^{207}Pb NMR of Solid Solutions of Divalent Metal Nitrates

Young-Sik Kye and Gerard S. Harbison*

Department of Chemistry, University of Nebraska at Lincoln, Lincoln, Nebraska 68588-0304

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^{207}Pb NMR spectra of mixed crystals of anhydrous lead and strontium nitrate show up to 13 lines, arising from lead ions with 0−12 Pb^{2+} nearest-neighbor cations replaced by Sr^{2+}. The shifted lines are further split by the multiplicity of inequivalent nearest-neighbor replacements. The average shift per Sr^{2+} ion is 21.8 ppm. Similar but somewhat smaller effects are seen in $[Pb,Ba](NO_3)_2$ mixed crystals. The intensities of the resonances can be fit to Monte Carlo models of Pb^{2+} and Sr^{2+} ion distributions and are consistent with like nearest-neighbor pairs being 120 J/mol lower in energy than unlike pairs.

The anhydrous nitrates[1] of Ba^{2+}, Pb^{2+}, Sr^{2+}, and Ca^{2+} and the cubic crystalline form[2] of $Cd(NO_3)_2$ which is stable above 160 °C are isomorphous and form a continuous set of solid solutions.[3] These crystals share the space group *Pa*3, with the cations in a face-centered cubic (fcc) lattice and the nitrate ions interspersed between them. The unit cell length varies from 0.759 nm at 25 °C for the calcium salt to 0.811 nm for the barium salt. We have previously examined the ^{14}N single-crystal NMR of the pure lead, barium,[4] and strontium[5] salts but were unable to get signals from mixed crystals. Attributing this failure to a distribution of quadrupole coupling constants in the crystal, we undertook a ^{207}Pb NMR study of these materials. ^{207}Pb, being spin $^1/_2$, has no quadrupolar interaction, yet it has a large dispersion of chemical shifts, and its high polarizability makes it a sensitive probe of its environment.

$Pb(NO_3)_2$ itself is widely used as an internal temperature standard in solid-state NMR;[6] its axially symmetric shielding tensor lies by symmetry along the crystallographic 111 direction, and it has a comparatively low anisotropy of around 55 ppm.[7,8] Figure 1a shows a typical magic-angle spinning spectrum[9] of the pure $Pb(NO_3)_2$; the single resonance is flanked by very weak rotational sidebands. Figure 1b shows the ^{207}Pb spectrum of a polycrystalline sample grown from a solution containing, on a molar basis, 40% $Pb(NO_3)_2$ and 60% $Sr(NO_3)_2$. Despite the high solution concentration of strontium, inductively coupled plasma (ICP) analysis of the crystals shows them to be 95.4% Pb and 4.6% Sr. In addition to the lead signal at its usual position, the spectrum shows a weak doublet which is 15.6 and 20.0 ppm more shielded than the signal from pure $Pb(NO_3)_2$. At higher concentrations of strontium, more lines appear. The spectrum in Figure 1c is for a sample containing 76.1% Pb and 23.9% Sr; that in Figure 1d from one with 44.1% Pb and 55.9% Sr.

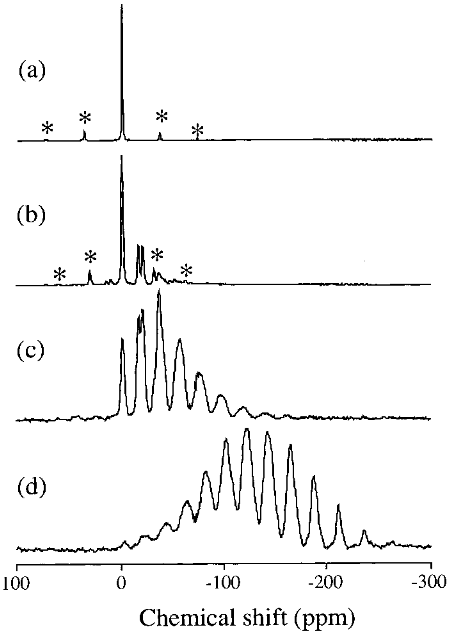

Figure 1. ^{207}Pb MAS NMR spectra of $(Pb,Sr)(NO_3)_2$ solid solutions, containing mole fractions of (a) 0%, (b) 4.6%, (c) 23.9%, and (d) 55.9% strontium. Rotational sidebands are indicated by asterisks.

If the first doublet is counted as a single line, then a total of 13 lines is observed. These 13 lines are seen in Figure 1d, albeit with very weak lines from lead surrounded by 12 other leads $[Pb(Pb_{12}Sr_0)]$ and from lead surrounded by 12 other strontiums $[Pb(Pb_0Sr_{12})]$. Samples resulting from evaporating such solutions to dryness show the full complement of lines even more clearly. However, such materials are highly inhomogeneous; the lower solubility of the lead salt means that crystals with a higher concentration of lead preferentially crystallize first; as lead is removed from solution, material with higher strontium concentrations is sequentially deposited. To avoid such fractionation, our samples were obtained from a large excess of saturated solution, and the solution concentration did not change more than 4% during crystallization.

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(9) Magic-angle spinning spectra were obtained at 63.76 MHz (7.1 T) using a one-pulse sequence. The ^{207}Pb $\pi/2$ pulse was 4.1 μs with recovery delays of 8 s. Spectra were obtained at spinning frequencies between 1.9 and 2.1 kHz. Mixed-crystal spectra were recorded with and without a small admixture of pure lead nitrate to account for any temperature differences between samples.

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The 13 resonances clearly derive from replacement of lead by strontium in the 12 nearest-neighbor cationic positions of the fcc unit. That nearest-neighbor effects dominate is shown by the invariance of the position of the $Pb(Pb_{12}Sr_0)$ line; it shifts by less than 5 ppm overall, even in crystals with a high mole fraction of strontium. Thus, more distant neighbors contribute very little to the shift. We attribute the splitting of the $Pb(Pb_{11}Sr_1)$ line to orientational inequivalence of the nearest neighbors with respect to the unique 111 axis. Six of these neighbors form a hexagon in the plane perpendicular to 111, and six form a distorted octahedron with 3-fold rotational symmetry about that axis. The shielding tensors of the two components of the doublet are very different, reflecting this orientational inequivalence. Resolved splittings are not observed for the $Pb(Pb_{10}Sr_2)$ line or those with more strontium; there is, however, a pronounced increase in inhomogeneous line width toward the middle of the series, indicating a multiplicity of different arrangements of ions into the two types of sites. The lines narrow again at high strontium concentrations, with the $Pb(Pb_0Sr_{12})$ line being especially narrow. The magnitude of the shift is 17.8 ppm/additional strontium ion at low strontium concentrations, increasing to 23.3 ppm/strontium at high concentrations.

The resolution of distinct resonances from lead ions with different nearest-neighbor compositions allows a microenergetic analysis of solid-solution formation because, for crystals of any given composition, we can determine the exact number of neighbors of each type. An analysis of the peak intensities shows a significant deviation from a random statistical distribution, indicating that the lead and strontium ions are weakly clustered in the crystal; Monte Carlo calculations of the intensities yield a nearest-neighbor pair energy for unlike pairs 120 J/mol higher than that of like pairs. Measurement of the lattice parameter of the solid solution as a function of composition (Figure 2)[10] confirms the nonideality of the solutions. Interestingly, however, the slight observed concave deviation from the linear dependence expected from Vegard's law for a perfect solid solution[11] is usually interpreted as evidence for favorable interactions between *unlike* ions, contrary to the NMR results which show clustering of *like* ions.

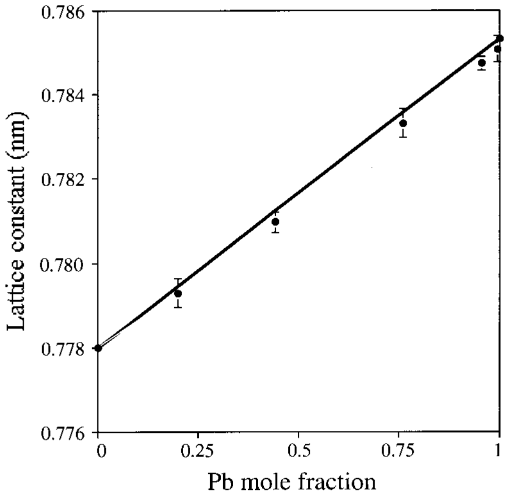

Figure 2. Lattice constant of $(Pb,Sr)(NO_3)_2$ solid solutions versus Pb mole fraction obtained by powder diffraction measurements as described in the text. Error bars are standard deviations calculated from all observable reflections. The straight line denotes the Vegard's law behavior for a perfect solid solution.

What is the origin of the shift? Pb^{2+} ions are slightly larger than Sr^{2+} ions, but it is unlikely that the size difference itself is the origin for the phenomenon. Preliminary data for $(Pb,Ba)(NO_3)_2$ solid solutions show a shift of identical sign to that seen for $(Pb,Sr)(NO_3)_2$ but of somewhat smaller magnitude,[12] yet Pb^{2+} is smaller, not larger, than Ba^{2+}. It is more likely, therefore, that the effect originates in polarizability differences. However, regardless of its origin, it provides an opportunity to conduct measurements on the microenergetics of solid solutions in these and similar systems.

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(10) X-ray powder diffractograms were obtained using Cu Kα radiation on a Rigaku D-Max/B diffractometer at a temperature of 25 °C, using 99.999% crystalline silicon as an internal standard. Elemental analysis of the crystals were obtained by inductively coupled plasma atomic emission spectrometry and have a reproducibility of ±0.8%.

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