12C/1999G075

EXAFS STUDY ON THE TRACE YTTERBIUM INCORPORATED IN CALCIUM CARBONATE CRYSTALS

Hiroshi TSUNO[1), 2), 4)], Hiroyuki KAGI[2)*], Yoshio TAKAHASHI[3)],
Tasuku AKAGI[4)] and Masaharu NOMURA[5)]

1) Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8569, Japan
2) Graduate School of Science, The University of Tokyo, Tokyo 113-0033, Japan
3) Faculty of Science, Hiroshima University, Hiroshima 739-8526, Japan
4) Faculty of Agriculture, Tokyo University of Agriculture and Technology, Tokyo, 183-8509, Japan
5) Photon Factory, Institute of Materials Structure Science, KEK, Ibaraki 305-0801, Japan

Introduction

The detailed chemical mechanism of dissolution and crystallization of calcium carbonate ($CaCO_3$) is one of the crucial issues in understanding the global cycling of CO_2 on the earth surface. Recently, substantial increase in the solubility of $CaCO_3$ was observed by the addition of trace amount of lanthanum (La) into the aqueous system [1]. The presence of La in the starting solution (≈ 5 µmol kg^{-1}) stabilized the labile phase of $CaCO_3$, vaterite, in the aquatic solution [2]. The local structure of trace lanthanum in $CaCO_3$ will be important to understand the chemical mechanism of the phenomena. It is difficult to obtain La-L_{III} XAFS spectra in a fluorescence mode due to the interference from the strong fluorescence of calcium as a matrix of samples. We attempted to measure and analyze XAFS spectra of trace amounts of ytterbium (Yb) which can be separated from Ca fluorescence using a solid-state detector (SSD). During the previous beam time of KEK-PF, we could carry out the estimation of the detection limits of Yb-L_{III} XAFS measurement in a fluorescence mode [3]. In the present work, we have investigated the local structure around Yb in $CaCO_3$ by the EXAFS technique.

Experimental

Calcium carbonate was precipitated from a mixed solution of 30 mM $CaCl_2$ aq and 30 mM $NaHCO_3$ aq with a given amount of ytterbium chloride. Concentrations of Yb were 5 µM in the starting solutions and 1.2×10^{-3} as Yb/Ca molar ratio in the precipitated calcium carbonate, respectively. Standard materials are listed in Table 1.

The Yb-L_{III} XAFS spectra were recorded in the fluorescence mode at the BL12C of KEK-PF [4] under the atmosphere and at room temperature. The fluorescent X-ray was measured by a 19 element pure-Ge SSD [5]. Some paper or/and aluminum foil were put on the front of detector as filter for decrease of the intensity of Ca-fluorescence. Analysis of the EXAFS spectra was performed with a PC program, REX2000 (Rigaku Co.).

Results and Discussion

XANES spectra suggested that Yb is incorporated in $CaCO_3$ as a substance different from Yb_2O_3, $Yb(OH)_3 \cdot n(H_2O)$ or $Yb_2(CO_3)_3 \cdot n(H_2O)$.

Fig. 1 shows Fourier transform of $k^3\chi$ of Yb-doped $CaCO_3$. A peak at 2≈ (no phase-shift correction) is attributed to the nearest Yb-O interaction. Fig. 2 shows the back Fourier transform of the first peak at 2 ≈ (see Fig.1) and its fitting result. The analysis results of the first shell of Yb in the various materials are shown in Table 1. The coordination number of Yb in $CaCO_3$ is extremely small (N ≈ 4) in contrast to the case for the standard materials. Furthermore, the Yb-O distance is approximately 4% shorter than those of other compounds. These data suggest that Yb-O bonding is compressed in the host $CaCO_3$ structure.

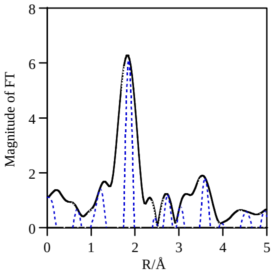

Fig. 1 Fourier transform of k^3weighted Yb L_{III} EXAFS of Yb in $CaCO_3$. Solid line: Radial structure function; Dashed line: imagenary part of FT.

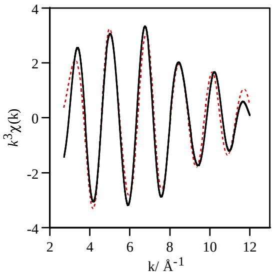

Fig. 2 Fit to the back Fourier transform of the first peak of Yb L_{III} FT-EXAFS in $CaCO_3$ shown in Fig. 1 (Yb-O). Solid line: experimentl; Dashed line: fitting.

Table 1: Results of the EXAFS analysis for Yb in $CaCO_3$ and various ytterbium compounds (the first nearest Yb-O shell).

Samples	$R_{Yb\text{-}O}$/≈	Coordination numbers
Yb in $CaCO_3$	2.25	4.1
$NaYb(CO_3)_2 \cdot n(H_2O)$	2.33	5.8
$Yb_2(CO_3)_3 \cdot n(H_2O)$	2.33	5.6
$Yb(OH)_3 \cdot n(H_2O)$	2.27	5.1
Yb in $NaHCO_3$-NaCl solution	2.33	7.8

References

[1]Akagi, T. and Kono, Y., Aquat. Geochem., 1, 231 (1995)
[2]Tsuno, H. *et al*., Bull. Chem. Soc. Jap., 74, 479 (2001)
[3]Kagi, H. *et al*., KEK Activity Report, 17, 153 (2000)
[4]Nomura, M. and Koyama, A., KEK Report, 95-15, 1 (1996)
[5]Nomura, M., KEK Report, 98-4, 1 (1998)

*kagi@eqchem.s.u-tokyo.ac.jp