



Temperature calibration for high-temperature MAS NMR to 913 K: ^{63}Cu MAS NMR of CuBr and CuI, and ^{23}Na MAS NMR of NaNbO_3

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ABSTRACT

The solid-state phase transitions of CuBr, CuI and NaNbO_3 can be readily observed using ^{63}Cu and ^{23}Na high-temperature magic-angle spinning nuclear magnetic resonance spectroscopy. Temperature has large, linear effects on the peak maximum of ^{63}Cu in each solid phase of CuBr and CuI, and there is large jump in shift across each phase transition. The ^{23}Na MAS NMR peak intensities and the line widths in NaNbO_3 also clearly show its high-temperature transition to the cubic phase. These data can be used to calibrate high-temperature MAS NMR probes up to 913 K, which is two hundred degrees higher than the commonly-used temperature calibration based on the chemical shift of ^{207}Pb in $\text{Pb}(\text{NO}_3)_2$.

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1. Introduction

High-temperature (here meaning temperatures above about 250 °C, where conventional organic polymer components become unstable), magic-angle spinning (MAS) NMR is a very useful technique to directly observe structural changes and dynamics in solids and in highly viscous glass-forming liquids, including cation and anion site exchange and phase transitions [1–12]. Accurate determination of sample temperature in any high-temperature (high T) NMR probe can be difficult because of electronic effects of locating a thermocouple in or adjacent to the RF coil [13]; temperature measurement is especially challenging in MAS probes because of the rapid rates of bearing and drive gas flow around the sample rotor, the likelihood of large thermal gradients that may depend on spinning rate [14], and sample heating through high-speed spinning [14–16]. Temperatures are generally based on one or more sensors located “upstream” and/or “downstream” of the sample in the gas flow path, but these readings must be calibrated. Although in some cases a test thermocouple can actually be inserted into a spinning MAS rotor [3], such calibrations usually are based on observing spectra of materials that go through solid–solid or solid–liquid phase transitions, including organic compounds at relatively low temperatures and inorganic phases at higher temperatures, e.g. of LiNaSO_4 at 791 K [6,17] and RbNO_3 at 446 K [6]. These have led to the development of secondary NMR “thermometers” based on the calibrated effects of temperature on chemical shifts such as for ^{207}Pb in $\text{Pb}(\text{NO}_3)_2$ [1,16] and somewhat less convenient contact shifts for ^{119}Sn in magnetic Pr and Sm stannates [6]. However, the commonly-used $\text{Pb}(\text{NO}_3)_2$ begins to decompose above about 720 K, suggesting the need for other, more refractory reference materials to reach the

maximum temperatures of modern high-T MAS probes, presently about 970 K. Ideally, such phases should have narrow, rapidly-observable NMR lines, large temperature effects on spectra, and at least short-term chemical stability in the neutral to reducing atmosphere generally present in such probes.

Early static (non-MAS) NMR studies of ^{63}Cu , ^{81}Br , and ^{127}I in CuBr and CuI showed large chemical shift changes with temperature [18,19]. Both compounds are diamagnetic and have three different solid phases with transformations between about 600 and 800 K: they are cubic at low temperature (eliminating quadrupolar line broadening and shift), change to a hexagonal structure at intermediate temperature, and then change back to cubic at higher temperature [18]. ^{63}Cu and ^{65}Cu MAS NMR data at room temperature for CuCl, CuBr, and CuI have been reported [20], as well as ^{63}Cu MAS NMR spectra for cuprous mixed halide solid solutions [21,22]. NaNbO_3 has orthorhombic symmetry at room temperature [23–25], and several structural transitions with increasing temperature. The ^{23}Na NMR relaxation rate shows large changes through the dynamic tetragonal to cubic phase transition at 913 K [24]. ^{63}Cu and ^{23}Na (both spin=3/2) have high natural abundances and conveniently high Larmor frequencies. We have thus used MAS NMR of these nuclides to observe the solid–solid phase transitions of CuBr, CuI, and NaNbO_3 and have applied these data to calibrate the sample temperature in a high-T MAS probe. We have also refined the temperature effects on the ^{63}Cu chemical shifts, which should be useful for temperature calibrations away from the transition temperatures.

2. Experimental

^{63}Cu and ^{23}Na MAS NMR spectra were collected on a Varian 14.1T spectrometer with a high-temperature MAS probe (Doty

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Scientific, Inc., Columbia, SC) at a spinning rate of 4 kHz at room temperature, and 5 kHz above 373 K. The samples were packed in 7 mm Si₃N₄ rotors with BN liners. Dry N₂ gas (liquid nitrogen source) was used for both rotor bearing and drive to prevent oxidation of the probe, rotor, and samples. Reagents were purchased from Alfa Aesar: copper(I) bromide, 98%; copper(I) iodide, 99.999% (metals basis); and sodium niobium oxide, 99.997% (metals basis). Prior to the NMR experiments the samples were tested for compatibility with the rotor liners by heating in BN capsules in an argon atmosphere in a tube furnace: no obvious interactions were observed other than some darkening of the originally white colors at temperatures below the melting points. The CuBr and CuI used for high-T MAS NMR were dried in argon at 473 K for 12 h; for the latter, the drying shifted the resonance significantly and narrowed it considerably. During high-T MAS NMR measurements, CuBr was heated to 742 K; CuI was heated to 818 K; and NaNbO₃ was heated to 926 K. Comparing the weights of the sample before and after these experiments, the CuBr lost 1.8 wt%, the CuI weight changed by less than 0.1 wt%, and the NaNbO₃ lost 0.9 wt%, indicating minimal decomposition or reduction by the BN rotor. ²³Na MAS NMR spectra were collected at 158.63 MHz with a recycle delay of 0.3 s and a radio frequency pulse length of 0.8 μs, which is a tip angle of π/10 for the liquid standard NaCl solution. ²³Na chemical shifts are reported relative to a 1.0 M NaCl solution at 0 ppm. ⁶³Cu MAS NMR spectra were collected at 158.94 MHz with a recycle delay of 0.5 s and a radio frequency pulse length of 0.8 μs, and are referenced to the room temperature peak maxima of cubic CuBr and CuI, respectively. The room temperature chemical shift of CuBr is at –58 ppm relative to that of CuI, consistent with an earlier ⁶³Cu MAS NMR study [20]. The latter also reported the chemical shift of CuCl (also used as a reference) as –2.8 ppm relative to CuI. Multiple spectra were collected at each temperature to check if the sample reached equilibrium, and the data were collected on cooling as well as on heating. 1000 acquisitions were required for each ²³Na spectrum and 400 acquisitions for ⁶³Cu, giving total acquisition times of 3–5 min. To test the calibration at relatively low temperatures, ²⁰⁷Pb MAS NMR spectra were measured for Pb(NO₃)₂ as in the previous ²⁰⁷Pb chemical shift thermometer study [1]. “Display temperatures” described below are based on the average of the values measured by thermocouples “upstream” and “downstream” of the rotor in the gas flow pathway, as corrected by the software supplied by the manufacturer of the probe. The manufacturer calibrated the “display temperatures” by inserting a thermocouple into the high-T probe without a spinning rotor (G. Entzminger, Doty Scientific, personal communication).

In principle, the melting points of CuI (878 K) and CuBr (771 K) could also be useful for temperature calibration, but we did not attempt to observe these by high-temperature MAS NMR because of concerns about rotor stability and, more fundamentally, the potential for changes in the melting point with small changes in Cu oxidation state or the Cu/halide ratios induced by volatilization in an unsealed rotor. Similar concerns may also apply to other potential melting point standards near the high end of the typical MAS NMR range, such as ²³Na spectra of Na₂Mo₂O₇ (*mp* = 960 K), ²³Na in NaWO₄ (971 K) and ²³Na and ⁵¹V in NaVO₃ (903 K).

3. Results and discussion

3.1. Temperature calibration

A calibration for the probe “display temperature” was developed from the ²⁰⁷Pb chemical shift for Pb(NO₃)₂ below about 673 K [1], combined with the known phase transition

temperatures of CuBr, CuI, and NaNbO₃. The phase transitions of the cuprous halides were observed by the changes in ⁶³Cu MAS NMR spectra (Figs. 1 and 2). As detailed below, each spectrum contains a single, narrow peak (except for the CuI β phase), for which the width (FWHM) ranges from 2 to 8 ppm at different temperatures. The ²³Na MAS NMR spectrum of NaNbO₃ also contains a single, narrow peak. The peak is asymmetrical at lower temperatures, as it contains signals from two different sodium sites [25], but becomes more symmetrical as temperature increases. The NaNbO₃ phase transition was clearly identified by the changes of linewidth and central peak/side band intensity ratios over temperature ranges of < 5 K. The actual sample temperatures are plotted against the display temperatures, including ²⁰⁷Pb chemical shift calibrated temperatures (Fig. 3). The data were least-squares fitted to a second order polynomial

$$T = 7.909 + 1.032T_D - 9.06 \times 10^{-5}T_D^2 \quad (1)$$

where *T* is the actual sample temperature (K) with uncertainty of ± 5 K, and *T_D* is the display temperature. This relationship is of course specific to this probe and the experimental conditions, especially the spinning rate, but can give some idea of corrections that may be needed more generally. Divergence from the displayed readings was large (> 10 K) only above about 650 K.

It is interesting to note the spinning speed effect on sample temperature. ⁶³Cu MAS NMR were also collected on a Varian 14.1T spectrometer at 192.4 MHz using a Varian/Chemagnetics T3 probe with 3.2 mm zirconia rotors spinning at 20 and 4 kHz for both heat-treated CuBr and CuI, respectively. The peak maxima shift down about 4.3 ppm for CuBr and 6.6 ppm for CuI when the spinning speed increased from 4 to 20 kHz, respectively. According to the chemical shift and temperature correlations given below, this corresponds to an increase in the sample temperature of about 25 K, consistent with previous studies of such effects in MAS NMR [14–16].

3.2. CuBr

⁶³Cu MAS NMR spectra for cuprous bromide were measured from room temperature to 742 K, where the β–α phase transition occurs (Fig. 1). The peak maximum at room temperature was used as the reference (0 ppm). For the low temperature γ phase, which has cubic point symmetry at the Cu position, peak maxima should correspond to the isotropic chemical shifts. The peak shifts to lower frequency with increasing temperature, and shows a linear relationship with temperature in each phase. This agrees with a previous static NMR study [18] of CuBr for the γ phase, but not for the β phase. Unlike the α and γ phases, β-CuBr has a non-cubic würtzite structure. The shift reported in the previous static ⁶³Cu NMR study at 13 MHz was “the position of the most pronounced maximum of the absorption signal line shape”, and thus was shifted from the true chemical shift by quadrupolar interactions. Data collected here are at much higher frequency (159 MHz) with additional line-narrowing by MAS. Therefore, the peak maxima reported should be much closer to the true chemical shift. The peak width (FWHM) is about 4.8 ppm at room temperature. This decreases with increase in temperature and narrows down to 2.1 ppm at 476 K, then starts to increase with temperature until the first phase transition, possibly due to relaxation effects. The FWHM is almost constant in the β phase (6.6 ppm), and increases to 8.2 ppm at the β–α phase transition. As noted above, the large changes in frequency of the peak maximum from one phase to another help us to identify the actual sample temperatures to within about 5 K (e.g. the phase transition of γ→β happens between 661 and 666 K). The data for γ and β phases

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