

Spin tube oxide obtained by topochemical dehydration

Dehydration is an essential reaction for maintaining biological functions such as maintaining a constant body temperature and is also involved in other simple organic reactions such as the synthesis of ethers from alcohols [1]. In the case of inorganic materials, dehydration reactions can be seen, for example, in the processes of molding and baking clay during which our ancestors made earthenware and pottery. The Hayabusa2 spacecraft, which succeeded in its mission in 2020, has shown that the near-Earth asteroid Ryugu has an unexpectedly low water content resulting from its surface material being composed of carbonaceous chondrites that have undergone heating and dehydration [2].

Oxides, which represent inorganic materials, exhibit various properties that make them function as magnets, batteries, catalysts, and superconductors among others. Interestingly, functionalities of oxide materials can be achieved through the successful control of oxygen content. For example, in the high- T_c oxide superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, the transition temperature of superconductivity can be tuned by adjusting the oxygen content x [3]. The main method of controlling the oxygen content of oxides has been to adjust the gas atmosphere during synthesis at high temperatures. Recently, however, it has been reported that low-temperature topochemical reactions using metal hydrides such as CaH_2 are powerful methods to remove oxygen ions from oxides during reduction reactions [4].

In this study, we have succeeded in obtaining a new material, SrCoO_2 , by electrochemical insertion

of a proton (H^+) into the oxide $\text{SrCoO}_{2.5}$, followed by heating and a dehydration reaction (Fig. 1(a)) [5]. Here, the cobalt valence is reduced from trivalence in the starting material $\text{SrCoO}_{2.5}$ to divalence in the reactant SrCoO_2 , indicating that this method of combining protonation and dehydration is a powerful reduction reaction process. Note that SrCoO_2 cannot be obtained by the reduction reaction using metal hydrides, which have been known as the strongest reducing agent.

We have performed soft X-ray absorption spectroscopy (sXAS) experiments at SPRING-8 BL25SU to investigate the local structure and valence state of $\text{SrCoO}_{2.5}$ and materials obtained by our developed new reduction reaction method using protonation and dehydration. Figure 1(b) shows the sXAS spectra around the Co L -edge for the samples before and after protonation and after subsequent dehydration in a vacuum. The electrochemical protonation of $\text{SrCoO}_{2.5}$ results in $\text{HSrCoO}_{2.5}$, indicating that the Co L -edge shifts to a lower energy accompanied by the reduction from Co^{3+} to Co^{2+} . On the other hand, after $\text{HSrCoO}_{2.5}$ is dehydrated at a high temperature, the position of the Co L -edge does not change, indicating that the divalent state Co^{2+} is retained during the dehydration reaction. However, the spectral shape changed significantly, indicating a significant change in the local structure around Co cations after dehydration. That is, the spectrum of $\text{HSrCoO}_{2.5}$ before dehydration contains a mixture of spectra corresponding to both octahedral and tetrahedral coordination around Co cations, but after heating and dehydration, the former spectrum

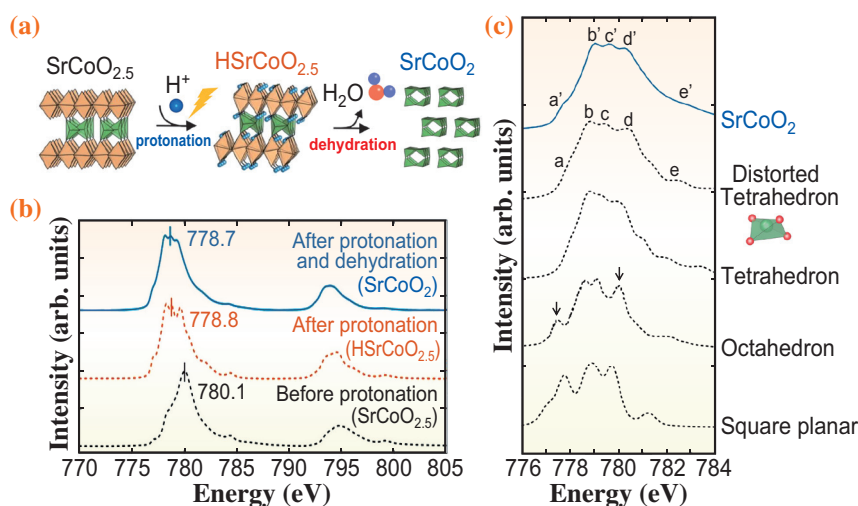


Fig. 1. (a) New reduction process using the combination of electrochemical protonation and subsequent dehydration discovered in this study. (b–c) Experimental results of sXAS measurements performed at SPRING-8 BL25SU.

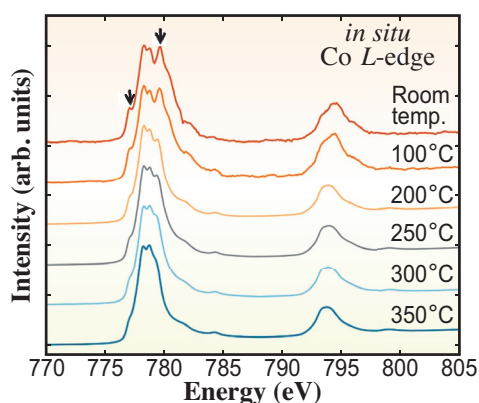


Fig. 2. *In situ* xXAS spectra of the Co L-edge of HSrCoO_{2.5} during heating in a vacuum. Arrows indicate the characteristic peaks of the CoO₆ octahedron, which disappear at high temperatures in a vacuum.

corresponding to octahedral coordination disappears and the only that corresponding to the distorted tetrahedral coordination is observed (Fig. 1(c)). This result was also confirmed by the results of *in situ* xXAS experiments (Fig. 2). This means that a large number of oxygen ions can be removed from HSrCoO_{2.5} at about 300°C during the dehydration reaction (HSrCoO_{2.5} → SrCoO₂ + 0.5H₂O). SrCoO₂ obtained through this reaction is a new material, and its crystal structure was also determined by scanning transmission electron microscopy (STEM) experiments and complementary theoretical calculations (Fig. 3(a)).

The feature of this new reduction reaction method is the existence of a protonated intermediate HSrCoO_{2.5} (Fig. 1(a) center), in which the CoO₆ octahedron is distorted upon protonation and destabilized under local strain. It is therefore considered that stable water (H₂O) can be removed along with oxygen ions from the crystal lattice of HSrCoO_{2.5} by heating and dehydration, resulting in SrCoO₂ (Fig. 1(a) right). Thus far, in perovskite-related ABO₂ (A, alkaline-earth metal ions or rare-earth metal ions; B, transition metal ions) compounds, only those with iron (Fe), copper (Cu), and nickel (Ni) at the B site are known to exist. Therefore, it is interesting and important to note that a new variation of cobalt Co was obtained in this study by a new reduction process in which the oxide is protonated followed by a dehydration reaction.

The insertion of H⁺ into oxide thin films using the ionic liquid gating technique is a recent subject of research worldwide. However, there has been no research on the concept of using an electrochemically protonated material as a precursor for a dehydration reaction to synthesize a new material with low oxygen content, as in this study. Therefore, this study is the first demonstration that the dehydration reaction after protonation is a powerful method of reduction reaction

to remove many oxygen ions from an oxide. In the future, it is expected that this reducing reaction will be used to develop new oxide functional materials. For example, it will be interesting to apply this method to powder samples and to develop reduced oxides with new structures in combination with the substrate strain arising from the thin film growth. In terms of applications, the potential utilization in the development of hydrogen storage materials holds promise. Moreover, SrCoO₂ obtained in this study has a unique crystal structure called a four-leg spin tube (Fig. 1(a) right and Fig. 3(b)). This structure closely resembles the “spin ladder structure” that has attracted attention in the field of condensed matter physics since the discovery of high-*T_c* cuprate superconductors. Therefore, it is expected to be a new platform for the emergence of novel quantum magnetism and superconductivity, and it will be interesting to see the future experimental and theoretical development of this research.

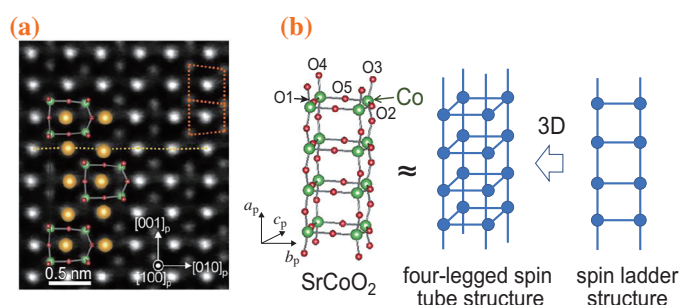


Fig. 3. (a) High-angle annular dark-field STEM image of SrCoO₂. (b) Schematic view of the relationship between four-legged spin tube structure of SrCoO₂ and spin ladder structure.

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