Acta Cryst. (1999). A**55**, 127–132

A study of $Li_2TiOSiO_4$ and $Li_2TiOGeO_4$ by X-ray powder and electron single-crystal diffraction, ^{17}O MAS NMR and O *K*-edge and Ti $L_{2,3}$-edge EELS

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(*Received 3 February 1998; accepted 15 May 1998*)

Dedicated to Professor A. F. Moodie on the occasion of his 75th birthday

Abstract

X-ray powder and electron single-crystal diffraction of crystals of $Li_2TiOSiO_4$ and $Li_2TiOGeO_4$ showed them to be tetragonal, space group *P*4/*nmm* unit-cell parameters $a = 6.4379\,(2)$, $c = 4.40032\,(2)$ Å for $Li_2TiOSiO_4$ and $a = 6.6110\,(8)$, $c = 4.4372\,(6)$ Å for Li_2TiGeO_4. The compounds are isostructural with their sodium analogues but are considerably compressed along the *c* axis owing to the smaller size of lithium compared with sodium atoms. Square-pyramidal TiO_5 groups are joined in these compounds by tetrahedral SiO_4 and GeO_4 groups, respectively. ^{17}O nuclear magnetic resonance spectra of the two compounds, isotopically enriched with ^{17}O, showed peaks due to the apical titanyl, Ti—O, and basal, bridging, Ti—O—Si or Ti—O—Ge, oxygen atoms of the title compounds. By comparison with reference spectra, oxygen *K* edges and titanium $L_{2,3}$ edges of electron energy-loss spectra were tentatively assigned.

1. Introduction

Titanium occurs in fourfold coordination in a number of compounds, in clearly fivefold coordination in the mineral fresnoite $Ba_2TiOSi_2O_7$ and its structural analogues (Masse *et al.*, 1967) but most commonly in octahedral coordination. Distorted octahedral TiO_6 geometries occur in a number of noncentrosymmetric structure types such as $LiNbO_3$, $BaTiO_3$ and $KTiOPO_4$ (KTP) that have important nonlinear optical properties and in centrosymmetric structures such as titanite, $CaTiOSiO_4$.

In the noncentrosymmetric KTP structure, chains of corner-sharing TiO_6 octahedra are cross linked by phosphate tetrahedra. The short Ti—O titanyl bond leads to essentially fivefold coordination of Ti and is the source of the large nonlinear optical coefficient in KTP. In the centrosymmetric titanite, structure chains of corner-sharing TiO_6 octahedra are cross linked by silicate tetrahedra (Speer & Gibbs, 1976; Taylor & Brown, 1976). The displacement of the titanium atom from the geometrical centre of the octahedron results in alternating long (1.974 Å) and short (1.766 Å) Ti—O bonds along the chains of octahedra.

A variety of diffraction and spectroscopic techniques has been used to investigate structure-to-property relationships in such materials. These suggest that the local bonding environment of titanium and oxygen atoms plays a key role in their properties. For example, nonlinear optical properties have been correlated with structure in extremely detailed studies by substitution chemistry (*e.g.* Thomas *et al.*, 1990; Phillips *et al.*, 1990).

Other spectroscopic studies include, for example, titanium *K*-edge near-edge structure (XANES) measurements of a series of Ti-containing model compounds with different titanium coordination numbers (Farges, 1996). Or again, the chemical shift measured from solid-state Si NMR has been found to vary (Balmer *et al.*, 1997) with the structure and local bonding in a series of titanosilicates.

In the present work, we have chosen to combine diffraction techniques, using X-rays and electrons, to obtain bond lengths and geometry with the spectroscopic techniques of electron energy-loss spectroscopy (EELS) and magic angle spinning (MAS) nuclear magnetic resonance (NMR) to obtain information on energy levels and local environment of the titanium and oxygen atoms that play a key role in the important physical properties of titanosilicates.

The titanosilicate we selected to study was $Li_2TiOSiO_4$. This material was chosen for several reasons: Firstly, as is shown below, it contains only two oxygen sites in the asymmetric unit of its unit cell, one O atom being a bridging Ti—O—Si and the other an apical O atom of a TiO_5 tetragonal pyramid. Thus, spectra are simpler to interpret than those of titanite, say, which has four crystallographically inequivalent bridging O atoms or those of KTP which has eight inequivalent bridging O

atoms and two distinct apical O atoms. Secondly, the method of preparation of the title compounds produced well faceted highly perfect crystals that had both reasonable enrichment in the ^{17}O isotope making them suitable for ^{17}O NMR study and very low proton content which allows excellent stability in the electron beam used for CBED and EELS. This requirement of low hydrogen content has been emphasized by A. F. Moodie on many occasions. Thirdly, a chemical substitution study was possible as ^{17}O isotopically enriched crystals of $Li_2TiOGeO_4$ could be prepared and these were found to be isostructural with the Si compound.

The ubiquity of oxygen in many important compounds gives ^{17}O NMR wide-ranging application to solid-state chemistry. For routine observation, ^{17}O NMR requires isotopic enrichment because of its low natural abundance (0.037%). The large isotropic chemical shift range of ^{17}O makes it a very sensitive probe of structure and in a wide range of ABO_3 and A_2BO_3 compounds (B = Ti, Zr, Sn) it was shown that the isotropic chemical shift was largely determined by the B cation. The multiplicity and extent of splitting of the ^{17}O resonances are a reflection of the crystal structure (Bastow, Dirken, Smith & Whitfield, 1996). Recently there have been extensive ^{17}O NMR studies of sol–gel produced oxides, *e.g.* TiO_2 (Bastow *et al.*, 1993) and HfO_2 (Bastow, Smith & Whitfield, 1996). One of the main advantages of NMR is that it is sensitive to short-range structure so that similar information is obtained from both crystalline and amorphous compounds. In TiO_2, both OTi_3 and OTi_4 local environments in the amorphous gel and subsequent conversion of anatase to rutile could be followed. Again, in TiO_2–SiO_2 gel, the formation of Ti—O—Si linkages could be clearly identified (Dirken *et al.*, 1995).

The high resolution that can now be obtained with EELS makes it a powerful technique for probing local environment. Further, the ability to record EELS for both titanium $L_{2,3}$ edge and oxygen K edges makes the technique especially attractive in studying bonding in titanosilicates.

2. Experimental

2.1. *Sample preparation*

SiO_2–TiO_2 mixed gels were prepared by co-hydrolysis by 10 at.% enriched $H_2{}^{17}O$ of an equimolar solution in 2-propanol of titanium *n*-propoxide [$Ti(OPr^n)_4$] and tetraethoxyorthosilicate. An equimolar amount of finely powdered lithium carbonate was added to the gel and the mixture stirred for 24 h and then dried under a current of nitrogen to remove ethanol and 2-propanol. The dry powder mixture was heated in a stream of nitrogen to 1170 K for 24 h. The incompletely reacted product was mixed with an equal mass of lithium chloride and reheated to 1170 K in a stream of nitrogen until the lithium chloride had completely evaporated. The product consisted of a finely crystalline powder which Rietveld analysis of its X-ray powder diffraction pattern showed to consist of $Li_2TiOSiO_4$ with 2% admixture of rutile, TiO_2, and 2% admixture of Li_2SiO_3.

$Li_2TiOGeO_4$ was prepared by hydrolysis, using ^{17}O isotopically enriched water, of a stoichiometric mixture of $Ti(OPr^n)_4$ and $Ge(OEt)_4$ followed by reaction with an equivalent amount of Li_2CO_3 at 1170 K. The incompletely reacted product was reheated with an equal mass of LiCl at 1170 K in a stream of nitrogen until the LiCl had completely evaporated. The product consisted of finely crystalline $Li_2TiOGeO_4$ with some admixture of rutile and lithium germanate. The preparation of $Li_2TiOGeO_4$ has not been reported to our knowledge.

2.2. *Data collection*

X-ray powder diffraction patterns were collected on a Siemens D-500 diffractometer using nickel-filtered Cu $K\alpha$ radiation and a graphite monochromator. The powder diffraction patterns were analysed using the Philips Quasar system for Rietveld analysis. This allowed refinement of unit-cell dimensions but not of atom coordinates.

Selected-area and convergent-beam electron diffraction patterns were recorded on an analytical Jeol 2010 electron microscope with an LaB_6 source. Crushed powders were dispersed with absolute ethanol onto holey-carbon-film-covered copper grids and dried in a vacuum oven before insertion into the microscope

High-resolution electron micrographs (HREM) were recorded on a high-resolution Jeol 4000 EX microscope with an LaB_6 source with a nominal resolution of 1.6 Å.

Electron energy-loss spectra were obtained using a dedicated UHV scanning transmission electron microscope (VG HB501) equipped with a Gatan energy-loss spectrometer (Gatan Imaging Filter model UHV 678). The system uses a cold field-emission source, which allows one to achieve an energy resolution (measured at the full width at half-maximum of the zero-loss peak) of 0.4–0.5 eV.

The MAS NMR experiments were carried out on a Bruker MSL 400 spectrometer (B_0 = 9.4 T) operating at 54.2 MHz for ^{17}O. Oxygen spectra were obtained using a 4 mm double-bearing magic angle probe used with 10–12 kHz spinning speeds, 20 s recycle delay and 1.5 ms pulses (flip angle $\sim \pi/4$). Chemical shifts (δ p.p.m.) were measured in parts per 10^6 from an external reference water at a defined shift, $\delta = 0$.

3. Results and discussion

X-ray powder diffraction shows crystals of both the title compounds to be tetragonal with unit-cell parameters (refined using the Rietveld analysis program) $a = 6.4379\,(2)$, $c = 4.4003\,(2)$ Å for $Li_2TiOSiO_4$ and $a = 6.6110\,(8)$, $c = 4.4372\,(6)$ Å for $Li_2TiOGeO_4$.

Selected-area and convergent-beam electron diffraction (CBED) of both compounds (Fig. 1) showed that they crystallize in a centrosymmetric tetragonal space group with the only space-group-forbidden reflections being $hk0$ for $h + k$ odd. This is consistent with $P4/nmm$, the space group confirmed for the corresponding sodium compounds $Na_2TiOSiO_4$ (Nyman *et al.*, 1978) and $Na_2TiOGeO_4$ (Verkhovskij *et al.*, 1970) by successful refinement of their structures from single-crystal X-ray data. This observation, together with the near coincidence of the lattice a parameters of $Li_2TiOSiO_4$ and $Na_2TiOSiO_4$, strongly suggested that these compounds are isostructural. The lattice c parameter of $Li_2TiOSiO_4$ is much less than that of $Na_2TiOSiO_4$ and this is consistent with the two crystals having the same layers of SiO_4 tetrahedra and TiO_5 square pyramids joined by sharing corners and separated by layers of Li^+ ions in the former compound and by the much larger Na^+ ions in the latter. Fractional atomic coordinates in Table 1 calculated to give the same dimensions of SiO_4 tetrahedra and TiO_5 square pyramids were used as a trial structure for calculation of the X-ray powder diffraction pattern. A Rietveld analysis of calculated and observed X-ray powder diffraction intensities gave a Bragg R value of 0.115 for 42 reflections confirming the trial structure is correct. The TiO_5 square pyramids have an apical Ti—O bond distance of 1.70 Å and a basal Ti—O bond distance of 1.99 Å.

Crystals of $Li_2TiOSiO_4$ were sufficiently stable in a 400 keV electron beam to obtain high-resolution electron micrographs (Fig. 2). These verify that the crystals have large regions of single phase without extended defects.

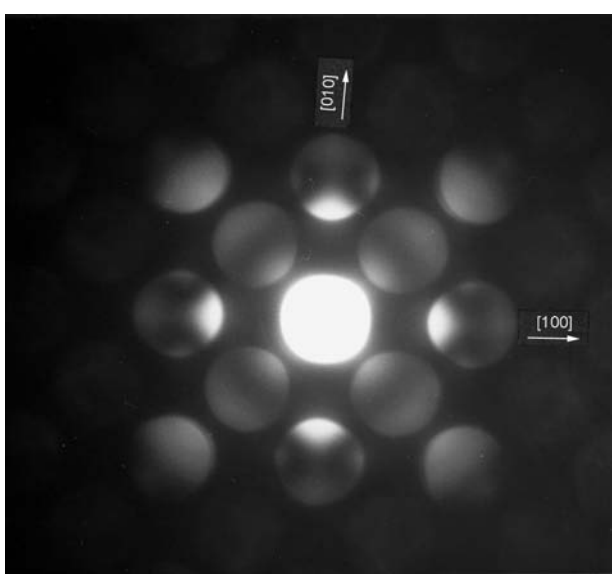

Fig. 1. CBED of $Li_2TiOSiO_4$ viewed along [001], showing systematic absences $hk0$ for $h + k \neq 2n$.

Table 1. *Fractional atomic coordinates of* $Li_2TiOSiO_4$

		x	y	z	B (Å^2)
Ti	2(c)	1/4	1/4	0.076	0.5
Li	4(e)	0	0	1/2	0.5
Si	2(a)	3/4	3/4	0	0.5
O(1)	8(i)	1/4	0.957	0.213	0.5
O(2)	2(c)	1/4	1/4	0.700	0.5

The ^{17}O MAS NMR spectra reveal details of the solid-state formation of $Li_2TiOSiO_4$ *via* an amorphous gel to a final crystalline product. The spectrum (Fig. 3, bottom) of the reaction mixture heated to 970 K is characteristic of an amorphous gel. There are two main resonances, one at ~0 parts in 10^6 and the other at ~180 parts in 10^6. By comparison with NMR data from TiO_2–SiO_2 gels (Dirken *et al.*, 1995), these can be assigned to Si—O—Si at 0 parts in 10^6 and Si—O—Ti at 180 parts in 10^6. There is also a minor peak at ~540 parts in 10^6, which is probably OTi_3. The amorphous nature, which was confirmed by XRD, is indicated by the line widths of the resonances associated with titanium. After heating to 1170 K, crystallization has clearly occurred from the much reduced line widths (Fig. 3, centre). Four peaks can be immediately identified at ~40, 372, 406 and 595 parts in 10^6. From the ^{17}O NMR shift data that already exist, the peak at 595 parts in 10^6 can be immediately identified as rutile (Bastow *et al.*, 1993) and the peaks at 372 and 406 parts in 10^6 as Li_2TiO_3. The resonance at ~40 parts in 10^6 has second-order quadrupolar structure and the decrease in width from the Si—O—Si linkage is indicative of a nonbridging silicate unit, and given the stoichiometry is probably a lithium silicate. XRD indicated that Li_2SiO_3 is present. This information could be gleaned directly from O MAS NMR if a sufficiently large database of ^{17}O spectra from crystalline compounds existed.

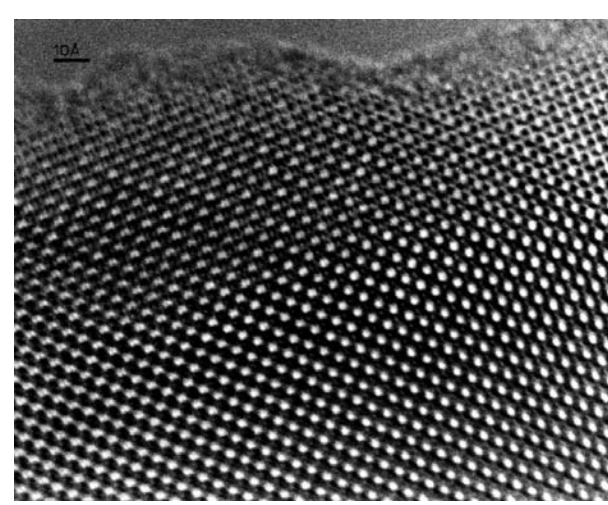

Fig. 2. High-resolution electron micrograph of $Li_2TiOSiO_4$ viewed along [001].

On heating to 1220 K, the ^{17}O MAS NMR spectrum becomes more complex (Fig. 3, top). The rutile and lithium silicate peaks have decreased in intensity whereas that from the Li_2TiO_3 has increased. There are new peaks, a prominent one at around 150 parts in 10^6 and a second at 730 parts in 10^6, which must be the oxygen resonances from $Li_2TiOSiO_4$. Recrystallization from an LiCl melt produced almost single-phase $Li_2TiOSiO_4$ (Fig. 4). There are two distinct oxygen sites in $Li_2TiOSiO_4$ in the ratio 4:1. The more populated from the Si—O—Ti linkages give rise to the peak at ~150 parts in 10^6. An experiment at 7.05 T showed that the width scaled inversely with the applied magnetic field as expected for a purely second-order quadrupolar broadened line shape. This was simulated to give a quadrupole constant, $\mathbf{C}_q$, of 3.05 MHz, asymmetry parameter of 0.35 and an isotropic chemical shift of 157.0 parts in 10^6. These shift data are extremely useful in confirming the assignment of resonances in this region from TiO_2–SiO_2 gels. The other resonance has a very high shift at 741 parts in 10^6. In coordination with titanium, ^{17}O can show a wide range of chemical shifts, depending strongly on the coordination number of the oxygen. At 741 parts in 10^6, this can be assigned to the nonbridging apical oxygen of the TiO_5 tetragonal pyramid. The highly linear nature of the local environment is reflected in the strong chemical-shift anisotropy, which gives rise to the extensive spinning sideband pattern from this site. The centre band, which is not the strongest peak, is identified from several long runs at different spinning frequencies.

The MAS NMR spectrum of ^{17}O from $Li_2TiOGeO_4$ (Fig. 4) is similar to that from the silicate, and the resonances from the apical and basal oxygens of the TiO_5 tetragonal pyramids can be unequivocally assigned. The resonance from the apical nonbridging atom occurs at 749 parts in 10^6 (*cf.* 741 parts in 10^6 for the silicate). The resonance at around 105 parts in 10^6 from the bridging Ti—O—Ge oxygen has characteristic second-order quadrupolar line shape with peaks at 82 and 128 parts in 10^6 (*cf.* 131 and 145 parts in 10^6 for the silicate). The bigger splitting of this peak in the germanate compared with the silicate is a reflection of the bigger $\mathbf{C}_q$ in the germanate. A simulation of the quadrupole broadened line shape for this resonance gave a quadrupole coupling constant of 4.80 MHz, asymmetry parameter of 0.22 and an isotropic chemical shift of 148 parts in 10^6. An excellent agreement between observed and simulated line shapes reflects the fact there is only one bridging oxygen site in the asymmetric unit of the unit cell.

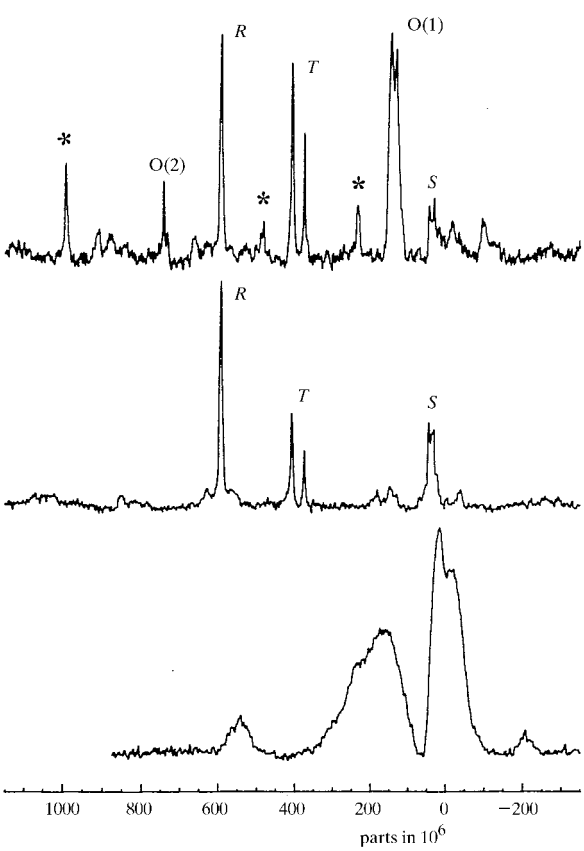

Fig. 3. ^{17}O MAS NMR of $TiO_2/SiO_2/Li_2CO_3$ reacted at 970 K (bottom), 1170 K (middle) and 1230 K (top). O(1), O(2) indicate resonances from $Li_2TiOSiO_4$, *T* from Li_2TiO_3, *S* from Li_2SiO_3, *R* from rutile and asterisks indicate side bands from the O(2) resonance.

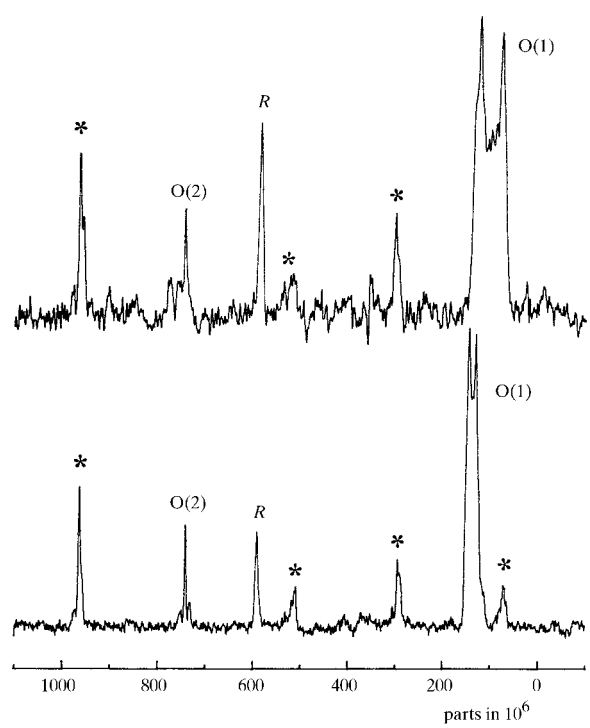

Fig. 4. ^{17}O MAS NMR of $Li_2TiOSiO_4$ (lower curve) and $Li_2TiOGeO_4$ (upper curve). Resonances from apical O(2) and bridging O(1) sites are indicated; *R* indicates resonance from rutile; spinning side bands from the O(2) resonances are indicated by asterisks.

The oxygen *K* edges in the EELS spectra of $Li_2TiOSiO_4$ and $Li_2TiOGeO_4$ show that there are mainly four peaks near the edge threshold and the energy of these changes significantly when comparing the two compounds (Fig. 5). These edges arise from transitions from the oxygen 1*s* core states to unoccupied states having *p* symmetry and probe the local electronic structure at the oxygen sites (therefore the O-*p* states). It is difficult to unambiguously associate the peak positions with particular energy bands without detailed molecular-orbital or band-structure methods but from reference spectra in the Ti—O and Si—O systems a general description of the peaks can be given.

In $SrTiO_3$, anatase, and rutile, the first peak of the O *K* edge is at about 530 eV (*e.g.* van der Laan, 1990) and it represents the hybridization of the O-2*p* band with the Ti-3*d* bands. In these reference materials and in titanite ($CaTiSiO_5$), the degeneracy of the 3*d* states is lifted due to the octahedral crystal field (even if distorted) and thus these states are split into t_{2g} and e_g bands which are clearly visible in the Ti $L_{2,3}$ edges of these compounds (*e.g.* Brydson *et al.*, 1992). In $Li_2TiOSiO_4$ and $Li_2TiOGeO_4$, the Ti $L_{2,3}$ edge (Fig. 6) does not show such even splitting between the two states owing to the lower symmetry of the square-pyramidal coordination of Ti and from this it can be deduced that such splitting (t_{2g} and e_g) should not be visible in the O *K* edge. The structure at about 535–536 eV is very similar in shape and position to the peak seen when oxygen is coordinating Si tetrahedrally [see for example the spectra of Wallis & Gaskell (1993)] and the peak arises from the mixing of the Si-3*s*/3*p* states with the O-2*p*. The similarity in energy positions of the Ti—O(1) and Si—O(1) peaks arises in part because of the comparable bond lengths in the reference materials and in our compounds. In fact, the Si—O bond length in the Si tetrahedra of $Li_2TiOSiO_4$ and in α-SiO_2 are very similar (~1.6 Å) and the Ti—O(1) bridging bonds in $Li_2TiOSiO_4$ and anatase (or rutile) are also very similar (~1.9 Å). Considering these similarities to spectra of Ti—O and Si—O compounds, we can see that the O *K* edges show the mixed bonding character when forming the Ti—O—Si bridges bonding with the Ti 3*d* bands and the Si 3*s*/*sp* bands at different energy levels.

From the shorter bond length Ti—O(2) of the apical oxygen (1.70 Å), it can be deduced that the peak position should be at higher energy than the 529 eV peak arising from Ti—O(1). The peak at 532–533 eV can therefore be assigned to the formation of this bond between the Ti-3*d* and the apical O-2*p*. Although detailed calculations are necessary to confirm the exact origin, the structure at about 540 eV can be tentatively assigned to more delocalized states mixing both together the Ti-4*s*/4*p* and the Si-3*s*/*sp* with the O-2*p* as similar structures are generally observed in transition-metal oxides and not in any of the Si—O reference materials.

We note that remarkable peak shifts are observed when comparing $Li_2TiOSiO_4$ and $Li_2TiOGeO_4$ spectra reflecting the change in bond distances. In particular, we note the separation between the high-energy peaks related to Si (and Ge) increases in the same way as the quadrupole coupling constant calculated from the NMR of the bridging O atoms.

4. Conclusions

Lithium titanium silicate, $Li_2TiOSiO_4$, and lithium titanium germanate, $Li_2TiOGeO_4$, were shown by selected-area and convergent-beam electron diffraction to have the space group *P*4/*nmm*. X-ray powder diffraction patterns were indexed and accurate cell dimensions for the two compounds determined. An excellent fit of calculated and observed X-ray powder diffraction was achieved.

^{17}O nuclear magnetic resonance spectra of the two compounds, isotopically enriched with ^{17}O, showed peaks due to the apical titanyl, Ti—O, and basal bridging Ti—O—Si or Ti—O—Ge oxygen atoms of the title compounds. By comparison with reference spectra, oxygen *K* edges and titanium $L_{2,3}$ edges of electron energy-loss spectra were tentatively assigned.

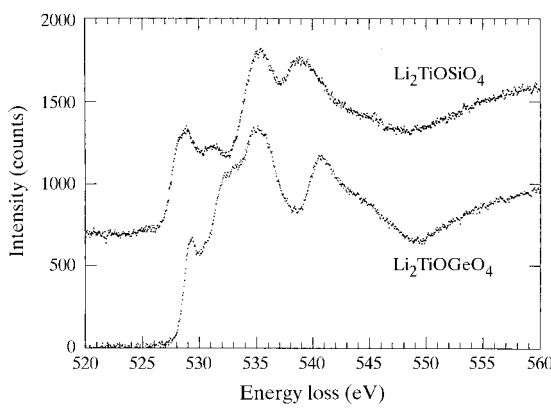

Fig. 5. EELS O *K* edge of $Li_2TiOSiO_4$ and $Li_2TiOGeO_4$.

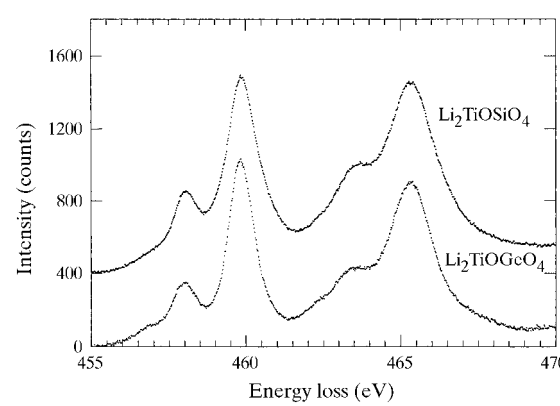

Fig. 6. EELS Ti $L_{2,3}$ edge of $Li_2TiOSiO_4$ and $Li_2TiOGeO_4$.

We plan to extend this work to ^{17}O NMR and oxygen *K*-edge and titanium $L_{2,3}$-edge EELS of more complex titanosilicates and of related titanophosphates and to make detailed calculations that will allow us to unambiguously associate the EELS peak positions to particular energy bands.

MES thanks EPSRC for funding ^{17}O NMR research through GR/L28647.

References

Balmer, M. L., Bunker, B. C., Wang, L. Q., Peden, C. H. F. & Su, Y. (1997). *J. Phys. Chem.* B**101**, 9170–9179.

Bastow, T. J., Dirken, P. J., Smith, M. E. & Whitfield, H. J. (1996). *J. Phys. Chem.* **100**, 18539–18545.

Bastow, T. J., Moodie, A. F., Smith, M. E. & Whitfield, H. J. (1993). *J. Mater. Chem.* **3**, 697–702.

Bastow, T. J., Smith, M. E. & Whitfield, H. J. (1996). *J. Mater. Chem.* **6**, 1951–1955.

Brydson, R., Sauer, H. & Engel, W. (1992). *Transmission Electron Energy Loss Spectrometry in Materials Science*, edited by M. M. Disko, C. C. Ahn & B. Fultz, pp. 131–154. Warrendale, PA: The Minerals, Metals and Materials Society.

Dirken, P. J., Smith, M. E. & Whitfield, H. J. (1995). *J. Phys. Chem.* **99**, 395–401.

Farges, F. (1996). *J. Non-Cryst. Solids*, **204**, 53–64.

Laan, G. van der (1990). *Phys. Rev. B*, **41**, 12366–12368.

Masse, R., Grenier, J.-C. & Durif, A. (1967). *Bull. Soc. Fr. Minéral. Cristallogr.* **90**, 20–23.

Nyman, H., O'Keefe, M. & Bovin, J.-O. (1978). *Acta Cryst.* B**34**, 905–906.

Phillips, M. L. F., Harrison, W. T. A., Gier, T. E., Stucky, G. D., Kulkarni, G. V. & Burdett, J. K. (1990). *Inorg. Chem.* **29**, 2158–2163.

Speer, J. A. & Gibbs, G. V. (1976). *Am. Mineral.* **61**, 238–247.

Taylor, M. & Brown, G. E. (1976). *Am. Mineral.* **61**, 435–447.

Thomas, P. A., Glazer, A. M. & Watts, B. E. (1990). *Acta Cryst.* B**46**, 333–343.

Verkhovskij, V. J., Kuz'min, E. A., Iljukhin, V. V. & Belov, N. V. (1970). *Dokl. Akad Nauk SSSR*, **190**, 91–93.

Wallis, D. J. & Gaskell, P. H. (1993). *Electron Microscopy and Analysis*, edited by A. J. Craven, pp. 47–50. Institute of Physics Conference Series No. 138. Bristol: Institute of Physics.