

Solid-State ^{207}Pb CP-MAS NMR of Lead(II) Compounds for the Structural Study of Molecular Routes to Lead-Based Perovskite-Phase Materials

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Crystalline, perovskite-phase metal oxide materials ABO_3 such as PbTiO_3 , PbZrO_3 , and $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ exhibit a variety of interesting properties such as ferroelectric, pyroelectric, and piezoelectric behavior.^{4–8} In order to take advantage of these properties, it is often necessary to develop low-temperature (<400 °C) synthetic routes to crystalline thin films. The preparation of these materials generally involves thermal decomposition of metal–organic lead, titanium, and zirconium compounds.^{8–11} However, these metal oxides are polymorphic and can crystallize in either the pyrochlore or perovskite phases.¹² The formation of the pyrochlore phase is undesirable because it does not exhibit the properties mentioned above. As with many metal–organic routes to solid-state inorganic materials, it is difficult to follow the structural evolution during thermal decomposition and the subsequent development of the final crystalline phase. Many studies have been focused on the control of stoichiometry and homogeneity, but there are few studies of the control of phase behavior in polymorphic systems. The polymorphic nature of the ABO_3 phase provides an opportunity to investigate such behavior.

We recently observed that lead α -hydroxy carboxylate compounds such as $\text{Pb}(\text{O}_2\text{CCR}_2\text{OH})_2$ react with Ti(IV) and Zr(IV) alkoxide compounds to form an intermediate which on thermolysis at 350 °C yields crystalline perovskite-phase ABO_3 .^{13–15} In order to better understand the phase behavior, we have sought techniques to follow structural changes during the amorphous to crystalline phase transition. Solid-state NMR spectroscopy can complement information obtained from other techniques (e.g. X-ray crystallography) and can provide structural information under circumstances in which other techniques are not effective, as is often the case in the characterization of amorphous materials.

Solid-state ^{207}Pb NMR spectroscopy utilizing both cross-polarization and magic angle spinning techniques is a promising method for characterizing metal–organic lead compounds in the solid state.^{16–18} Much of the work to date has focused on

compounds containing lead–carbon bonds,^{18–21} and there have been only three studies of compounds in which lead chelates through oxygen.^{22–24} A review by Wrackmeyer and Horchler²⁵ predicted that this technique would be widely used for characterization of lead-containing materials in the solid state. However, since this review, few studies utilizing solid-state ^{207}Pb NMR spectroscopy have been published as a result of the difficulty in obtaining high-quality spectra. There are two reasons for this: (1) the chemical shift range is large, and there are insufficient data available to enable prediction of chemical shifts in many cases; (2) the relaxation mechanism is poorly understood, so the proper instrumental parameters are not known. In this paper, we address these problems via preliminary results of a study of the solid-state ^{207}Pb NMR data for crystalline $\text{Pb}(\text{O}_2\text{CCR}_2\text{OH})_2$ compounds, crystalline perovskite-phase PbMO_3 ($\text{M} = \text{Ti}, \text{Zr}$), and an amorphous PbTiO_3 precursor and proton T_1 relaxation times to investigate the potential of this technique to follow solid-state structural changes.

The solid-state ^{207}Pb CP-MAS NMR results are given in Table 1 and were measured in crystalline samples as determined by X-ray diffraction, except in the case of the PbTiO_3 precursor, which is amorphous.²⁶ The solid-state ^{2107}Pb NMR spectrum of $\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2$ displays a single center band at –2031 ppm, about 67 ppm upfield (to lower frequency) of the value obtained in D_2O solution. All of the lead carboxylates and glycolates studied gave δ values more negative than their solution values, by 50–600 ppm. The observation of a single center band for $\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2$ is consistent with the single-crystal X-ray diffraction data, which indicate a single crystallographic Pb site

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- (26) Solid-state ^{207}Pb NMR spectra were obtained on a Chemagnetics console interfaced to a General Electric 1280 data station and pulse programmer and a wide-bore 4.7-T magnet (199.6 MHz for ^1H) constructed by Nalorac Cryogenics. Chemical shifts are reported vs tetramethyllead, with positive shifts to higher frequency. Chemical shifts were calibrated by substitution of an external secondary standard (1.0 M aqueous $\text{Pb}(\text{NO}_3)_2$, $\delta = -2961.2$ ppm vs PbMe_4). Spectral width was 100 kHz, and the spectrometer frequency was varied from 41.58 to 41.78 MHz to observe the chemical shift range from +1400 to –5500 ppm vs tetramethyllead. Samples were packed into 7.5 mm o.d. zirconia rotors and spun about the magic angle. Center bands were identified by varying the spinning rate over the range 2000–6000 Hz. Tetraphenyllead was used for initial setup and optimization of cross-polarization parameters. Proton T_1 relaxation times were measured by the pulse saturation technique while the ^{207}Pb cross-polarization signal was observed, and ^1H – ^{207}Pb cross-relaxation times were determined by varying the CP contact time from 1 to 40 ms. ^{207}Pb T_1 relaxation times were determined by pulse saturation using direct polarization. The results of these measurements were used to optimize the CP contact time and recycle delay for each sample. Typical optimum values of CP contact time were 3–10 ms, while recycle delays ranged from 3 s for lead(II) acetate and lead(II) dimethylglycolate to 40 s for lead(II) glycolate. Spectra were obtained in 64–512 acquisitions although a larger number of acquisitions was occasionally used (up to 48 000) to improve the signal to noise ratio.

Table 1. Solid-State ^{207}Pb NMR Results

compound	δ (ppm)	$^1\text{H } T_1$ (s)	$T_{\text{H-Pb}}$ (ms)
$\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2$	-2031	24 ± 2	2.2 ± 0.07
$\text{Pb}(\text{O}_2\text{CCH}_3)_2 \cdot 3\text{H}_2\text{O}$	-1897	0.56 ± 0.09	1.6 ± 0.46
$\text{Pb}(\text{O}_2\text{CC}(\text{CH}_3)_2\text{OH})_2$	-1177		6.2 ± 1.7
	-2077	0.2 ± 0.1	4.0 ± 0.5
	-2623		4.8 ± 1.1
$\text{Pb}(\text{C}_6\text{H}_5)_4$	-136	199 ± 10	1.5 ± 0.15
	PbZrO_3	-1000	<i>a</i>
PbTiO_3	-1340	<i>a</i>	<i>a</i>
	-1408	<i>a</i>	<i>a</i>
$[\text{Pb}(\text{O}_2\text{CCMe}_2\text{O})_2\text{Ti}(\text{O}-i\text{-Pr})_2]_n$	-1500	1.1 ± 0.1	<i>b</i>

^a Cross polarization not used. ^b Not measured.

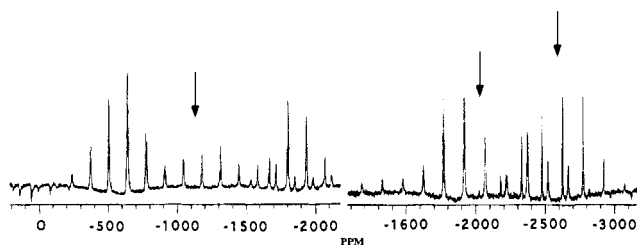


Figure 1. Solid-state CP-MAS ^{207}Pb NMR spectrum of $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ showing the three chemically inequivalent isotropic resonances (arrows) in a 2:2:1 ratio.

in this compound (see supplementary material).¹⁵ For comparison, the ^{207}Pb CP-MAS spectrum of lead(II) acetate trihydrate also exhibits a single center band with ~ 50 -kHz shielding anisotropy, consistent with the X-ray diffraction data. The chemical shift of this center band is -1897 ppm, compared with -1337 ppm for a 1 M aqueous solution and -1521 ppm for a 1 M solution in glacial acetic acid.

The solid-state ^{207}Pb NMR spectrum of $\text{Pb}(\text{O}_2\text{CC}(\text{CH}_3)_2\text{OH})_2$ displays three center bands at -1177 , -2077 , and -2623 ppm; see Figure 1. These center bands give total integrated intensities (center band + associated sidebands) in the ratio 1.96:2.00:1.04, respectively. X-ray data for this compound indicate three chemically distinct lead sites in a ratio of 2:2:1 (see supplementary material). From the integrated intensities, we can assign the NMR center band at -2623 ppm to the central lead atom, but the other two resonances cannot be assigned on the basis of their integrated area. We propose that the high-field shift of the central lead atom is consistent with the apparent absence of a stereochemically active lone pair. In contrast, $\text{Pb}(2)$ and $\text{Pb}(3)$ both exhibit coordination environments which can accommodate stereochemically active lone pairs. It is interesting to note that there is little difference in the coordination environments of $\text{Pb}(2)$ and $\text{Pb}(3)$, yet they exhibit a chemical shift difference of approximately 1000 ppm. In contrast, the same compound dissolved in aqueous solution exhibits a single ^{207}Pb NMR chemical shift at -1875 ppm, presumably as a result of disruption of the hydrogen-bonded solid-state structure.

The relaxation time data in Table 1 correlate well with the known structural features of these compounds. The $^1\text{H } T_1$ was measured by observing the changes in intensity of the ^{13}C cross-polarization spectra as a function of delay time. Solid-state ^1H NMR spectra were not observed directly, although the solution data have been reported.¹³ The trend in proton T_1 relaxation times follows the degree of flexibility of the proton-containing parts of the molecule. The methylene groups in $\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2$ are unable to rotate, which leads to a relatively long (24 s) $^1\text{H } T_1$ value. In contrast, both $\text{Pb}(\text{O}_2\text{CC}(\text{CH}_3)_2\text{OH})_2$ and $\text{Pb}(\text{O}_2\text{CCH}_3)_2 \cdot 3\text{H}_2\text{O}$ contain methyl groups which are free to rotate, thus lowering the proton T_1 values by 2 orders of magnitude.

The ^1H - ^{207}Pb cross-relaxation times give an indication of the distance through space between the lead nucleus and the cross-polarizing protons. Our values indicate that the proton-to-lead distances increase in the order acetate < glycolate < dimeth-

ylglycolate. It was hoped that these values might allow for unambiguous distinction between the two unassigned ^{207}Pb chemical shifts in the solid-state spectrum of $\text{Pb}(\text{O}_2\text{CC}(\text{CH}_3)_2\text{OH})_2$. However, there are only small differences in the nonbonded $\text{Pb}(2)\text{---H}$ and $\text{Pb}(3)\text{---H}$ distances, so further interpretation within the limits of error on the data are inappropriate.

Crystalline perovskite PbZrO_3 gives rise to two ^{207}Pb NMR resonances at -1000 and -1340 ppm corresponding to the two chemically inequivalent lead environments observed crystallographically.²⁷ Estimation of the peak heights of the two resonances and their associated spinning sidebands showed equal relative intensities, consistent with the crystallographic data. Crystalline PbTiO_3 gives rise to one ^{207}Pb NMR resonance at -1408 ppm, consistent with the single chemical environment expected for tetragonal PbTiO_3 .

To investigate whether it is possible to observe an amorphous intermediate in the formation of PbTiO_3 according to the strategy outlined above,¹³⁻¹⁵ the intermediate derived from the reaction between $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ and $\text{Ti}(\text{O}-i\text{-Pr})_4$ was studied. The characterization data for this species has been described elsewhere.¹³ A single resonance was observed at -1500 ppm, close to the value observed for crystalline PbTiO_3 . The intensity of the signal for the lead precursor, relative to other crystalline materials studied, showed that this resonance was representative of the bulk of the material. This similarity may indicate the presence of similar coordination environments in the precursor and PbTiO_3 , which could account for the observed low crystallization temperature of the precursor. It is not possible to assign coordination environment as a function of ^{207}Pb chemical shift at this stage, because a larger data base which correlates ^{207}Pb chemical shift with coordination environment in compounds that have been structurally characterized is required. However, these data show that solid-state ^{207}Pb NMR spectroscopy is a sensitive technique for the investigation of lead coordination environment. The use of solid-state ^{113}Cd NMR for the distinction of structural isomers of a crystalline cadmium thiolate compound was recently reported.²⁸ Furthermore, this technique could be a valuable supplement to X-ray crystallographic data for the characterization of crystalline solid-state compounds and could be crucial for the characterization of the lead environment in amorphous materials. We have demonstrated that it is possible to observe solid-state ^{207}Pb NMR data for amorphous materials and that the ^1H - ^{207}Pb cross relaxation times provide structural information. However, we find that it is harder to obtain high-quality ^{207}Pb NMR data for samples that do not contain H than we had expected on the basis of literature data.

Further studies are in progress to determine the utility of this technique for structural elucidation during amorphous to crystalline transitions in lead-based perovskite-phase metal oxide systems.

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Supplementary Material Available: Figures showing the local Pb coordination environment in $\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2$ and $\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2$ based on X-ray crystallographic data (2 pages). Ordering information is given on any current masthead page.

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