

Determining the Rh dopant site structure in Rh:SrTiO₃ photocatalysts

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Photoelectrochemical water splitting is a potentially attractive method for producing hydrogen from water with the help of sunlight. The process relies on a semiconductor photoelectrode that absorbs sunlight and injects either photoexcited electrons or holes into water, producing either hydrogen or oxygen. A *p*-type semiconductor, such as Rh-doped SrTiO₃ can be used as a water-stable hydrogen evolution electrode material. Unfortunately, doped oxide semiconductors such as Rh:SrTiO₃ exhibit exceedingly short, picosecond scale photocarrier lifetimes and mobilities that are far below the Hall mobility when the same material is doped to a metallic state, i.e., Nb:SrTiO₃. The purpose of this work is to use x-ray fluorescence holography (XFH) to determine what types of dopant-related defect structures form in Rh:SrTiO₃ and to develop doping schemes that may reduce carrier trapping and improve the energy conversion efficiency of a photoelectrode.

XFH measurements were performed on Rh⁴⁺:SrTiO₃ and Rh³⁺:SrTiO₃ thin film samples at SPring-8 BL13XU. Reconstructions of atomic positions around the Rh dopant site are shown for a Rh³⁺:SrTiO₃ film in Fig. 1. The detected atomic positions were compared with possible defect cluster structures and two of the most likely defects types were identified: the formation of Rh-V_O-Rh clusters, and metallic Ti-Rh-Ti clusters where the dopant atom occupies the oxygen site. The structural models for these defect clusters are shown in Fig. 1. This work shows that XFH is an effective tool for uniquely identifying dopant site structures in perovskites, providing useful information for designing electronically cleaner doping schemes and synthesis procedures.

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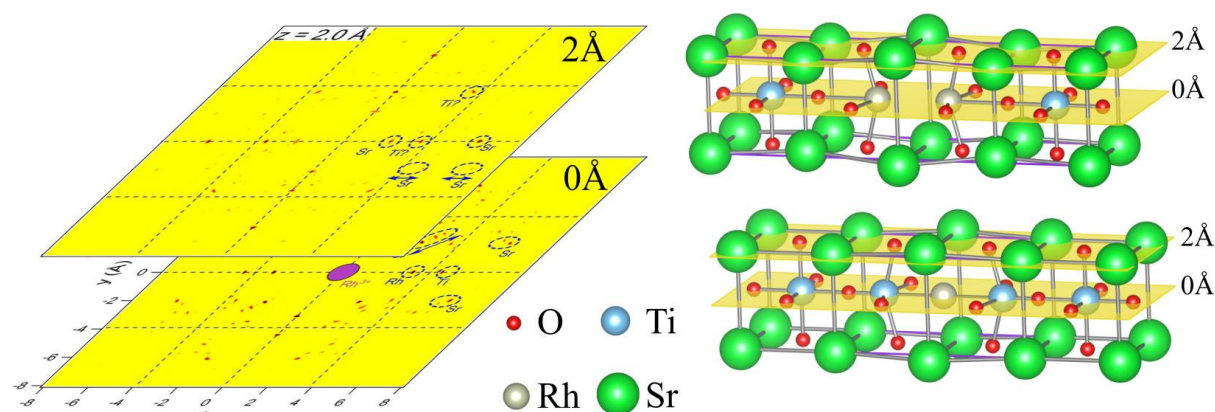


Fig. 1 X-ray fluorescence holography reconstructions of atom positions in two planes and the corresponding structural models for a cluster combining two Rh atoms with an oxygen vacancy and a metallic cluster where the Rh atom occupies the oxygen site.