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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 Fe^{4+}) perovskites, electron carrier doping by substitution of an aliovalent cation La^{3+} for 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 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.

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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 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 La^{3+} ion was substituted by small 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}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 Fe^{3+} and 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.

Keywords: novel perovskite, unusual high valence iron, high-pressure synthesis

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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 (N_2 , O_2 , H_2 , etc.) and even full-shell molecules (CH_4 , 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- H_2 [2], CH_4 - H_2 [3], and more recently Xe- 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 H_2 . Kr and 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 H_2 molecule. Three intramolecular H-H vibrons are observed at higher frequencies than those of pure, solid H_2 at the same pressure.

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High pressure compounds in xenon-hydrogen mixtures

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The study of binary mixtures of atomic (He, Ar, Xe, etc.) and diatomic (N₂, O₂, H₂, etc.) molecular solids is relevant for a better understanding of the interior of the giant planets. It has led to the discovery of a new type of compound – the van der Waals (vdW) compound – and provides essential information on the interactions among simple molecules.

It was long believed that group 18 elements were inert and unreactive and could not form compounds. A new chemistry field started in 1962, when the first noble gas compound, xenon hexafluoroplatinate, was synthesised [1]. Since then, many compounds have been created combining noble gases with other chemical elements [2].

Here we present a study of vdW compound formation in the xenon-hydrogen system under high pressure. We have studied several compositions (between 7% and 15% vol Xe) to map the binary phase diagram. Complex phase behaviour as a function of composition and pressure was observed with the formation of different stoichiometric phases.

These novel Xe-H₂ compounds have been characterized by single-crystal and powder x-ray diffraction at beamline I15 of Diamond Light Source. We find three separate phases with orthorhombic, hexagonal and rhombohedral structures as function of pressure and composition. These novel structures will be presented in relation to other rare gas-hydrogen compounds, in particular Ar(H₂)₂ [3], Kr(H₂)₄ [4], and the previously reported Xe(H₂)₈ [5].

A rare gas hydrogen system not only offers the possibility of the discovery of unusual stoichiometric compounds, but also allows the study of the hydrogen molecule in a modified environment compared to pure H₂ solid. The study of the detailed intra-molecular response of H₂ to compression can give insight into new pathways to hydrogen metallization. This has been suggested for the Ar(H₂)₂ compound [3]. In the Ar-H system the H₂ vibron is seen to increase continuously under pressure. In contrast our Raman spectroscopic measurements on rhombohedral Xe(H₂)₈ show shifted vibron frequencies relative to the pure (bulk) H-H stretching mode which soften with pressure and appear to cross the pressure-frequency trajectory of the pure H₂ vibron around 50 GPa.

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Keywords: high pressure, molecular solids, diffraction

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Neutron diffraction study on the pressure-induced cubic-tetragonal structural distortion in LaD₂ using total scattering spectrometer NOVA

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Rare-earth metals absorb large amount of hydrogen to form di and trihydrides. For a dihydride LaH₂, in which hydrogen atoms are accommodated in the tetrahedral interstitial sites of the host fcc metal lattice alone and the octahedral sites remain empty, we found a pressure-induced phase separation by synchrotron radiation X-ray diffraction [1]. We also found a lattice distortion from the cubic to a tetragonal one before the phase separation. X-ray diffraction measurements, however, provided no information on the hydrogen positions and occupancies in the metal lattice. They are crucial for understanding the origin of the lattice distortion and hence the mechanism of the phase separation.

High-pressure neutron diffraction experiments were performed for LaD₂ with a total scattering spectrometer NOVA constructed at J-PARC [2]. Rietveld analysis of an ambient pressure profile of a powder sample yielded a lattice constant $a=5.652(2)\text{\AA}$ and hydrogen occupancies 0.94(4) at T-site and 0.09(6) at O-site. In the high pressure experiments, we used a Paris-Edinburgh cell [3]. High pressures up to 10 GPa and above were generated with single toroid anvils made of tungsten carbide and double toroid anvils of sintered diamond, respectively. LaD₂ powder was encapsulated in a gasket made of TiZr null alloy together with a pressure medium of deuterated methanol-ethanol 4:1 mixture. We obtained diffraction profiles at ten pressure conditions from 0.1 to 17GPa.

The fcc lattice of LaD₂ began distortion to a tetragonal lattice around 7GPa. The peak splitting arising from the tetragonal distortion increased in magnitude on further compression to the phase separation pressure of 11 GPa. A similar lattice distortion has been reported for superstoichiometric LaH_{2+x}, in which excess hydrogen atoms occupy the O-sites to make the cubic lattice distorted [4]. Partial transfer of the T-site D atoms into the O-sites in LaD₂ is one possible cause for the distortion. Refinement of the diffraction profiles measured for the tetragonal phase at several pressure points are carrying out now. The microscopic mechanism of the cubic-tetragonal structural transition and the following phase separation will be discussed on the basis of the refined structural parameters.

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High pressure structure and magnetism of one 1-D molecular magnetic material

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Molecular magnetic materials(MMM) have been attracted much attention for increasing demands on smaller size magnetic memory devices and interest in the interpretation of the mechanism for complicated magnetic interactions. Many studies focus on investigating the magnetic coupling mechanism and the magneto-structural correlation. Many methods can be used to control magnetic property.