SIZE EFFECTS IN THE NMR OF SnO₂ POWDERS

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ABSTRACT

Using tin dioxide powders obtained from different thermal treatments, we investigated the effects of powder granule size on parameters such as chemical shift, linewidth, and spin-lattice relaxation, via magic-angle spinning (MAS) room temperature nuclear magnetic resonance (NMR) on the ¹¹⁹Sn nucleus. Mean size, as determined by the Scherrer formula applied to the X-ray diffraction data, varied from 4 to 32 nm. We compared the properties of the ¹¹⁹Sn power samples with normal 10 µm cassiterite SnO₂ bulk properties. Linewidth showed a general broadening as size decreased, but there was evidence in the anisotropy of the chemical shift, and in the spin-lattice relaxation, of a size-dependence effect. The largest modification in bulk properties occurred at about 8 nm. We discuss the correlation between anisotropy and spin-lattice relaxation in relation to the change of vibrational modes, as observed by Raman spectroscopy, as particle size decreases. © 2000 Elsevier Science Ltd

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INTRODUCTION

Tin dioxide is a semiconductor, which in its as-grown state typically is n-type. For application as a gas sensor [1], it is formed as a ceramic. It is thought that it is the surface resistance of the granules forming the ceramic that controls the overall resistance of the sensor; this resistance is the parameter that changes in the presence of gas. Since the surface plays such an important role, we thought it useful to assess the value of the nuclear magnetic resonance (NMR) technique in probing surface states in such powders, by looking at the NMR parameters of a series of samples with powder sizes varying from 4 to 32 nm. In this paper, the $^{119}$Sn NMR data collected is compared with data for standard bulk cassiterite SnO$_2$ (~10 μm) powder.

EXPERIMENTAL

An 8.7876 g sample of SnCl$_2$·5H$_2$O was dissolved in 100 ml of deionized water. This was then mixed with a nitrate solution in the molar ratio 1:1 to obtain a transparent solution. The transparent solution was then heated at 150°C for 12 h in a Teflon vessel and cooled to room temperature. A white SnO$_2$ powder comprised of nanometer-sized particles was thus obtained. The powder was sintered at 200, 400, 600, and 800°C for 6 h. The particle size ($t$) was determined from powder X-ray diffraction data, using Scherrer’s equation:

$$ t = \frac{(0.9\lambda)}{(\beta\cos\theta)} $$

where \(\lambda\) is the wavelength of the copper K\(\alpha\) radiation, \(\beta\) is the full-width at half-maximum (FWHM) of the X-ray line, and \(\theta\) is Bragg’s diffraction angle for the line. Figure 1 shows the relation between sintering temperature and average particle size in a powder sample.

The NMR experiments were undertaken on an MSL 500 Bruker spectrometer, at a field of 11.75 T, using spinning speeds of about 6 kHz, and at a resonance frequency of 186.5 MHz. Static NMR linewidths of about 10 kHz break up under MAS into several sidebands, and it is the amplitude, width, and position of these sidebands that provide the raw data for analysis. We restricted our analysis to data on the central feature and on the ±1 and ±2 sideband.
orders; outside this range, the sidebands were very weak and the excitation radio frequency pulses would have had to be narrower, and the acquisition times much longer, to give accurate values of amplitudes. Spin-lattice relaxation times, $T_1$, were measured by the saturation recovery method, with a comb of 20 pulses providing the initial saturation, followed by a variable delay of up to 50 s and an observation pulse. The saturation was effective in reducing the nuclear polarization to zero, and the observation pulse was kept reasonably narrow, to ensure uniform spectral coverage. The recovery of the central transition was monitored to provide values of $T_1$, and the recoveries were well described by single exponentials.

RESULTS AND DISCUSSION

The X-ray diffraction data are shown in Figure 2. In comparison with the X-ray data on similar powders by Shek et al. [2], our data revealed a steady broadening of standard tetragonal structure peaks as size diminished, with an apparent split developing in the $2\theta = 27^\circ$ peak for the 5 and 4 nm samples. This may be evidence that the samples with the smallest particles show a tendency to become orthorhombic [2].

A series of Raman spectra are shown in Figure 3. There is a clear progression from domination by bulk phonon modes $A_1$, $A_2$, and $A_3$ in the samples with larger particles to domination by surface modes $B_1$ in the samples with smaller particles. The 8 nm sample is situated at the transition from bulk-dominated to surface-dominated. Again, the bulk peaks, while weakening as particle size diminishes, also broaden, rather like the X-ray diffraction patterns (Fig. 2). The Raman spectra were taken using a Renishaw-2000 He–Ne laser.

The NMR chemical shifts of bulk SnO$_2$ cassiterite are well-known. Clayden et al. [3] used graphical analysis of the sideband pattern [4] of magic-angle spinning (MAS) NMR to
establish values of $-560, -560, -685,$ and $-604.3$ ppm as the chemical shift components of $^{119}\text{Sn}$ for $\delta_{11}, \delta_{22}, \delta_{33},$ and $\delta_{\text{iso}}$, respectively. In a more detailed study at higher magnetic fields, Cossement et al. [5] produced values of $-550, -573, -686,$ and $-603$ ppm for the same parameters. The deviation from the tetrahedral symmetry of the crystal was explained on a first-, second-, and third-nearest neighbor model of the interactions that generate the chemical shifts at the central site. For comparison, the Cossement et al. [5] also analyzed the shifts in SnO and other compounds, showing that Sn exhibits a large range of shifts in different compounds, and that, in particular, SnO exhibits a very much greater anisotropy and a very different isotropic chemical shift, compared to SnO$_2$. Indeed, Clayden et al. [3] had already shown significant variation of $^{119}\text{Sn}$ shifts over a large range of solid tin compounds. From these two studies, it seems that the three contributing factors in the determination of on-site chemical shifts are (i) the valence charge density on the central tin nucleus, (ii) the immediate oxygen environment of that nucleus, and, more weakly, (iii) the arrangement of more distant neighbors around it. $^{119}\text{Sn}$ and $^{117}\text{Sn}$ exhibit dilute nuclei due to their low abundance, thus dipolar broadening is small. Neither Clayden et al. [3] nor Cossement et al. [5] note any distorting effects from dipolar interactions, and, given that our measurements were undertaken at higher magnetic fields, we can safely ignore dipolar distortions to the relative sideband intensities.

Figure 4 shows typical NMR spectra from two of the samples over the frequency range encompassing the two pairs of sidebands that were used in the subsequent analysis to deduce tensor components of the chemical shift. Apart from the much larger widths and the detailed variation of the amplitudes of the sidebands, these spectra are not dissimilar to those displayed in refs. 3 and 5. Figure 5 shows these NMR linewidth data as a function of mean particle size, demonstrating a steady broadening as size diminishes, rather similar again to the
X-ray diffraction broadening (Fig. 2). The linewidths quoted here are of the central MAS-NMR response forming part of the pattern of spinning sidebands and as such should represent the developing inhomogeneity of shift in our samples as size decreases. We had hoped at the outset for some sign of a separating “surface” tin signal, which, given the known dispersion of tin shifts, would have split-off from the bulk signal. In $^{195}$Pt metal dispersions, such separate contributions are identifiable [6]. We observed, however, only a steady broadening. The amount of broadening of the NMR signal shown in Figure 5 correlates rather well with the broadening of the dominant $A_2$ peak (Fig. 3) in the Raman spectra.

Figure 6 shows the chemical shift data analyzed through ratios of sideband amplitudes and use of graphical analysis, one of the techniques used by earlier studies on SnO$_2$ [3,5]. The 10 μm data in this graph are from ref. 3. Isotropic shifts appear to show little dependence on particle size. But the individual components of the chemical shift tensor, $\delta_{11}$, $\delta_{22}$, and $\delta_{33}$, show some size dependence. Perhaps the most significant is the size dependence of $\delta_{22}$, which is larger in the bulk 10 μm particles, and shows a minimum at the 8 nm size. It may be, therefore, that the surface structures show isotropic chemical shifts that are unchanged from isotropic shifts in bulk structures. The electron symmetry around tin nuclei changes in the surface, however, to produce this effect on the anisotropy. This trend in the value of the anisotropy may be connected to the observation from X-ray diffraction data of a splitting of the 27° peak for the smallest particle sizes.

The analyzed NMR spectra from the 32 and 5 nm samples, both taken at about 5.7 kHz. The shifts are referenced with respect to tetramethyl tin. Note the substantial rise in linewidth as the particle size diminishes.
The skew parameter measures the symmetry of a chemical shift tensor, ranging in value from $+1$ for a tensor with $\delta_{22} = \delta_{11}$, through 0 when $\delta_{22}$ lies in the middle of the spectrum, and on to $-1$ when $\delta_{22} = \delta_{33}$. In Figure 7, we show the trend in the skew parameter over the particle size range; there is a significant minimum at the 8 nm particle size. The NMR spectrum for the sample with this particle size is noticeably more symmetric in appearance.

Figure 8 charts the behavior of the spin-lattice relaxation time, showing a marked minimum at the 8 nm size. Thus, skew anisotropy of shift appears to be correlated with spin-lattice relaxation rate.

The key elements of behavior in the properties of this series of powder samples, thus, are (i) the appearance of specific surface modes in the Raman spectra; (ii) a marked development
of the inhomogeneity in the sample, as witnessed by the growth of the NMR linewidth and
the broadening of the X-ray linewidths as the size diminishes; (iii) trends in the anisotropy
of shift showing a smooth dip in the skew, the largest at the 8 nm particle size, while the
isotropic shift is relatively independent of particle size; and (iv) trends in the spin-lattice
relaxation rate, with a peak at the 8 nm particle size.

If the spin-lattice relaxation mechanism is, as would be expected, a Raman mechanism [7]
involving vibrations of the lattice coupling to the nucleus via the chemical shift, then the
anisotropy of the shift could be the driving mechanism for spin-lattice relaxation, in spite of
the fact that the isotropic shift is not much changed by the local symmetry changes invoked
by a particular vibration of the lattice. The correlation of the developing skew anisotropy of
shift with relaxation rate would be understandable if the developing difference \( \delta_{22} \) and \( \delta_{11} \)
couples to a particular vibrational mode to create an oscillating magnetic field and, hence, a
relaxation mechanism. It may well be that the surface vibrational modes are important, with
the efficient relaxation of local \(^{119}\text{Sn}\) surface nuclei being communicated to the bulk \(^{119}\text{Sn}\)
nuclei by nuclear spin diffusion. The decrease of relaxation rate for samples with particle sizes below 8 nm would then be linked to the decrease of skew anisotropy in this range of particle sizes, presumably reflecting a further trend in the local valence charge/symmetry as size decreases.

It should be observed also that there is little or no evidence in these NMR studies that the surface states that start to dominate the properties as the particle size decreases bear any resemblance to SnO states. It might be argued that such surface states would show oxygen deficiency and, hence, start to resemble SnO. Given the huge differences in shift characteristics between SnO and SnO$_2$, commented upon earlier, the NMR evidence clearly rules this out.

**CONCLUSION**

We conclude then by noting that the isotropic chemical shift in these nanoparticles is insensitive to the “bulk” to “surface” transition associated with diminishing particle size. In the particular systems studied, a correlation was found between NMR relaxation and skew anisotropy, with the maximum deviation from bulk values occurring at a particle size of 8 nm. This is the region of particle size where, as size diminishes, surface modes start to appear in the vibrational spectra of these materials.

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**REFERENCES**