

$\sin\theta/\lambda < 1.0 \text{ \AA}^{-1}$, 6692 reflections with $F/\langle F \rangle > 3\sigma/F$, $R=2.53\%$) evidences that KGP and KTP are isostructural. The structures of these two crystals differ mainly in the following features: $[\text{GeO}_6]$ -octahedra are essentially less distorted than $[\text{TiO}_6]$ ones, besides, there was hardly any alteration of long and short chemical bonds in the chains of metal-oxygen octahedra. For instance, the corresponding bond lengths are as follows: $\text{Ge}(1)-\text{O}(\text{Ge}2)$ 1.801, $\text{Ge}(1)-\text{O}(\text{Ge}1)$ 1.791, $\text{Ge}(2)-\text{O}(\text{Ge}2)$ 1.813, $\text{Ge}(2)-\text{O}(\text{Ge}1)$ 1.823 Å. The results obtained for KGP are compared to the data available for similar KMeOPO_4 compounds, where $\text{Me} = \text{Sn}$ and V , as well as for KTP crystals irradiated by fast neutrons.

PS-08.04.10 TEMPERATURE DEPENDENCE OF THERMAL VIBRATION AND POSITIONAL PARAMETERS OF ATOMS IN MAGNETITE. By H. Okudera*, K. Kihara and T. Matsumoto, Department of Earth Sciences, Faculty of Science, Kanazawa University, Japan.

Crystallographic parameters and their thermal changes in natural magnetite (Fe_3O_4) have been studied with single crystal X-ray diffraction method in the range from room temperature to 1069K. The cell dimension (a), oxygen coordinate (u -parameter), and atomic mean-square displacements (MSD's) are reversible as a function of temperature below 773K. The cell dimensions of four specimens are determined within the range from 8.3925(7) to 8.3962(3) (Å) at room temperature before heating and agree with the previous reports (e.g., Hamilton, W. C., Pys. Rev., 1958 110, 1050-1057; Fleet, M. E., Acta Cryst., 1981, B37, 917-920). The cell dimension a with increasing temperature is fitted with the quadratic form:

a (Å) = $8.3845 + 2.3947 \times 10^{-6} T + 9.338 \times 10^{-8} T^2$ in the range from 299K to 773K. Discontinuity of the first derivative of expansion at 865K, reported by Gorton *et al.* (Trans. Metal. Soc. AIME, 1965, 233, 1519-1525), is not observed in the present magnetite.

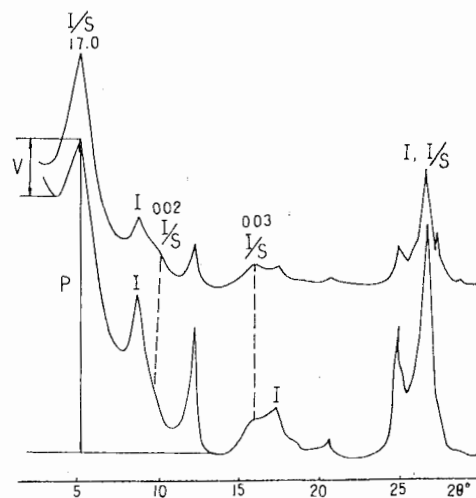
The u -parameter remains nearly constant at $u = 0.25487(3)$, but begins to increase at 623K, suggesting random distribution of Fe^{3+} and Fe^{2+} over the tetrahedral and octahedral cation sites. This suggests that the structure would be ideally inverse type below 623K and Fe^{2+} and Fe^{3+} cations would be slightly disordered above the temperature. At the octahedral cation site, the MSD's of atom normal to $[111]$ has smaller values than that along $[111]$ at a low temperature. The former, however, has a larger rate of increase with increasing temperature, and becomes larger than the latter above 623K.

PS-08.04.11A PRACTICAL V/P METHOD FOR ESTIMATING SMECTITE LAYERS PERCENTAGE IN MIXED-LAYER ILLITE/SMECTITE AND A STUDY OF FACTORS OF INFLUENCING THE V/P VALUES. By Xi-sheng Lin and Nai-Xuan Zheng, Scientific Research Institute of Petroleum Exploration and Development, Beijing, China.

Smectite layers percentage (%S) has been used to quantitatively describe mixed-layer illite/smectite (I/S). According to the method (R. C. Reynolds, 1970, 1980), the %S should be identified based upon the positions of 002 and 003

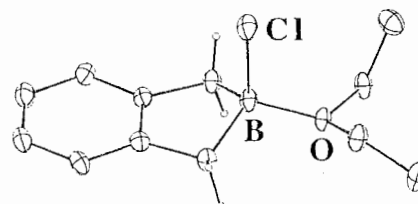
reflections of illite/smectite. However, these two peaks are often overlapped with 001 and 002 reflections of illite respectively. An equation $(\%)S = 66 \cdot \frac{V}{P} + 39$ (shown in Figure) has been derived here, according to the least squares principle, and by using information from E. Perry and J. Hower (1970) and our analyzed data. Obviously, it is easier to use the equation to determine the %S, and the error is 10%. The results suggest that both slit size of diffractometer and contents of I/S in samples affect the V/P values. Size of divergence slit should be fixed at 1° or $\frac{1}{2}^\circ$

and the equation be changed to $(66 \cdot \frac{V}{P} + 39) \cdot \sigma_i$ ($i=1, 2, 3$) because of the influence of the contents. σ_i are: $\sigma_1 = 1.888 - 0.1952 \ln x$, for $(\%)S \geq 75$; $\sigma_2 = 1.633 - 0.14 \ln x$, for $50 \leq (\%)S < 75$; $\sigma_3 = 1.129 - 0.0013x$, for $37 \leq (\%)S < 50$. Here, x are referred to the contents. The other factors such as crystallite thickness and lattice distortion, which influence the V/P values, are also discussed in brief.



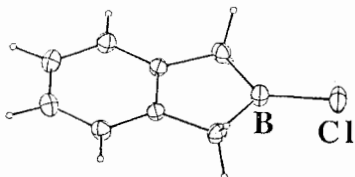
V/P of 17A peak of ethylene glycol treated mixed-layer illite/smectite
I, illite I/S, illite/smectite

PS-08.04.12 RECONSTRUCTIVE CRYSTAL-TO-CRYSTAL CONVERSION IN THE SOLID STATE. By U. Eigendorf, G.E. Herberich, T. Wagner, and U. Englert*, Institut für Anorganische Chemie, RWTH Aachen, Prof.-Pirlet-Straße 1, D-5100 Aachen, Germany. Crystals of the etherate



08-Inorganic and Mineralogical Crystallography

($P2_1/n$, $a = 13.477(2)$, $b = 7.015(1)$, $c = 26.323(2)$ 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}C ISOTOPE INFLUENCE ON DIAMOND STRUCTURE. By T. Yamanaka¹⁾, S. Morimoto¹⁾ and S. Sasaki
 1) College of General Education, Osaka University
 2) Res. Lab. of Engin. Material, Tokyo Institute of Technology

Diamond with ^{13}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}C and ^{13}C isotopes were prepared by high pressure apparatus. The specimens with the size of about 20µm 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 κ -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}C and ^{13}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}C and ^{13}C and with the force constant. The shift is not a linear relation with the

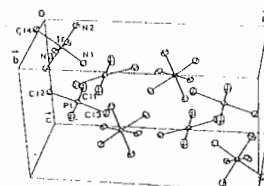
reduced mass but is represented by a binary equation. This relation is consistent with the lattice constant variation mentioned above. It has been clarified that the lattice vibration gives an effect to the thermal atomic displacement and the thermal conductivity induced from the phonon dispersion.

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

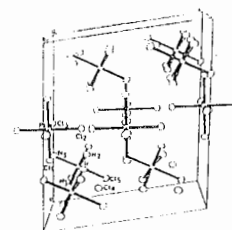
PS-08.04.14 CRYSTAL STRUCTURE OF SOME CATALYTIC PRECURSORS WITH Pt-Ir COMPLEXES. By E. Gamier* and M. Belć, Cristalochimie Minérale, Université de Poitiers, 40 Av. du Recteur Pineau, 86022 Poitiers cedex, France.

Multimetallic formulations are currently used to improve the properties of metal catalysts. We grew Pt-Ir complexes by diffusion of $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$, PtCl_4^{2-} , $\text{Pt}(\text{NH}_3)_4^{2+}$, 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 H_2 to get the bimetallic aggregates. (A) crystallises with nearly octahedral $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$ cations and planar PtCl_4^{2-} anions. The coordination of these ions is 6/6. The structure of (C) is constituted of Cl^- and 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 PtCl_6^{2-} layer and two other layers, each of these two layers containing 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): $\text{Pt}(\text{NH}_3)_4\text{IrCl}_5(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$,
 $I4_1/a$,
 $a = 15.655(2)\text{Å}$,
 $c = 23.554(3)\text{Å}$,
 $Z = 16$, $R = 0.0404$.

