EXAFS Investigation of Rare Earth Elements in Synthetic Zircon

R. J. Finch,[1] A. J. Kropf,[1] J. M. Hanchar[2]
[1]*Argonne National Laboratory, Argonne, IL, U.S.A.*
[2]*The George Washington University, Washington, DC, U.S.A.*

Introduction

Both natural and synthetic zircon ($ZrSiO_4$) crystals commonly display several orders of magnitude increase in the concentrations of trivalent rare earth elements (REE^{3+}) between La and Lu.[1] The reasons for such a large difference in REE incorporation depend, in part, on the relative compatibilities of large REE^{3+} ions at the Zr site in the zircon structure; however, an additional constraint on the replacement of Zr^{4+} by REE^{3+} is the ability of the zircon structure to accommodate charge-compensating substitutions, such as $P_{+1}Si_{-1}$. Determining the mechanisms of REE substitutions and the role of structural strain on limiting REE incorporation into zircon would improve our understanding of how REE may partition between zircon crystals and an REE-bearing liquid, and what the role of strain is in compositional zoning in zircon.[2]

The ionic radius of eight-coordinated Zr^{4+} is 0.84 Å. Because of the lanthanide contraction (ionic radii for trivalent lanthanides range from 1.160 to 0.977 Å for La and Lu, respectively), heavy lanthanides and Y are more compatible than lighter lanthanides in the zircon structure. This is consistent with Y and lanthanides (REE) replacing Zr^{4+} in REE-substituted zircon ($ZrSiO_4$), although, to our knowledge, this has not yet been unambiguously demonstrated.

A recent single-crystal x-ray diffraction (XRD) study of structural changes arising from the xenotime-type substitution ($REE_{+1}P_{+1}Zr_{-1}Si_{-1}$) in synthetic zircon crystals doped with individual REE demonstrated the overall magnitude of strain at the Zr and Si sites caused by substitution of REE and P into these sites in the zircon structure.[3] Because XRD reveals changes in bond lengths averaged over all equivalent sites in a crystal, we have obtained extended x-ray absorption fine structure (EXAFS) data in order to analyze local REE coordination in REE-substituted synthetic zircon crystals. The synthetic zircon crystals analyzed by EXAFS contain only one REE in each sample, eliminating potential absorption-edge interferences caused by neighboring lanthanide elements.

Results

We obtained EXAFS spectra at REE L-edges for selected synthetic zircon crystals containing 1.4 to 2.5 mol % REE. These spectra confirm that REE occupy the eight-coordinated Zr site in the zircon structure. Local distortions to bond lengths around REE^{3+} ions include lengthening of REE-O, REE-Si, and REE-Zr distances relative to similar distances in pure $ZrSiO_4$. There are two distinct Zr-O bond distances in pure $ZrSiO_4$ (2.130 Å and 2.275 Å), but our data strongly suggest that those Zr sites occupied by REE^{3+} ions display only a single REE-O bond distance. The magnitude of the REE-O bond distance varies with the ionic radius of the substituting REE^{3+} cation, e.g., Dy-O = 2.37(s) Å, Yb-O = 2.32(s) Å, and Lu-O = 2.33(s) Å. Notably, REE-O bond lengths in synthetic zircon crystals determined by EXAFS agree well with single bond distances predicted from bond-valence parameters.[4] Furthermore, bond distances determined by EXAFS are in excellent agreement with (bulk) average bond lengths determined by XRD when scaled with the average REE concentration in each crystal.[1]

Acknowledgments

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (BES), under Contract No. W-31-109-ENG-38. The MRCAT is funded by the member institutions and BES under contracts DE-FG02-94ER45525 and DE-FG02-96ER45589.

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