

Paramagnetic interactions in the ^{31}P NMR spectroscopy of rare earth element orthophosphate (REPO_4 , monazite/xenotime) solid solutions

AARON C. PALKE* AND JONATHAN F. STEBBINS

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.

ABSTRACT

We present the results of a variable-temperature (VT) ^{31}P magic angle spinning NMR (MAS-NMR) study of a series of solid solutions between different synthetic rare earth (RE = Y, La, Ce, Pr, Nd, Eu, Dy) orthophosphates (REPO_4) taking either the monoclinic monazite or tetragonal xenotime (zircon) crystal structure. Solid solutions were formed by mixing a small amount of a paramagnetic REPO_4 material (RE = Ce, Pr, Nd, Eu, Dy) with either diamagnetic LaPO_4 or YPO_4 , which take the monoclinic and tetragonal crystal structures, respectively. Mixtures were made with up to 10 mol% (nominal content) of the paramagnetic component. ^{31}P spectra of these materials contained several paramagnetically shifted resonances indicating some dissolution of the paramagnetic rare earth into the host LaPO_4 or YPO_4 phase; however, it is clear that none of the samples studied here reached a state of complete solid solution. The use of multiple paramagnetic species in dilute solid solution with two diamagnetic materials taking different crystal structures enabled an investigation of the probable mechanisms of paramagnetic interactions in the ^{31}P NMR experiments. A peak assignment model is introduced for the ^{31}P spectra. Our analysis indicates that the paramagnetic interactions are dominated by the Fermi contact shift with a secondary contribution from the so-called “pseudocontact” shift.

Keywords: NMR spectroscopy, monazite, xenotime, paramagnetic shifts, phosphates