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Development of ultrahigh field solid state NMR techniques for the elucidation of titanium environments in materials

Although titanium is a component of many technologically important and scientifically interesting materials and there is intense interest in the role it plays in determining the properties of these materials, many of which are chemically or physically disordered, there is only limited information about the local structure. NMR is in principle an ideal microscopic probe of structure being element and site specific. However there have been very few reports of solid state titanium NMR to date. The difficulty in undertaking titanium NMR has been that the two NMR active isotopes have a relatively low natural abundance (~ 6%) and a small magnetic moment so that the signal is small and, most importantly, both isotopes have quite a large quadrupole moment so that in most materials the titanium lines are very broad. The broadening of the titanium line due to the quadrupole interaction is inversely proportional to magnetic field and furthermore the sensitivity increases with field thus the best chance of successfully undertaking titanium NMR is to work at high magnetic field. This project was to investigate the feasibility of using titanium NMR as a microscopic local probe of the titanium environment using a 'state of the art' 14.1 T (600 MHz) NMR spectrometer.

The project has been successful in that during this study we have been able to observe titanium resonances in a large number of different materials and have significantly extended understanding of the sensitivity of the titanium NMR parameters to structure in a number of ways. In the ATiO_3 perovskite and ilmenite compounds (an important group of materials with a framework structure consisting of corner sharing TiO_6 octahedra) we found that although some of these had a relatively large quadrupole coupling constant (up to ~ 16 MHz) and thus a wide line we were able to deduce the NMR parameters. In these compounds the electric field gradient at the titanium site correlated well with the shear strain of the TiO_6 octahedron. Interestingly the electric field gradient for Zn_2TiO_4 , which has an inverse spinel structure, is close to that predicted from the shear strain suggesting that this correlation may be generally useful in titanium compounds. The chemical shift was found to cover a range of ~ 170 ppm becoming more positive as the mean Ti-O distance increased with a slope ~ 2500 ppm/ for the perovskites.

Because the lines are usually too broad to be narrowed by Magic Angle Spinning the lineshape will be affected by chemical shift anisotropy. The effect of this was assessed by synthesising some compounds from isotopically pure material. Typical chemical shift anisotropies were found to be small (~ 50-100 ppm) but sufficient to have a noticeable affect on the NMR parameters deduced from a single field fit to the spectrum.

Attempts were made to determine the effect of titanium coordination on the chemical shift as there is considerable controversy about this coordination in disordered materials. However there are relatively few compounds with well defined TiO_4 sites and these are often very difficult to synthesise. Nevertheless we have succeeded in making some of these. Preliminary data indicate that the shift does seem to be more positive than TiO_6 but only by ~100 ppm which is unlikely to be sufficient to uniquely determine the coordination of titanium via NMR.

One use we have already made of titanium NMR in a practical situation is in a study of a series of nanocrystalline samples of TiO_2 . These are a complex mixture of rutile and anatase (and possibly brookite). As the titanium NMR characteristics of these phases are different the composite spectra can be deconvolved to quantify the amount of each phase present. The inherent direct quantitativity of NMR gives it a distinct advantage compared with XRD in this sort of investigation.

In summary solid state titanium NMR has been shown to be both feasible and useful for investigating materials provided high magnetic field spectrometers are available.