# High pressure studies and chemical bonding analysis of $Rh_3Bi_{14}$ and $Rh_3Bi_{12}Br_2$ compounds

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## Introduction

X-ray diffraction at high pressure permits insight into structural properties of the materials, through structural and physical changes when the pressure is varied. The present work reports the synthesis, crystal structure of $Rh_3Bi_{14}$, and high pressure studies, chemical bonding analysis for the influence of different ions in channels on bonding and stability.

## Methods and Materials

$Rh_3Bi_{14}$ single crystals were grown from Bi-flux and separated by centrifuging. Single crystal X-ray diffraction data of $Rh_3Bi_{14}$ were collected on an Oxford CCD diffraction system. High pressures were generated up to *ca* 30 GPa by the ETH DAC using the ruby chips for pressure calibration. A mixture of methanol and ethanol (4:1) served as the pressure transmitting medium. Powder diffraction measurements were carried out at the SNBL, ESRF, Grenoble ($\lambda$ = 0.70933 Å).

## Results and discussions

Crystallographic data are summarized in *Table 1*.

*Table 1. Crystallographic data for $Rh_3Bi_{14}$.*

| | |
|---|---|
| Formula | $Rh_3Bi_{14}$ |
| Crystal system, Space group | Orthorhombic, *Fddd* (No. 70) |
| Lattice parameters | a = 6.8802(3) Å, b = 17.3228(8) Å, c = 31.6682(15) Å |
| Cell volume, Z | 3774.4(3) Å$^3$, 8 |

The $Rh_3Bi_{14}$ is isostructural with $Rh_3Bi_{12}Br_2$ [1], consists of a 3D framework of edge-sharing cubes and square antiprisms [$RhBi_8$] (*Fig. 1*). It is closely related to the intermetallic compound $RhBi_4$ [2], in which two frameworks of antiprisms interpenetrate [3]. In $Rh_3Bi_{14}$ and $Rh_3Bi_{12}Br_2$, additional bismuth and bromine anions, respectively, fill the channels of the 3D polyhedral cationic framework formed by covalently bonded rhodium and bismuth atoms.

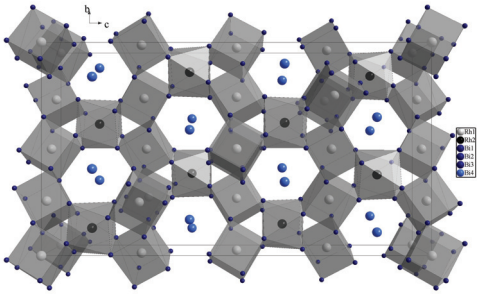

*Fig.1. Perspective view of crystal structure of $Rh_3Bi_{14}$ along [100].*

The X-ray diffraction diagrams measured at elevated pressures indicate that both compounds remain stable up to *ca* 30 GPa (*Fig. 2*). After determination of peak positions in diffraction diagrams measured at various pressures, the unit cell parameter were refined by means of least-squares procedure. A 2nd-order Birch-Murnaghan equation of state can be fitted to experimental data (*Fig. 3*).

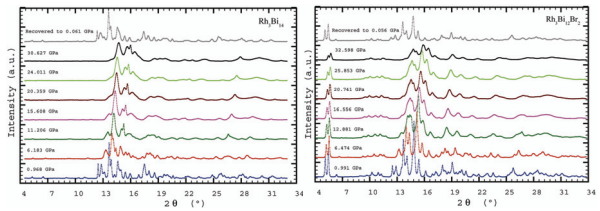

*Fig. 2. Some representative powder diffraction patterns of $Rh_3Bi_{14}$(left), $Rh_3Bi_{12}Br_2$ (right) shown measured at different pressures.*

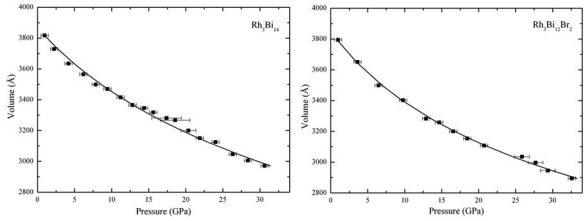

*Fig.3. Volume per unit cell as a function of pressure for (left)$Rh_3Bi_{14}$, (right)$Rh_3Bi_{12}Br_2$. The solid line corresponds to the 2nd-order Birch-Murnaghan equation of state with a bulk modulus $K_0$=70(5)GPa and $K_0$=67(4) GPa for $Rh_3Bi_{14}$ and $Rh_3Bi_{12}Br_2$, respectively.*

The role of chemical bonding in unexpectedly high stability of the 3D framework, its flexibility in accommodating different atoms in the channels is shown by applying the electron localization function (ELF) as bonding indicator (*Fig. 4*).

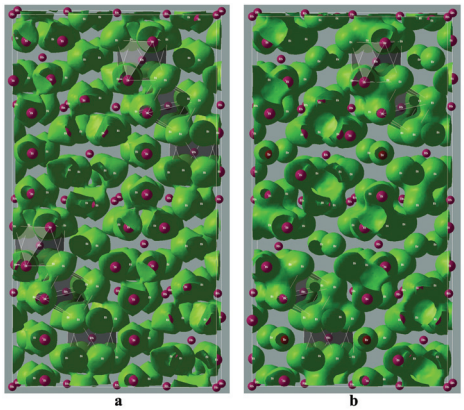


*Fig.4. Crystal structure and electron localization function of (a) $Rh_3Bi_{14}$ (b) $Rh_3Bi_{12}Br_2$ with $\eta$ =0.45 showing the positions of the bonding attractors.*

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**References**

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