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Combinatorial chemistry using fluorescence XAFS imaging

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Introduction

2D observation of fluorescence X-ray absorption fine structure (XAFS) can be performed just by replacing a conventional X-ray detector with a non-scanning X-ray fluorescence (XRF) imaging system equipped with a CCD camera [1]. Roughly speaking, it provides 1000 × 1000 XAFS spectra simultaneously in a short time (XRF imaging) [2]. This report describes a feasibility test for its application to combinatorial chemistry.

Experimental

Several manganese cobaltite spinel $MnCo_2O_4$ samples [3] were prepared from an aqueous solution containing 0.25 M $MnCl_2$ and 0.5 M $CoCl_2$. Drops (0.5 μl) were put on an alumina plate with several different amounts of nitric acid, and heated on a hot plate. The temperature of the plate was changed stepwise from 350 °C to 220 °C with the spotting. Then, as shown in Fig.1, nine different products were prepared after drying. XAFS imaging experiments were carried out by repeating exposures of the XRF image during the monochromator scans.

Results and Discussion

Fig.2 shows a 1000 × 1000 XRF image observed when the primary X-ray energy is 6.57 keV (just above the Mn K edge). The XAFS spectrum for each product can be obtained just by UL1 and UR integrating X-ray intensities in the pixel in each area (LL1, LR1, C1, 1) for all images collected as a function of X-ray energy. Although some parts appeared bright, reflecting 3D sape of the sample surface, it does not affect XAFS spehctra. Fig 3 shows spectra near the Mn-K edge. One can clearly see the differences in spectral features. When both the HNO_3 concentration and heating level were low (LL1), unreacted chloride remained, and therefore the spectrum resembled that of manganese chloride (the pink-color of the spot in Fig. 1 also shows the remaining salts). If either the HNO_3 concentration or heating was sufficient (LR1, UL1, or UR1), the chemical shifts show a higher oxidation state of manganese, and the spectra agreed with those of $MnCo_2O_4$. For comparison, normal XAFS experiments were performed at BL-10B [3], and a good agreement was confirmed including quite fine but significant differences in spectral features observed in LR1, UL1, and UR1. The technique seems very promising for combinatorial chemistry research on more practical systems. Further studies are now under way. The authors gratefully thank Prof. I. Nakai (Sci. Univ. of Tokyo) for his valuable discussion at the early stage of this research.

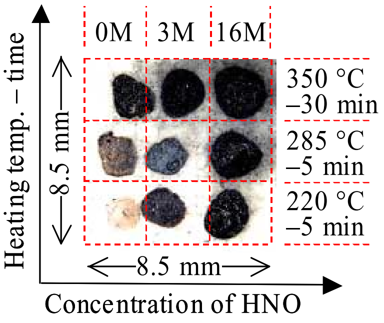

Figure 1 Variation in HNO_3 concentration in the reactant solution (0.25 M $MnCl_2$ and 0.5 M $CoCl_2$), and heating condition on an alumina plate. 9 spots in the picture are products obtained.

References

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[2] K. Sakurai and M. Mizusawa, Photon Factory Activity Report 2001 #19, 223 (2002).
[3] H. Eba and K. Sakurai, to be submitted.

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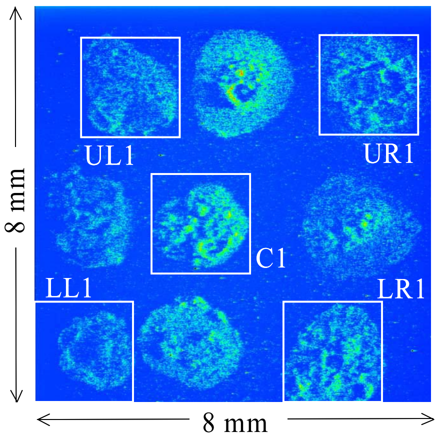

Figure 2 XRF image (1000 × 1000 pixels) from the sample (picture in Fig. 1) at the incident energy 6.57 keV and by 1 sec exposure.

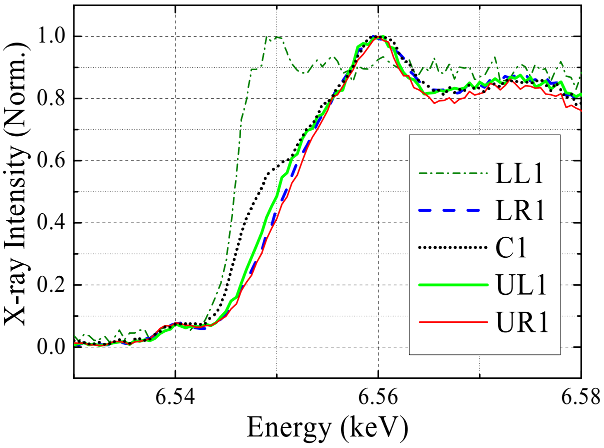

Figure 3 XAFS spectra obtained from the sequential images. Integration has been carried out on the areas indicated in Fig. 2.