Structure analysis of $Ca(Mn_{1-x}Ru_x)O_3$ perovskite-type compounds by using XRD and XAFS

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1. Introduction

In order to make a breakthrough in metal recycling technology, it is essential to develop a technique for converting noble metals (especially, Ru, Rh, Ir) contained in noble metal waste material into compounds which dissolve readily in HCl. So far, we have found that $Ca(Mn_{1-x}Ru_x)O_3$ (x = 0.1, 0.3, 0.5) perovskite-type compounds (CMRO) dissolve readily in hot concentrated HCl. To make clear the mechanism of dissolution of CMRO into HCl, the averaged structures of CMRO were investigated by Rietveld refinements of powder XRD data as well as the valences of Ca, Mn, and Ru and the local structures around these metals were evaluated by SR- and laboratory-XAFS analyses.

2. Experimental

The raw materials of RuO_2 (3N), $CaCO_3$ (4N), and MnO_2 (3N) were weighed and wet planetary ball-milled so as to be molar ratios of cations satisfying $Ca(Mn_{1-x}Ru_x)O_3$ (x = 0.1, 0.3, 0.5) compositions. The mixtures were uniaxially-pressed under 0.2 MPa and then fired at 1273 K for 10 to 40 hrs in air. Powdered reaction products were investigated by X-ray diffractometry and the lattice constants and crystal structure parameters were refined by the Rietveld method. The XAFS measurements for Ca *K*- and Ru *L*-edges were carried out at BL-13 of the SR center (Ritsumeikan University). That for Mn *K*-edge was performed using a laboratory XAFS spectrometer (Technos, EXAC-820) at AIST.

3. Results and Discussion

Rietveld refinement results of XRD data revealed that the each reaction product after firing for 40 hrs includes more than 91 mol% of CMRO (x = 0.1, 0.3, 0.5) having a target composition (All CMRO have a $GdFeO_3$-type perovskite structure, crystal system: orthorhombic, space

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group: *Pnma* (No.62)[1]) [2]. Figure 1 shows the composition dependence of the bond valence sums (BVSs) of Ca, Mn, and Ru ions, as well as weighted average BVS of (Mn,Ru) sites in CMRO based on Rietveld refinements. With an increase in Ru content (x), the BVS of Ca increased from 2.11 to 2.12 (by 0.01). On the other hand, the BVS of Mn decreased from 3.93 to 3.52 (by 0.41) and that of Ru from 4.89 to 4.38 (by 0.51) with increasing Ru content (x). The weighted average BVSs of (Mn, Ru) sites were as follows: 4.02 (x = 0.1), 3.94 (x = 0.3), and 3.95 (x = 0.5). The Ru L_3-edge XANES spectra using a total electron yield method for CMRO, $Sr_2(Y, Ru)O_6$, and $CaRuO_3$ are depicted in Fig. 2. It is noticed from Fig. 2 that with increasing Ru content (x), the splitting of two peaks decreases and each peak shifts to lower energy, suggesting the valence of Ru approaches from +5 to +4 with increasing x [1, 3]. Figure 3 shows the Mn K-edge XANES spectra for CMRO, $CaMnO_3$, and $GdMnO_3$. The peak position shifts to lower energy with increasing Ru content (x), suggesting the valence of Mn approaches from +4 to +3 [1, 4]. The Ca K-edge XANES spectra did not show clear and systematic peak shift with a change of composition (x). The XRD and XAFS analyses revealed that the Mn and Ru ions in CMRO exist as the redox pairs of $Mn^{3+/4+}$-$Ru^{4+/5+}$, which is expected to be involved in HCl solubility of CMRO.

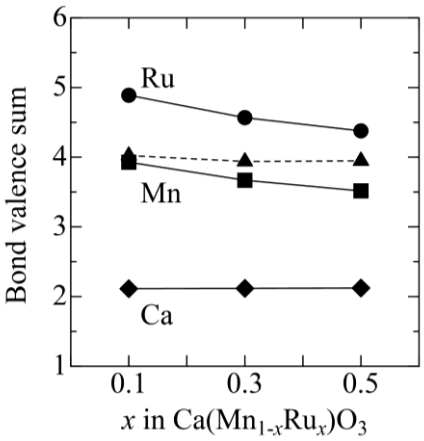

Fig. 1 Bond valence sums (BVSs) of Ca (◆), Mn (■), and Ru (●) ions, as well as weighted average BVS of (Mn,Ru) sites (▲) in $Ca(Mn_{1-x}Ru_x)O_3$ (x = 0.1, 0.3, 0.5) (CMRO) based on Rietveld refinements.

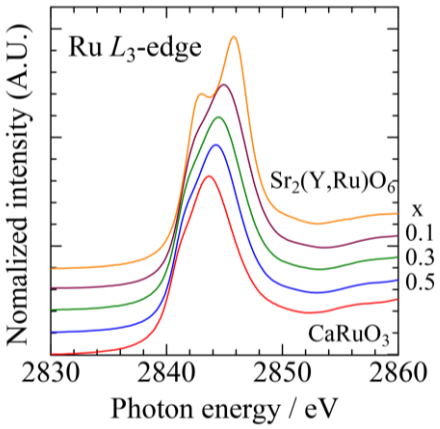

Fig. 2 Ru L_3-edge XANES spectra using a total electron yield method for $Ca(Mn_{1-x}Ru_x)O_3$ (x = 0.1, 0.3, 0.5) (CMRO), $Sr_2(Y, Ru)O_6$, and $CaRuO_3$.

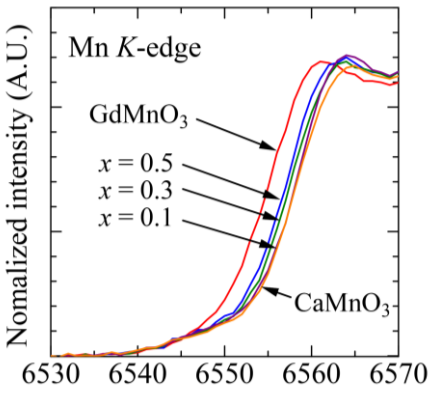

Fig. 3 Mn K-edge XANES spectra for $Ca(Mn_{1-x}Ru_x)O_3$ (x = 0.1, 0.3, 0.5) (CMRO), $CaMnO_3$, and $GdMnO_3$.

References

[1] Q. Zhou, B.J. Kennedy, Z. Zhang, L-Y. Jang, and B. Aitken, *Chem. Mater.*, **21**, 4203 (2009).

[2] K. Nomura, H. Kageyama, K. Mitsuhara, and T. Ohta, *"Proceedings of the 51st Annual Conference on X-ray Chemical Analysis"*, pp.103-104 (2015).

[3] Z. Hu, H. von Lips, M.S. Golden, J. Fink, G. Kaindl, F.M.F. de Groot, S. Ebbinghaus, and A. Reller, *Phys. Rev.*, B**61**, 5262 (2000).

[4] G. Subias, J. Garcia, M.G. Proietti, and J. Blasco, *Phys. Rev.*, B**56**, 8183 (1997).