Crystal structure refinement of Pt-base perovskites

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

A novel Pt-based perovskite Ca\textsubscript{3}Pt\textsubscript{4}O\textsubscript{12} (CCPO) has been reported [6]. CCPO is an antiferromagnetic insulator with \( T_\text{N} = 40 \) K. In the course of electron carrier doping for CCPO, we successfully obtained an AA′B\textsubscript{4}O\textsubscript{12}, type perovskite phase from a nominal starting composition of La\textsubscript{2}Ca\textsubscript{4}Pt\textsubscript{4}O\textsubscript{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 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 1/6 deficiency at B-site, with the chemical formula of Ca\textsubscript{3-La}La\textsubscript{2}Ca\textsubscript{4}Pt\textsubscript{4}O\textsubscript{12}. LCPO is the first example that contains a significant amount of B-site cation deficiency in AA′B\textsubscript{4}O\textsubscript{12}, type perovskite, suggesting that the possibility of B-site cation deficiency should be considered in the structural analysis of AA′B\textsubscript{4}O\textsubscript{12}, type perovskite in some cases.


Keywords: platinum perovskite, vacancy, high-pressure synthesis

High pressure synthesis, structure, and physical properties of a novel iron-based perovskite YCu\textsubscript{4}Fe\textsubscript{2}O\textsubscript{12}

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Iron-based perovskites A\textsubscript{4}Cu\textsubscript{2}Fe\textsubscript{2}O\textsubscript{12} (A = Ca\textsuperscript{2+} and La\textsuperscript{3+}), which were recently synthesized under high pressures of 10–15 GPa, demonstrate intriguing electronic phase transitions. Ca\textsubscript{3}Cu\textsubscript{2}Fe\textsubscript{2}O\textsubscript{12} shows ferromagnetic and charge disproportionation (CD) transitions (2Fe\textsuperscript{4+} → Fe\textsuperscript{3+} + Fe\textsuperscript{5+}) at 210 K [1]. In contrast, La\textsubscript{3}Cu\textsubscript{2}Fe\textsubscript{2}O\textsubscript{12} (LCFO) exhibits antiferromagnetic and intesite 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 YCu\textsubscript{2}Fe\textsubscript{2}O\textsubscript{12} (YCF0), in which large La\textsuperscript{3+} ion was substituted by small Y\textsuperscript{3+} ion, to study the ionic size effect in the A\textsubscript{4}Cu\textsubscript{2}Fe\textsubscript{2}O\textsubscript{12} perovskite.

YCF0 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 isotothermal magnetization data indicated a ferromagnetic transition at 250 K. Fe Mössbauer spectra exhibited that a single Fe\textsuperscript{5+} species of B-site at room temperature split into multiple magnetic sextets at 4 K, indicating the CD of Fe\textsuperscript{5+} into Fe\textsuperscript{3+} and Fe\textsuperscript{5+} species (8Fe\textsuperscript{5+} → 5Fe\textsuperscript{3+} + 3Fe\textsuperscript{5+}). The above-mentioned electronic properties of YCF0, which are in contrast to those of LCFO, imply that the ionic size of A-site cation influences the electronic phase transition in A\textsubscript{4}Cu\textsubscript{2}Fe\textsubscript{2}O\textsubscript{12}. We will discuss the ionic size effect, comparing the local structure of YCFO and LCFO.


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

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\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}) and even full-shell molecules (CH\textsubscript{4}, SiH\textsubscript{4}, etc.) interact with each other in solid form under high pressure; novel stoichiometric van der Waals compounds have been synthesized for example in the systems He-Ne, Ar-H\textsubscript{2}, CH\textsubscript{2}-H\textsubscript{2}, and more recently Xe-H\textsubscript{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\textsubscript{2}, Kr and H\textsubscript{2} are miscible in the liquid phase. A solid phase with stoichiometry Kr(H\textsubscript{2})\textsubscript{30} 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\textsubscript{2} molecule. Three intramolecular H-H vibrions are observed at higher frequencies than those of pure, solid H\textsubscript{2} at the same pressure.