

Hybrid structure analysis: Accurate and precise determination of the structure parameters of mono- and bimetallic spinels via iterative and alternating refinements of powder X-ray diffraction and X-ray absorption fine structure spectroscopy

Several complex oxides are a subject of interest to physicists and chemists owing to their intriguing physical properties, such as ferroelectricity and superconductivity. Understanding these properties requires an investigation of the structures and electronic states of these oxides. Single-crystal X-ray diffraction (SCXRD) and powder X-ray diffraction (PXRD) are commonly used for structure analysis. SCXRD provides high-precision three-dimensional structures, aiding in elucidating structure-property relationships. Although SCXRD is a powerful tool, it requires good single crystals. In industrial applications, where most materials are not single crystals, PXRD is used instead of SCXRD. However, PXRD provides limited information, and thus, the accurate determination of structures is challenging. This limitation is more pronounced for materials with light and heavy elements, such as oxides. As X-rays are scattered by electrons, it is generally difficult to distinguish between different elements, particularly when they are close in the periodic table. Consequently, the development of solid materials often involves repetitive trial-and-error processes, highlighting the need for a rational design method for streamlined synthesis and performance evaluations.

The concept proposed in this study involves a hybrid structure analysis of metal oxides with high accuracy and precision by combining PXRD and X-ray absorption fine structure (XAFS). PXRD was used to determine the cell parameters and information of heavy atoms accurately, providing high-precision structure parameters through the Rietveld analysis. However, this method is not accurate for light atoms. On the other hand, XAFS offers element-selective information on coordination environments and oxidation states, but has lower precision. This study aimed to leverage the strengths of both methods alternately by incorporating accurate XAFS information into precise PXRD Rietveld refinement. The hybrid analysis alternates between PXRD and extended XAFS (EXAFS) refinements, gradually refining the structure parameters until they converge to physically and chemically reasonable values. To validate this concept, spinel-structured Co_3O_4 was analyzed to demonstrate the effectiveness of the proposed strategy for obtaining accurate and precise structure information. We then applied this “hybrid structure analysis” to the more complicated bimetallic spinel Co_2MnO_4 . In this study, we focused on Co_2MnO_4 owing to space limitations [1].

Co_2MnO_4 is an electrocatalyst for the oxygen evolution reaction in water electrolysis and operates for more than 1,000 h under highly acidic conditions [2]. The structure analysis of Co_2MnO_4 using PXRD is much more difficult than that of Co_3O_4 because Co and Mn have similar atomic numbers and are located on the same metal site. Thus, the objective of this study was to extract accurate structure information, including cation distribution.

This strategy is illustrated in Fig. 1. To exploit the element-selective nature of XAFS, we used the K absorption edges of both Co and Mn. EXAFS can provide information on the distribution of elements, that is, element- and site-specific occupancy. Conversely, PXRD can be used to estimate the total occupancy of each site as long as the chemical species at the site are known. Hence, the following strategy was proposed: the total occupancy of the site was refined using PXRD and distributed to the occupancies by elements using information from EXAFS. Information on the average oxidation states of Co and Mn obtained via X-ray absorption near-edge structure (XANES) was also used to construct a model for the Rietveld analysis. PXRD and XAFS experiments were performed at SPing-8 BL44B2 [3] and BL14B2, respectively.

Step 0 (XANES): The average oxidation states of Co and Mn were estimated by comparing the energy of the absorption edge in the XANES spectra with those of the standard samples.

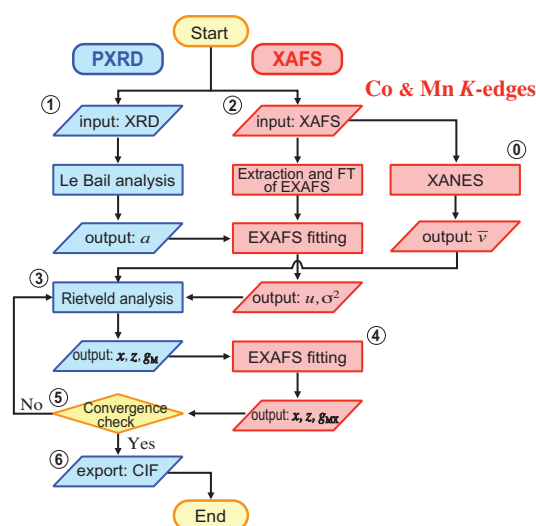


Fig. 1. Strategy of hybrid analysis of Co_2MnO_4 .

Step 1 (PXRD): The cell parameter a was refined by Le Bail analysis using RIETAN-FP software [4].

Step 2 (EXAFS): From the EXAFS results, we created an initial structure model in which Co was located on both sites A and B, whereas Mn was located on site B. Then, we refined the position of the oxygen using the Artemis software [5]. The value of the cell parameter obtained in Step 1 was fixed.

The fit was poor when the common coordinates of oxygen were adopted for both Co and Mn. The fit significantly improved when different coordinate values were used. This indicated that the local environments of Co and Mn were different.

Step 3 (PXRD): Rietveld analysis was performed to refine the occupancies with the position of oxygen fixed. Based on the results of Step 2, it was postulated that A site was occupied only by Co^{2+} , while B site was occupied by Co^{2+} , Co^{3+} , Mn^{3+} , and Mn^{4+} .

The oxygen atoms were split to incorporate the effects of different local environments around Co and Mn. We constructed two different models and compared their results. The “triple-disordered model,” where the oxygen atom was split into three to describe the disorder around the body diagonal, was adopted. The occupancy parameter for each atom was refined with the sum at each site maintained constant.

Step 4 (EXAFS): In Step 2, a simplified structure model, in which Mn was located only at the B site, was postulated. In fact, there was a small peak in the third coordination shell of the radial structure function at the Mn K -edge, indicating the presence of Mn at the A site. Therefore, the element- and site-specific occupancy parameters were refined, including the occupancy of Mn at the A site and g_{MnA} (where g_{MX} denotes the occupancy of metal M at site X).

Step 5 (PXRD): Because the discernment of Co and Mn using X-ray diffraction is difficult, the total occupancy of each site ($g_{\text{A}} (=g_{\text{CoA}} + g_{\text{MnA}})$, $g_{\text{B}} (=g_{\text{CoB}} + g_{\text{MnB}} = 1)$, and g_{O}), which is the sum of the occupancies of all atoms located at the site, was refined while retaining the Co/Mn ratio. The soft restraints of the bond lengths of $\text{M}_\text{A}-\text{O}$ and $\text{M}_\text{B}-\text{O}$ were set using the standard uncertainties derived from the EXAFS fitting in Step 4.

Step 6 (EXAFS): A refinement similar to that in Step 4 was conducted with a fixed oxygen position to update the element- and site-specific occupancy parameters.

Step 7: PXRD and EXAFS refinements were repeated, with the parameters updated until they satisfied the criteria for convergence in both PXRD and XAFS. Figure 2 shows the results of the hybrid structure analysis of Co_2MnO_4 during the final steps of the Rietveld and EXAFS analyses.

The results of the hybrid structure analysis showed that the A sites were occupied by Co and Mn in a ratio of 3:1. This matches the fact that Co^{2+} ions prefer sites

A to B. Moreover, the contribution of Mn at the A site improved the Mn K -edge EXAFS fitting compared with the result when no Mn at the A site was assumed in Step 2, which is reflected in the third coordination shell around Mn.

This study established a hybrid structure analysis method using PXRD and XAFS to determine the Co_3O_4 and Co_2MnO_4 parameters accurately. This method has been proven to be effective for bimetallic oxides. The hybrid approach, which combines XAFS selectivity and PXRD precision, revealed the detailed metal distribution through iterative refinements. The results demonstrate that high-quality structure analysis, such as SCXRD, can be achieved with powder samples through hybrid analysis and that it is applicable to catalysts. This method can analyze solid material structures, hinting at future *in situ* applications. In the era of data and computational science, our approach satisfies the growing requirements for precise structure analyses, accelerating mechanistic investigations and material explorations.

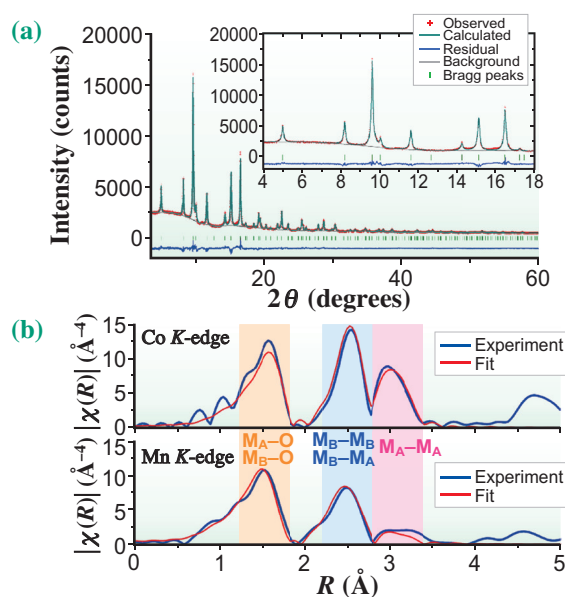


Fig. 2. Results of the hybrid structure analysis of Co_2MnO_4 . (a) Rietveld analysis and (b) EXAFS analysis at the final step (upper panel: Co K -edge; lower panel: Mn K -edge).

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