were of good quality. CsNiP crystals exhibited translucent luster having a well-developed morphology with growth striations prominently along ‘c’ axis. The size of crystal is of 0.5 to 2.5 mm with honey yellow colour Fig. 1. 2($LiZnHP_2O_7$) crystals exhibited subvitreous luster and having a size of 0.5–2.5 mm Twinning is almost absent Fig. 2.

3. Results and discussions

Solubility study is an important parameter for the successful growth of phosphates and phosphides in the form of single crystals. The lack of adequate solubility data could be responsible for the earlier failures in the growth of single crystals of phosphates and phosphides by hydrothermal methods. The solubility measurements were carried out by weight loss method. Here, a crystal is kept in equilibrium at the desired conditions for a known period in solvent media (HCl, H_3PO_4 and H_2O) in order to understand the growth process and to optimize the growth conditions. By linear fitment, the temperature coefficient of solubility (dS/dT) of CsNiP and 2($LiZnHP_2O_7$) have been calculated (Table I and II) and they have shown positive dS/dT (Fig. 3 and 4). In the present experiments, maximum percent of solubility is observed at the temperature of 250°C.

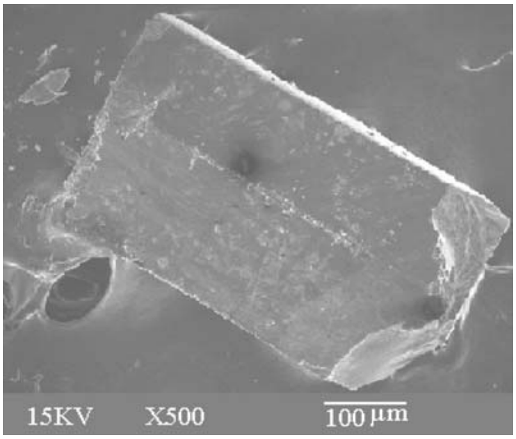

Figure 2 SEM photograph of 2($LiZnHP_2O_7$).

TABLE I Solubility data of CsNiP

T(K)	HCl (5N)	H_3PO_4 (5N)	H_2O
	Solubility (moles /L		
323	0.71	0.60	0.65
348	0.74	0.64	0.68
373	0.76	0.68	0.71
398	0.79	0.72	0.74
423	0.82	0.76	0.77
448	0.85	0.80	0.80
473	0.88	0.84	0.83
498	0.91	0.88	0.86
523	0.93	0.92	0.89
dS/dT m/L^{-1}T^{-1}	1.1×10^{-3}	1.6×10^{-3}	1.2×10^{-3}
ΔH kJ/mol	21.74	22.99	22.04

The logarithm of solubility of CsNiP and 2($LiZnHP_2O_7$) are found to be basically linear function of the reciprocal of the absolute temperature (10^3/TK). The enthalpy (ΔH) of dissolution has been determined from an Arrhenius equation:

$$\text{Log } S = A - \Delta H / 2.303^* RT$$

where ΔH = enthalpy (dissolving heat in kJ/mol) T = absolute temperature (K) R= constant of perfect gas (J/k mol) and A= constant for special reaction, which is intercept of Log S-1/T straight line.

The ΔH have been given in Tables I and II and represented in Fig. 5 and 6. The ΔH is relatively high and showing positive dS/dT of solubility. Based on this result, it was able to optimize the growth conditions (T= 250 – 265°C and P = 60–80 bars) and obtained relatively bigger size single crystals (2.5 mm).

Single crystal X-ray studies of CsNiP and 2($LiZnHP_2O_7$) were made on a DIPLabo Imaging Plate system with graphite monochromatered radiation (MoK$_\alpha$) [16]. Thirty-six frames of data were collected by

TABLE II Solubility data of $2(LiZnHP_2O_7)$ in H_3PO_4

T(K)	2N	4N	6N	8N	10N
323	0.26	0.33	0.36	0.43	0.48
373	0.36	0.43	0.48	0.52	0.58
423	0.46	0.53	0.6	0.63	0.7
473	0.6	0.65	0.7	0.76	0.82
523	0.75	0.8	0.86	0.89	0.95
ds/dt ($gL^{-1}T^{-1}$)	2.4×10^{-3}	2.3×10^{-3}	2.5×10^{-3}	2.2×10^{-3}	2.3×10^{-3}
ΔH (kJ/mol)	23.24	22.15	22.19	22.36	22.59

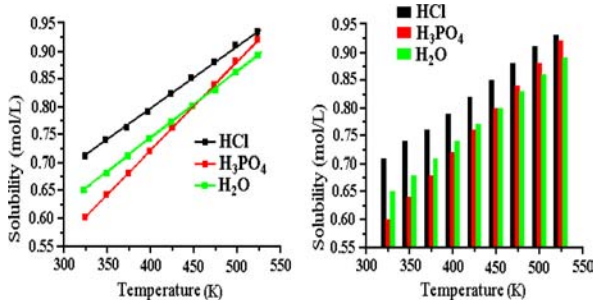

Figure 3 Solubility of curve of CsNiP.

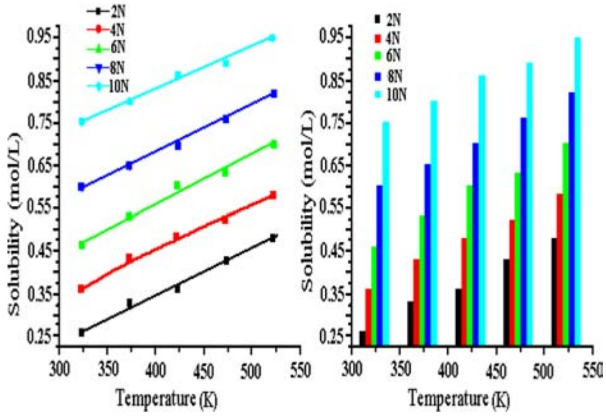

Figure 4 Solubility diagram of $2(LiZnHP_2O_7)$.

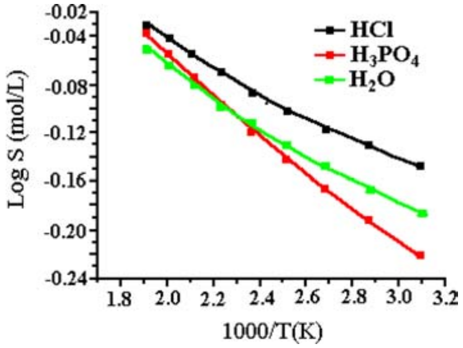

Figure 5 Lag *S* Vs 1000/*T* of CsNiP.

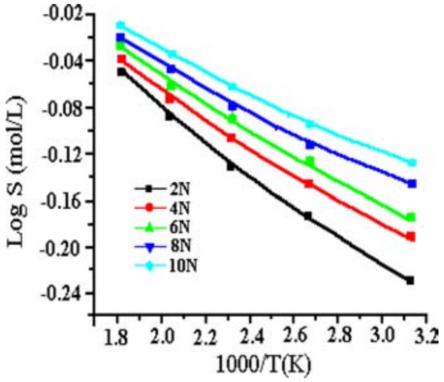

Figure 6 Lag S Vs 1000/T of $2(LiZnHP_2O_7)$.

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 [17]. All frames have indexed with hexagonal primitive lattice for CsNiP and orthorhombic primitive lattice for $2(LiZnHP_2O_7)$. The phase set with the highest combined figure of merit gave the positions of all the non-hydrogen atoms. Least-squares refinement was made using SHELXL-97 [18].

Fig. 7 represented the ORTEP diagram of CsNiP [19], the molecules with thermal ellipsoids at 50% probability. All the three atoms were at special positions. Ni atom lies on six-fold axis with six phosphorous atoms at their symmetry equivalent positions.

Fig. 8 represented the ORTEP diagram of $2(LiZnHP_2O_7)$, the molecule with 50% probability.

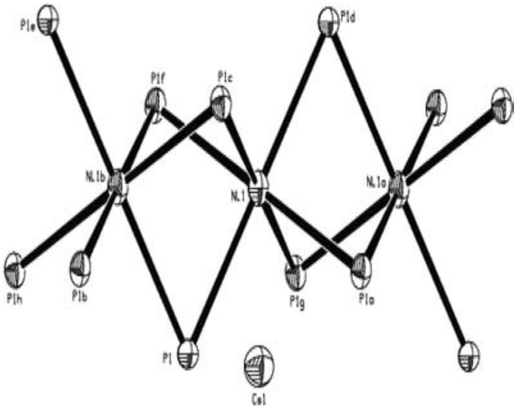

Figure 7 ORTEP Perspective diagram of the molecule with thermal ellipsoids at 50% probability.

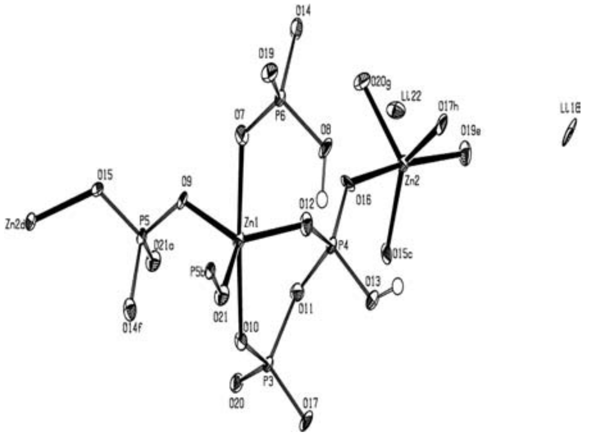

Figure 8 Perspective diagram of the molecule with thermal ellipsoids at 50% probability.

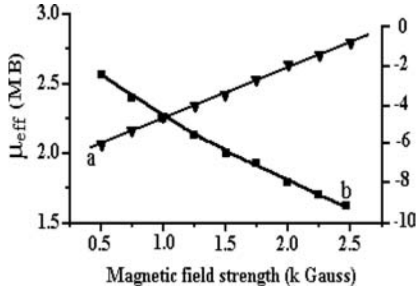

Figure 9 Magnetic susceptibility of (a) CsNiP and (b) $2(LiZnHP_2O_7)$.

The 3-dimensional representation of the molecules exhibited open-framework structure with four-member, six-member and fourteen-member apertures. Detailed structural data will be published elsewhere.

[

Symmetry Codes: a. (x,− 1 + y, z), b. (1 − x, − 1 − y, 1/2 + z), c. (1 − x, − y,1/2 + z),d. (1/2 − x, y, 1/2 + z), e. (−1/2 + x, − 1− y, z), f. (1/2 + x, 1− y, z), g. (x, 1 + y, z), h. (1− x, − y, + z)]

Magnetic susceptibility measurements were done using Gouy's balance method in the field strength ranging of 0.5–2.5 K gauss at 300°K (Fig. 9). Magnetic moments (μ_{eff}) of Nickel (II) derivatives have two unpaired electrons, either high spin octahedral with μ_{eff} of 2.81-3.93 BM or low spin octahedral with lesser μ_{eff} of (< 2.83 BM) [20]. Here, Nickel derivative of cesium bearing phosphide has μ_{eff} range of 2.17–2.60 BM, lower than the low spin octahedra. It could be attributed due the Ni^{2+} ion has octahedral coordination directly with the P^{3-} ions. It has positive correlation with field strength and hence it is a frequency dependent paramagnetic.

$2(LiZnHP_2O_7)$ has exhibited negative correlation (−1.3812 to −2.405BM) with the field strength and it is a diamagnetic in nature (Fig. 9). Detailed magnetic properties will be discussed elsewhere.

4. Conclusions

CsNiP and $2(LiZnHP_2O_7)$ crystals were synthesized by hydrothermal method in the form of single crystals. X-ray studies revealed, CsNiP has crystallized in hexagonal system with space group P63/mmc and exhibited channel type structures and it is a prospective paramagnetic material. $2(LiZnHP_2O_7)$ crystallized in orthorhombic system with space group Pca21 and having ring type of cavities with open aperture in the structure and it is a diamagnetic with negative correlation.

Acknowledgments

The authors would like to express thanks to DST, Government of India for financial assistance under the project SP/S2/M-44/96-97, CSIR financial assistance under the fellowship awarded No. 9/119(151)/2004 – EMR – I Dated 24.06.04 and Dr. B. Basavalingu for providing SEM results.

References

1 H. G. DANIELMEYER, G. HUBER, W. W.KRUHLER and J. F. JESSER, *Appl. Phys.* **2** (1973) 335.
2 H. P. WEBER, T. C. DAMEN, H. G. DANIELMEYER, and C. C. TOFIELD, *Appl. Phys. Lett.* **22** (1973) 534.
3 H. Y. P. HONG, *Mat. Res. Bull.* **11** (1976) 173.
4 J. B. GOODENOUGH, H. Y. P. HONG and J. A. KAFALAS, *ibid.* **11** (1976) 203.
5 C. DELNE, R. OLAZCUAGE, G. LE FLEM, P. HAGENMULLER, F. CHERKAOUE and R. BROCHU, *ibid* **16** (1981) 285.
6 K. ISSLEIB and A. TZSCHACH, *Chem. Bar.* **92** (1959) 1118.
7 E. FLUCK, K. ISSLEIB and B.TELL, *Naturforsch Z.* **20** (1965) 1123.
8 J. ACKERNANN and A. WOLD, *J. Phys. Chem. Solids* **38** (1977) 1013.
9 YI XIE, HUILAN SU, BIN LI and YITAI QIAN, *Mat. Res. Bull*, **35** (2000) 675.
10 K. KURIYAMA, K. KUSHIDA and R. TAGUCHI, *Solid. State. Commun.*, **108** (1988) 429.
11 I. SHIROTANI, TAKAFUMI ADACHI, KENJI SAKAE TODO, KIYOKAZU NOZAWA, TAKEHIKO YAGI and MINORU KINOSHITA. *J.Phys. Chem. Solids.* **57** (1996) 211.
12 I. SHIROTANI, M. TAKAYA, I.KANEKO, C. SEKINE and T. YAGI, *Solid. State. Commun.* **116** (2000) 683.
13 T. SAKON, A. KOBAYASHI, M. KUBOTAM Y. NAKANISHI, H. NOJIRI, S. MITSUDO, S. TAKAGI and S SUZUKI, *Physica B*, **300** (1999).259.
14 H. BARZ, H.C. KU, G.P. MEISNER, Z. FISK AND B.T. MATIAS, *Proc. Natl. Acad. Sci. USA* (1983) 77.
15 M. MAHENDRA, S.P. MADHU, B.H. DORESWAMY, G.S. GOPALAKRISHNA, M.A. SRIDHAR, J. SHASHIDHARA PRASAD, and K.G. ASHAMANJARI, *Mater. Res. Bull.* **38** (2003) 1309.
16 Z. OTWINOWSKI, AND W. MINOR, in Methods in Enzymology, edited by C. W. Carter jr. and R. M. Sweet, Academic Press: New York, Vol. 276 (1997) p. 307.
17 G.M. SHELDRICK, *SHELXL-97*. Program for the Refinement of Crystal Structures. University of Gottingen. Germany 1997.

18 G.M. SHELDRICK, *SHELXL-97*. Program for the Refinement of Crystal Structures. University of Gottingen. Germany (1997).

19 G.S. GOPALAKRISHNA, H. DORESWAMY, M.J. MAHESH, M. MAHENDRA, M.A. SRIDHAR,. J. SHASHIDHARA PRASAD and K. G. ASHAMANJARI, *Bull. Mater. Sci*, **27** (2004) 27.

20 RAJ RANIAN D.K. JHA and J. P. MISHRA *Asian J. Chem.* **11** (1999) 694.

Received 23 August 2004
and accepted 30 April 2005