

XAFS Study of Rare Earth Element Coordination in Calcite

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Introduction: Rare earth element (REE) patterns are valuable indicators of provenance and alteration for minerals and rocks. More recently, interest in trivalent REEs has developed because of expected similarities with the chemical behavior of trivalent actinide species (e.g., Am^{3+} , Cu^{3+} , Pu^{3+}), which pose serious threats as contaminants associated with radionuclide waste sources. Ca-bearing minerals are commonly enriched in REEs relative to other phases, reflecting the ease with which REEs substitute for Ca. In this EXAFS study, we characterized the local coordination environment of a series of trivalent REEs (Sm, Nd, Yb, and Dy) coprecipitated with CaCO_3 .

Methods and Materials: The REE-doped calcite samples were synthesized in room temperature aqueous solutions following procedures described by Gruzensky [1]. The samples were washed in deionized water, dried at 50 °C, and then ground to a fine powder for bulk EXAFS analysis. REE concentrations in the calcites were determined to be <2000 ppm in all cases. EXAFS scans were taken over the L_3 -edges at near liquid nitrogen temperature. The fluorescence yield was monitored using a 13-element solid-state Ge detector. Spectra of Sm_2O_3 , Dy_2O_3 , Yb_2O_3 , $\text{Nd}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Sm}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Dy}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$, and $\text{Yb}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ were collected using transmission methods for use as model compounds. Data analysis was done using WinXAS2.0 [2] in combination with FEFF7 [3].

Results: Figure 1 shows the Fourier transforms of the k^3 -weighted χ spectra of the REE doped calcite solids. The spectra are dominated by a single low- R peak attributable to the first shell of oxygen atoms. Smaller peaks at higher R are consistent with shells from C, O, and Ca, confirming REE^{3+} substitution in the Ca^{2+} site during coprecipitation. Comparison of the EXAFS determined first-shell REE-O distances to the ionic radii from Shannon [4] indicates a difference in the first shell REE-O coordination between the LREE's (Sm and Nd) and the HREE's (Yb and Dy). As shown in Figure 2, the HREE-O distances are consistent with 6-fold O coordination, whereas the LREE-O distances are consistent with 7-fold O coordination. This difference between the HREE and LREE oxygen coordinations possibly reflects differences in the mechanism of charge compensation when substituting trivalent REE for divalent Ca in the calcite structure, and may affect the relative stability of the HREE-calcite solid solutions versus the LREE-calcite solid solutions.

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References:

- [1] Gruzensky P.M. (1967) In H.S. Peiser (ed.), *Crystal Growth*, Pergamon Press, New York, p. 365-367.
 [2] Ressler T. (1997) *J. Physique IV*, 7, C2-269.
 [3] Zabinsky S.I., Rehr J.J., Ankudinov A., Albers R.C., and Eller M.J. (1995) *Phys. Rev. B* 52, 2995-3009.
 [4] Shannon R.D. (1976) *Acta Cryst.* A32, 751-767

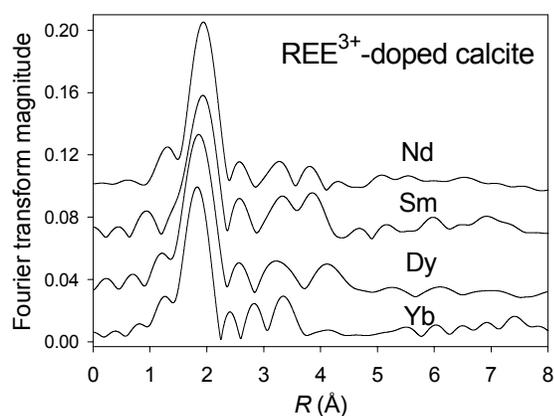


Figure 1. RSFs of the REE-calcite solid solutions.

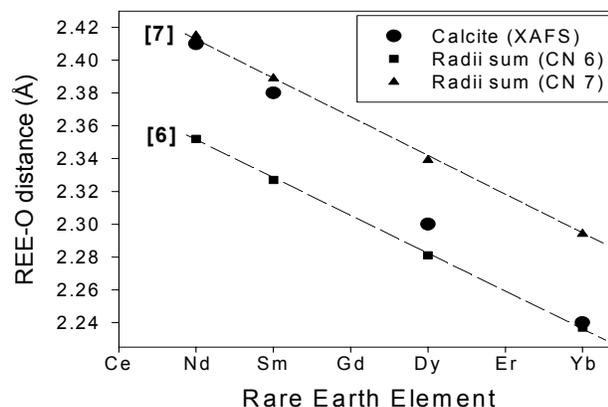


Figure 2. Shannon radii for 6- and 7 fold REE-O coordination compared to the experimentally determined REE-O distances.