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Powder x-ray diffraction analysis of bis(1,2-cyclohexanedione-dioximato) palladium(II) under high pressure

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Introduction

Interesting electrical and optical behaviors of one-dimensional bis(dimethylglyoximato)metal(II), $M(dmg)_2$ have been observed at high pressures[1-3]. The insulator-to-metal-to-insulator (IMI) transitions for Pt complexes occur at high pressures. The metal-metal (M-M) distance along the one-dimensional chain for $M(dmg)_2$ decreases rapidly with increasing pressure. The crystal structures of bis(1,2-cyclohexanedionedioximato)palladium(II), $Pd(niox)_2$, and $Pd(dmg)_2$ are orthorhombic. The both compounds are isostructural with $Pt(dmg)_2$. Using synchrotron radiation, we have studied powder x-ray diffraction of $Pd(niox)_2$ at high pressure and room temperature.

Experimentals

The powder x-ray diffraction of $Pd(niox)_2$ was studied with a diamond-anvil cell and an imaging plate up to 20 GPa. The x-ray beam with a wavelength of λ=0.6199Å was collimated to 80μm in diameter. High pressure diffraction experiments were performed at BL-18C. A 4:1 methanol-ethanol solution was used as the hydrostatic pressure fluid. The pressure in a diamond-anvil cell was determined from a pressure shift in the sharp R-line fluorescence spectrum of ruby.

Results and Discussion

The powder x-ray diffraction patterns have been measured with synchrotron radiation for $Pd(niox)_2$ at high pressures. The change of the powder x-ray diffraction patterns with the phase transition for both complexes is not observed up to 20 GPa. When pressure is reduced from 20 GPa to the ambient pressure, the diffraction patterns at normal pressure appear again at room temperature. Figure 1 shows ratio of lattice constants (l/l_0, l_0=the value at ambient pressure) vs pressure curves for $Pd(niox)_2$. The lattice constants decrease with increasing pressure up to 10 GPa. The crystal structure of this complex is anisotropic. The lattice constant of each axis shows the different pressure dependence. The b-axis shows a larger decrease compared with the a-axis. The ratios of lattice constants at high pressures to those at atmospheric pressure show the largest shrinkage along the c-axis. Figure 2 shows ratio of cell volumes vs pressure curves for $Pd(niox)_2$, $Pd(dmg)_2$ and $Pd(dpg)_2$. The pressure vs. volume curves are fitted by a Birch equation of state. Bulk modulus of $Pd(niox)_2$, $Pd(dmg)_2$ and $Pd(dpg)_2$ are 7.6(5) GPa, 9.9(7) GPa and 10.2(3)GPa, respectively.

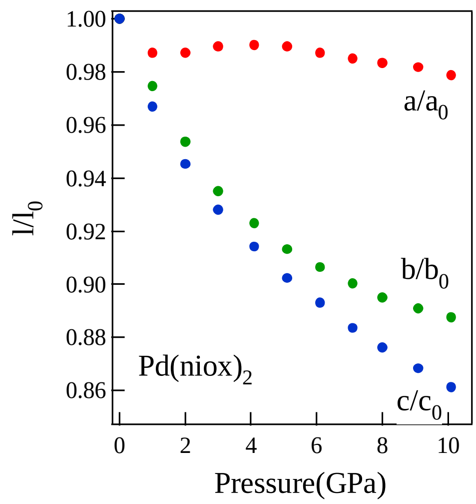

Figure 1 Ratio of lattice constant (l/l0) vs. pressure curves for $Pd(dmg)_2$ and $Pd(dpg)_2$ at room temperature.

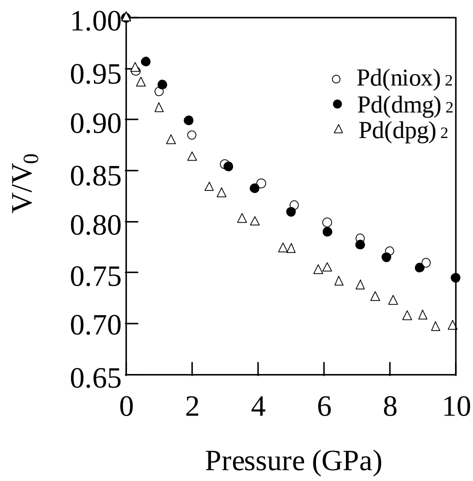

Figure 2 shows ratio of cell volume vs pressure curves for $Pd(niox)_2$ and $Pd(dmg)_2$ and $Pd(dpg)_2$.

References

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