

[1] G.A. Medvedkin, T. Ishibashi, T. Nishi, K. Sato, *Physics of technique semiconductors* **2001**, 35, 3, 305-309. [2] L.G. Khvostantsev, L.P. Vereshagin, A.P. Novikov. *High Temp.-High Pressure* **1977**, 9, 6, 637-639.

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## MS19.P10

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### Crystal structure refinement of Pt-base perovskite

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$AA'_3B_4O_{12}$ -type perovskites have been extensively investigated because of their intriguing structural and physical properties. In  $\text{CaCu}_3B_4\text{O}_{12}$  ( $B = \text{Mn}^{4+}$  and  $\text{Fe}^{4+}$ ) perovskites, electron carrier doping by substitution of an aliovalent cation  $\text{La}^{3+}$  for  $\text{Ca}^{2+}$  at  $A$ -site induces drastic changes in structural and physical properties [1], [2], [3], [4]. However,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  does not accept effective electron carriers by this type of substitution because of high stability of  $\text{Ti}^{4+}$  valence state in oxide. The resulting compound contains 1/3 deficiency at  $A$ -site, having a chemical formula of  $\text{La}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$  [5].

A novel Pt-based perovskite  $\text{CaCu}_3\text{Pt}_4\text{O}_{12}$  (CCPO) has been reported [6]. CCPO is an antiferromagnetic insulator with  $T_N = 40$  K. In the course of electron carrier doping for CCPO, we successfully obtained a  $AA'_3B_4O_{12}$ -type perovskite phase from a nominal starting composition of  $\text{LaCu}_3\text{Pt}_4\text{O}_{12}$  (LCPO). LCPO exhibited a spin-glass-like behavior below 4 K, whereas it remains an electrical insulator, suggesting that effective electron carriers were not introduced. Our structural refinement based on the synchrotron X-ray powder diffraction data implies that the LCPO has 1/16 deficiency at  $B$ -site, with the chemical formula of  $\text{LaCu}_3\text{Pt}_{3.75}\text{O}_{12}$ . LCPO is the first example that contains a significant amount of  $B$ -site cation deficiency in  $AA'_3B_4O_{12}$ -type perovskite, suggesting that the possibility of  $B$ -site cation deficiency should be considered in the structural analysis of  $AA'_3B_4O_{12}$ -type perovskite in some cases.

[1] Z. Zeng et al., *Phys. Rev. Lett.* **1999**, 82, 3164-3167. [2] J.A. Alonso et al., *Appl. Phys. Lett.* **2003**, 83, 2623-2625. [3] I. Yamada et al., *Angew. Chem. Int. Ed.* **2008**, 47, 7032-7035. [4] Y.W. Long et al., *Nature* **2009**, 458, 60-63. [5] A. Deshanvres et al., *Bull. Soc. Chim. Fr.* **1967**, 11, 4077-4078. [6] I. Yamada et al., *Inorg. Chem.* **2010**, 49, 6778-6780.

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### High pressure synthesis, structure, and physical properties of a novel iron-based perovskite $\text{YCu}_3\text{Fe}_4\text{O}_{12}$

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Iron-based perovskites  $\text{ACu}_3\text{Fe}_4\text{O}_{12}$  ( $A = \text{Ca}^{2+}$  and  $\text{La}^{3+}$ ), which were recently synthesized under high pressures of 10–15 GPa, demonstrate intriguing electronic phase transitions.  $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$  shows ferromagnetic and charge disproportionation (CD) transitions ( $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$ ) at 210 K [1]. In contrast,  $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$  (LCFO) exhibits

antiferromagnetic and intersite charge transfer (CT) transitions at 400 K, accompanied by a large volume change [2]. The essential factor determining the type of electronic phase transitions (CD or CT) has still been unsolved issue. To elucidate the above issue, we synthesized a novel perovskite  $\text{YCu}_3\text{Fe}_4\text{O}_{12}$  (YCFO), in which large  $\text{La}^{3+}$  ion was substituted by small  $\text{Y}^{3+}$  ion, and studied the ionic size effect in the  $A^{3+}\text{Cu}_3\text{Fe}_4\text{O}_{12}$  perovskite.

YCFO was successfully synthesized at high pressure of 15 GPa. The synchrotron X-ray powder diffraction data in the temperature range of 100–450 K showed no abrupt volume change attributed to the CT, unlike LCFO. Magnetic susceptibility and isothermal magnetization data indicated a ferromagnetic transition at 250 K.  $^{57}\text{Fe}$  Mössbauer spectra exhibited that a single  $\text{Fe}^{3.75+}$  species of  $B$ -site at room temperature split into multiple magnetic sextets at 4 K, indicating the CD of  $\text{Fe}^{3.75+}$  into  $\text{Fe}^{3+}$  and  $\text{Fe}^{5+}$  species ( $8\text{Fe}^{3.75+} \rightarrow 5\text{Fe}^{3+} + 3\text{Fe}^{5+}$ ).

The above-mentioned electronic properties of YCFO, which are in contrast to those of LCFO, imply that the ionic size of  $A$ -site cation influences the electronic phase transition in  $A^{3+}\text{Cu}_3\text{Fe}_4\text{O}_{12}$ . We will discuss the ionic size effect, comparing the local structure of YCFO and LCFO.

[1] I. Yamada et al., *Angew. Chem. Int. Ed.* **2008**, 47, 7032-7035. [2] Y.W. Long et al., *Nature* **2009**, 458, 60-63.

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### Novel high-pressure van der Waals compound in solid hydrogen-krypton mixtures

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Bonding interactions in molecular systems can be dramatically changed upon compression; atomic rare gases, diatomic ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ , etc.) and even full-shell molecules ( $\text{CH}_4$ ,  $\text{SiH}_4$ , etc.) can interact with each other in solid form under high pressure; novel stoichiometric van der Waals compounds have been synthesised for example in the systems He-Ne [1], Ar- $\text{H}_2$  [2],  $\text{CH}_4$ - $\text{H}_2$  [3], and more recently Xe- $\text{H}_2$  [4], [5].

The study of binary mixtures of hydrogen is of particular interest because they are relevant to the study of the interior of the giant planets and are of technological relevance for hydrogen storage.

Here we present a study of the binary system krypton-hydrogen. A diamond-anvil cell was loaded with a mixture of 8% in volume high purity Kr and  $\text{H}_2$ . Kr and  $\text{H}_2$  are miscible in the liquid phase. A solid phase with stoichiometry  $\text{Kr}(\text{H}_2)_4$  was observed to form at a pressure of 5.3 GPa.

The structure of this novel van der Waals compound has been determined by single crystal diffraction at beamline I15, Diamond Light Source. Krypton atoms assemble in a face-centred cubic structure forming octahedral clusters with Kr-Kr bond distances comparable to the Kr bond distance in pure Kr solid.

Complementary Raman spectroscopic measurements were performed to better characterize the environment of the  $\text{H}_2$  molecule. Three intramolecular H-H vibrons are observed at higher frequencies than those of pure, solid  $\text{H}_2$  at the same pressure.

[1] P. Loubeyre, M.J. Louis, R. LeToullec, *Phys. Rev. Lett* **1993**, 70, 178. [2] P. Loubeyre, R. LeToullec, J-P. Pinceaux, *Phys. Rev. Lett* **1994**, 72, 1360. [3] M. Somayazulu et al., *Science* **1996**, 271, 1400. [4] M. Somayazulu et al., *Nature Chemistry* **2010**, 2, 50-53. [5] M. Amboage, A.K. Kleppe, and A.P. Jephcoat, to be published.