

XANES study on the trace amounts of ytterbium ions incorporated in calcite: Spontaneously induced reduction of trivalent ytterbium in calcite

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Introduction

Trace amount of rare earth elements (REEs) induces significant effects on the crystal growth and dissolution of calcium carbonate. The substantial increase in the solubility of CaCO₃, the stabilization of the vaterite (labile phase of CaCO₃) and the inhibition of calcite growth were caused by the addition of trace amount of lanthanum into the aqueous system [1-4]. The uptake mechanism and chemical state of REEs incorporated into calcium carbonate were unclear. In the present work, we investigated the chemical species of ytterbium incorporated in calcite using X-ray absorption near edge structure (XANES) technique.

Experimental

Calcite (CaCO₃) was precipitated from a mixed solution of 30 mM CaCl₂ aq and 30 mM NaHCO₃ aq with a given amount of ytterbium chloride. Concentrations of Yb were 5 M in the starting solutions and 1.2×10⁻³ as Yb/Ca molar ratio in the precipitated calcium carbonate, respectively. Yb(OH)₃, NaYb(CO₃)₂·n(H₂O), Yb₂O₃, Yb₂(CO₃)₃·n(H₂O) and 5 mmol kg⁻¹ YbCl₃ solution were used as standard materials of XANES measurements. The Yb-L_{III} XAFS spectra were recorded in the fluorescence mode at the BL12C of KEK-PF [5]. XANES spectra of solid samples were measured at approximately 20K. The fluorescent X-ray was measured by a 19 element pure-Ge SSD [6]. Multiple scans (typically 3-5 times) were carried out and then averaged for each sample. XANES spectra were analyzed with REX2000 (Rigaku Co.).

Results and Discussion

Every XANES spectrum of the calcite and Yb-bearing standard materials had a significant white line around 8948 eV, which was assigned to electron transition 2p→5d6s of Yb³⁺ [7, 8]. The XANES spectra of Yb in calcite show a discernible shoulder in the lower energy side of the main white line (around 8940 eV). Fig. 1 shows the deconvoluted XANES spectrum of Yb in calcite. A small peak (Peak A in Fig. 1) was resolved from the spectra of calcite. Resultant peak position, peak height and FWHM of Lorentzian curve for Peak A are 8940.2 eV, 0.14 a.u. (arbitrary unit) and 6.1 eV, and those for Peak B are 8948.6 eV, 0.88 a.u. and 6.1 eV. The

position of Peak A was in lower energy by 8 eV than that of Peak B and is close to that of the absorption of Yb²⁺ [7-10]. Thus, we attributed peak A to Yb²⁺. These results indicate that significant proportion of ytterbium existed as divalent ions in the calcite structure. Tanaka et al. (1993) suggested that the ratio of areas of peak A and B indicates directly the relative amounts of Yb²⁺ and Yb³⁺ [8]. Based on the report, we calculated that the 14-17% of Yb exist as Yb²⁺ in calcite. Thermodynamic calculation indicates that [Yb²⁺]/[Yb³⁺] ratio in the starting solution is smaller than 10⁻³¹. In the starting solutions trivalent ytterbium was predominant and divalent ion was negligible. This suggests that a part of Yb was reduced on calcium carbonate formation. Further information of this result is described in Tsuno et al. (2003) [11].

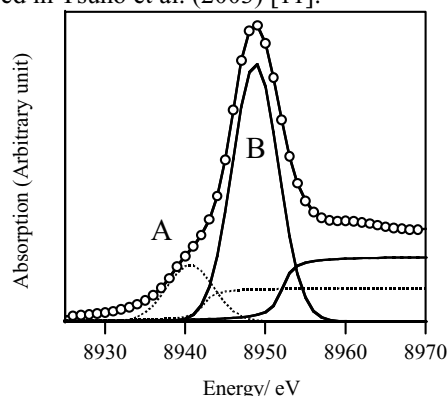


Fig. 1. Yb L_{III}-edge XANES and the deconvoluted spectra of Yb incorporated in calcite. A: Yb²⁺, B: Yb³⁺.

References

- [1]Akagi, T. and Kono, Y., *Aquat.Geochem.* 1, 231 (1995).
- [2]Tsuno, H., et al., *Bull. Chem. Soc. Jpn.*, 74, 479 (2001).
- [3]Tsuno, H., et al., *Chem. Lett.*, 2002, 960 (2002).
- [4]Kamiya, N., et al., *Chem. Lett.*, 2002, 890 (2002).
- [5]Nomura, M. and Koyama, A., *KEK Report*, 95-15, 1 (1996).
- [6]Nomura, M., *KEK Report*, 98-4, 1 (1998)
- [7]Hatwar, T. K., et al., *Solid State Commun.*, 34, 617 (1980).
- [8]Tanaka, T., et al., *Jpn. J. Appl. Phys.*, 32, 481 (1993).
- [9]Rao, C. N. R., et al., *Chem. Phys. Lett.*, 76, 413 (1980).
- [10]Baba, T., et al., *J. Chem. Soc., Faraday Trans.*, 89, 3177 (1993).
- [11]Tsuno, H., et al., *Chem. Lett.*, 32, 500 (2003).

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