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Relationship between ^{207}Pb NMR chemical shift and the morphology and crystal structure for the apatites $Pb_5(AO_4)_3Cl$, vanadinite (A = V), pyromorphite (A = P), and mimetite (A = As)

Otto E.O. Zeman[1], Rupert Hochleitner[2], Wolfgang W. Schmahl[2,3], Konstantin Karaghiosoff[1], and Thomas Bräuniger[1,*]

[1]Department of Chemistry, University of Munich (LMU), Butenandtstrasse 5-13, 81377 Munich, Germany
[2]Mineralogical State Collection Munich (SNSB), Theresienstrasse 41, 80333 Munich, Germany
[3]Department of Earth and Environmental Sciences, Section Crystallography, University of Munich (LMU), Theresienstrasse 41, 80333 Munich, Germany

Abstract

In this paper, we discuss information on crystal structure and morphology available from nuclear magnetic resonance (NMR) spectroscopy of ^{207}Pb for the mineral family $[Pb(4f)]_2[Pb(6h)]_3(AO_4)_3Cl$ with A = V (vanadinite), P (pyromorphite), and As (mimetite). The isotropic chemical shift of the ^{207}Pb atoms at Wyckoff positions 4*f* and 6*h* was (re-)determined from either static single-crystal or magic angle spinning NMR experiments. This isotropic shift can be linearly correlated to the unit-cell volume within the mineral family, and in the wider context of lead-bearing minerals, to the shortest Pb-O distance for position 4*f*, in which ^{207}Pb is solely coordinated by oxygen. By evaluating the number of resonances and their respective line widths in the ^{207}Pb-NMR spectra of these three naturally grown minerals, it could be established that vanadinite forms single-domain macroscopic crystals with very small mosaicity, whereas pyromorphite crystals show NMR characteristics, which can be interpreted as being caused by significant mosaicity. In some instances, this mosaic spread could be quantitatively approximated by a Gaussian distribution with a standard deviation angle of $\sigma = 5°$. In contrast, our mimetite specimen was composed of multiple sub-crystals with a very high variability of orientations, going beyond mere mosaicity effects. By extending the NMR methodology presented here to other minerals, it may be possible to gain new insights about structure-property relationships and the morphology of natural grown minerals.

Keywords: ^{207}Pb-NMR, single-crystal NMR, chemical shift, vanadinite, pyromorphite, mimetite