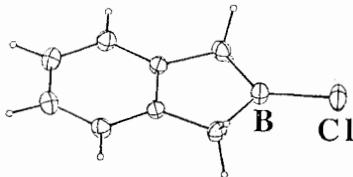


## 08-Inorganic and Mineralogical Crystallography

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( $P2_1/n$ ,  $a = 13.477(2)$ ,  $b = 7.015(1)$ ,  $c = 26.323(2)$  Å,  $\beta = 92.828(8)^\circ$ ,  $Z = 8$ , 2292 reflections, 303 variables,  $R = 0.051$ ,  $R_w = 0.071$ ) in *vacuo* loose the boron-coordinated solvent molecule; crystals of the boraindane



( $C2/c$ ,  $a = 11.234(2)$ ,  $b = 10.133(1)$ ,  $c = 7.507(1)$  Å,  $\beta = 118.133(9)^\circ$ ,  $Z = 4$ , 649 reflections, 64 variables,  $R = 0.050$ ,  $R_w = 0.073$ ) are obtained. Vacuum treatment of single crystals with known orientation matrices reveals that reorientation of the molecules occurs and that the solid state reaction is entirely reconstructive.

**PS-08.04.13**  $^{13}\text{C}$  ISOTOPE INFLUENCE ON DIAMOND STRUCTURE. By T. Yamanaka<sup>1)</sup>, S. Morimoto<sup>1)</sup> and S. Sasaki  
1) College of General Education, Osaka University  
2) Res. Lab. of Engin. Material, Tokyo Institute of Technology

Diamond with  $^{13}\text{C}$  isotope doped has been paid a large attention for the new material with the enormous extension of thermal conductivity. The influences of the isotope ratio on the lattice parameter and structure of diamond were investigated by X-ray diffraction study using four-circle diffractometer and positron synchrotron radiation (2.5GeV 300mA) at Photon Factory, Tsukuba together with Raman spectroscopy. A finely monochromated radiation of  $\lambda = 0.697148 \pm 0.000028\text{Å}$  was used as an incident beam.

Single-crystals of diamonds composed of various ratios of  $^{12}\text{C}$  and  $^{13}\text{C}$  isotopes were prepared by high pressure apparatus. The specimens with the size of about 20 $\mu\text{m}$  in diameter were used for the diffraction studies. The isotope concentrations in the synthesized diamonds were analyzed by secondary ion mass spectroscopy (SIMS).

The isotope dependence on the lattice constant  $a$  of diamond is expressed by  $a(A) = 3.56712 - 0.00155x + 0.00066x^2$ , where  $x = ^{13}\text{C} / (^{12}\text{C} + ^{13}\text{C})$ . The variation of the lattice constant with the isotope ratio,  $^{12}\text{C}/^{13}\text{C}$  is in the same fashion as those of  $^3\text{He}/^4\text{He}$ ,  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{74}\text{Ge}/^{72,6}\text{Ge}$ . All isotopes having a greater atomic weight in each element are characterized by the smaller lattice constant. The present equation is different from a linear function reported by Holloway et al., (1991).

Influence of the nuclear weight on the valence electron density is examined by the refinement of  $\kappa$ -parameter in  $\psi(\kappa, r)$ . After extinction and absorption correction, the least-squares refinements converged within less than  $R = 0.01$ .

In order to elucidate the isotope dependence on anharmonic thermal vibration of atoms, refinements of thermal parameters have been made by 3-dimensional Gram-Charlier expansion up to 4th order parameters of the trivariate Gaussian probability density function. Anharmonic potentials along with the directions,  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  of  $^{12}\text{C}$  and  $^{13}\text{C}$  diamond have been also evaluated.

Raman peak shift of  $F_{2g}$  proved that the lattice vibration is varied with the isotope mass difference between  $^{12}\text{C}$  and  $^{13}\text{C}$  and with the force constant. The shift is not a linear relation with the

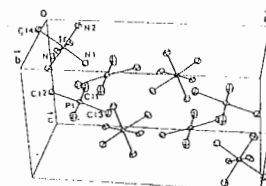
reduced mass but is represented by a binary equation. This relation is consistent with the lattice constant variation mentioned above. It has been clarified that the lattice vibration gives an effect to the thermal atomic displacement and the thermal conductivity induced from the phonon dispersion.

H. Holloway, K.C. Hass and M.A. Tamor  
Phys. Rev. B. 44, 7133 (1991)

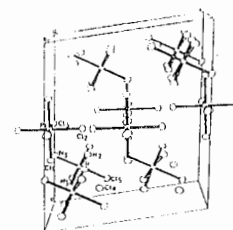
**PS-08.04.14** CRYSTAL STRUCTURE OF SOME CATALYTIC PRECURSORS WITH Pt-Ir COMPLEXES. By E. Gamier\* and M. Belé, Cristalochimie Minérale, Université de Poitiers, 40 Av. du Recteur Pineau, 86022 Poitiers cedex, France.

Multimetallic formulations are currently used to improve the properties of metal catalysts. We grew Pt-Ir complexes by diffusion of  $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$ ,  $\text{PtCl}_4^{2-}$ ,  $\text{Pt}(\text{NH}_3)_4^{2+}$ ,  $\text{IrCl}_6^{3-}$  in tetramethoxysilane or sodium metasilicate gels. Five precursors have been prepared: (A) =  $\text{Ir}(\text{NH}_3)_5\text{ClPtCl}_4$ , (B) =  $\text{Ir}(\text{NH}_3)_5\text{ClPtCl}_6$ , (C) =  $(\text{Ir}(\text{NH}_3)_5\text{Cl})_2\text{PtCl}_6 \cdot \text{Cl}_2$ , (D) =  $(\text{Pt}(\text{NH}_3)_4)_3(\text{IrCl}_6)_2$  and (E) =  $\text{Pt}(\text{NH}_3)_4\text{IrCl}_5(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$ . These precursors are crystallised in the porosity of alumina and reduced with  $\text{H}_2$  to get the bimetallic aggregates. (A) crystallises with nearly octahedral  $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$  cations and planar  $\text{PtCl}_4^{2-}$  anions. The coordination of these ions is 6/6. The structure of (C) is constituted of  $\text{Cl}^-$  and  $\text{PtCl}_6^{2-}$  anions and  $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$  cations. It can be regarded as ion layers parallel to (001): successively one  $\text{PtCl}_6^{2-}$  layer and two other layers, each of these two layers containing  $\text{Cl}^-$  and  $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$ . (E) is a layered compound. Each layer, parallel to (001) is stoichiometric. These structures possess an extended hydrogen bonding network involving the amino hydrogens and the chlorides.

(A):  $\text{Ir}(\text{NH}_3)_5\text{ClPtCl}_4$ ,  
 $Pnma$ ,  
 $a = 16.563(2)\text{Å}$ ,  
 $b = 8.111(1)\text{Å}$ ,  
 $c = 9.458(2)\text{Å}$ ,  
 $Z = 4$ ,  $R = 0.0282$ .



(C):  $(\text{Ir}(\text{NH}_3)_5\text{Cl})_2\text{PtCl}_6 \cdot \text{Cl}_2$ ,  
 $C2/m$ ,  
 $a = 11.243(2)\text{Å}$ ,  
 $b = 7.894(2)\text{Å}$ ,  
 $c = 13.406(2)\text{Å}$ ,  
 $\beta = 99.44(2)^\circ$ ,  
 $Z = 2$ ,  $R = 0.0290$ .



(E):  $\text{Pt}(\text{NH}_3)_4\text{IrCl}_5(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$ ,  
 $I4_1/a$ ,  
 $a = 15.655(2)\text{Å}$ ,  
 $c = 23.554(3)\text{Å}$ ,  
 $Z = 16$ ,  $R = 0.0404$ .

