Kent Academic Repository

Full text document (pdf)

Citation for published version

Chadwick, Alan V. and Pickup, David M. and Ramos, Silvia and Cibin, G. and Tapia-Ruiz, N. and Breuer, S. and Wohlmuth, D. and Wilkening, M. (2017) An X-Ray Absorption Spectroscopy Study of Ball-Milled Lithium Tantalate and Lithium Titanate Nanocrystals. IOP Conference Series: Materials Science and Engineering, 169 (1). 012015. ISSN 1757-8981.

DOI

https://doi.org/10.1088/1757-899X/169/1/012015

Link to record in KAR

http://kar.kent.ac.uk/64978/

Document Version

Publisher pdf

PAPER • OPEN ACCESS

An X-Ray Absorption Spectroscopy Study of Ball-Milled Lithium Tantalate and Lithium Titanate Nanocrystals

To cite this article: A.V. Chadwick *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **169** 012015

View the article online for updates and enhancements.

An X-Ray Absorption Spectroscopy Study of Ball-Milled Lithium Tantalate and Lithium Titanate Nanocrystals

A.V. Chadwick[1], D.M. Pickup[1], S. Ramos[1], G. Cibin[2], N. Tapia-Ruiz[3], S. Breuer[4], D. Wohlmuth[4] and M. Wilkening[4]

1 School of Physical Sciences, University of Kent, Canterbury, Kent CT2 7NH

2 Diamond Light Source, Diamond House, Harwell Campus, Didcot, Oxfordshire, OX11 0DE

3 Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH

4 Institute for Chemistry and Technology of Materials, Christian Doppler Laboratory for Lithium Batteries, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

E-mail: a.v.chadwick@kent.ac.uk

Abstract. Previous work has shown that nanocrystalline samples of lithium tantalate and titanate prepared by high-energy milling show unusually high lithium ion conductivity. Here, we report an X-ray absorption spectroscopy (XAS) study at the Ti K-edge and the Ta L_3 edge of samples that have been milled for various lengths of time. For both systems the results show that milling creates amorphous material whose quantity increases with the milling time. The more extensive data for the tantalate shows that milling for only 30 minutes generates ~25% amorphous content in the sample. The content rises to ~60% after 16 hours. It is suggested that it is the motion of the lithium ions through the amorphous content that provides the mechanism for the high ionic conductivity.

1. Introduction

There are numerous reports in the literature that atomic migration in nanocrystals is unusually fast compared to the parent bulk material. In ionic materials the origin for enhanced diffusion has been assigned to atomic disorder along interfaces and surfaces [1-4], however, in many cases, the experimental data are ambiguous. The data for the binary and ternary oxides is particularly varied and is very dependent on the method of sample preparation [5-9] as this controls the microstructure of the material. A simple and rapid method of producing relatively large quantities of nanomaterials is high-energy ball-milling [10-13]. However, it is now clear that for simple binary oxides, like alumina, Al_2O_3 [14] and zirconia, ZrO_2 [15] it produces samples that have a large (tens of per cent) amorphous content; the nanocrystalline core is surrounded by a shell of amorphous material. The effect on the atomic migration of this microstructure is not clear. In contrast, ball-milled ternary oxides can show unusually enhanced ionic mobility.

The first ternary ball-milled system that was studied in any depth was lithium niobate, $LiNbO_3$, and the samples exhibited very high lithium ion diffusivity and conductivity [16-18];

the material in bulk crystalline form is normally regarded as an insulator. [7]Li nuclear magnetic resonance (NMR) studies of ball-milled $LiNbO_3$ with particle sizes down to 16 nm showed lithium ion mobility was increased by several orders of magnitude [16]. Nb K-edge X-ray absorption spectroscopy (XAS) of ball-milled $LiNbO_3$ showed a highly attenuated Extended X-ray Absorption Fine Structure (EXAFS) indicative of a significant amorphous content [17]. A very thorough study by Heitjans and co-workers [18] of ball-milled and sol-gel prepared $LiNbO_3$ using a wide range of techniques confirmed the amorphous nature of the surface of the nanocrystals and that this was the origin of the high lithium ion mobility.

Currently there is intense interest in improving the performance of lithium-ion batteries and a necessary requirement of components is high lithium ion mobility [19]. Hence the observations for ball-milled $LiNbO_3$ have led to the study of other similar materials. Ball-milled $LiTaO_3$ with a particle size of about 20 nm exhibits an ionic conductivity five orders of magnitude higher than bulk crystals [20]. Similarly ball-milling Li_2TiO_3 [21, 22] increases the lithium ion conductivity by some three orders of magnitude. As in the case of $LiNbO_3$ the increased lithium ion diffusion is assigned to the generation of amorphous material. In this contribution we confirm and quantify the presence of amorphous material in these two materials using XAS measurements.

2. Methodology

2.1 Materials

Micron sized commercial powders of Li_2TiO_3 and $LiTaO_3$ were ball-milled using the procedures described in previous papers [20-22]. For Li_2TiO_3 only two samples were studied; micron powder and after 8 hours milling. In the case of $LiTaO_3$ micron powder and samples after 0.5, 1, 4, 8 and 16 hours of milling were investigated. For the XAS measurements the powders were mixed with cellulose diluent and pressed into 13 mm diameter pellets.

2.2 XAS measurements

XAS scans were collected for the appropriate edge (Ti K-edge and Ta L_3-edge) at room temperature on beam line B18 at the Diamond Light Source [23]. Data collection used transmission mode with ion chamber detectors. Continuous scanning (QEXAFS) was employed; an individual scan required 180 s and several scans were performed to improve the signal-to-noise ratio. The synchrotron energy and current were 3 GeV and 300 mA, respectively. The beam size at the sample
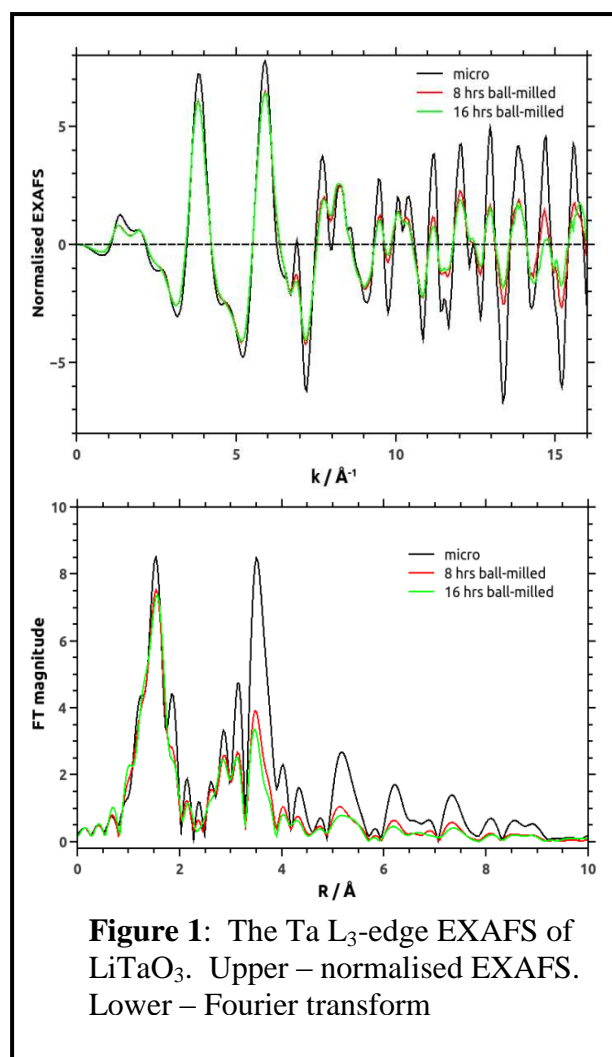
Figure 1: The Ta L_3-edge EXAFS of $LiTaO_3$. Upper – normalised EXAFS. Lower – Fourier transform
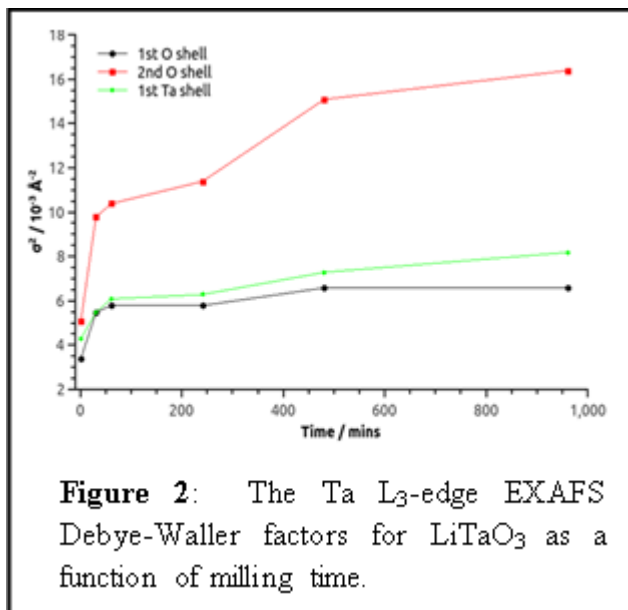
was 700×700 microns. Powdered samples were mixed with cellulose as a diluent and pressed into 13 mm diameter pellets. The spectra were normalized in Athena and fitted to scattering models in R-space produced by FEFF in Artemis [24].

3 Results and discussion

3.1 LiTaO$_3$ XAS measurements

All the spectra were analysed to yield the details of the local structure, i.e. bond lengths, R, Debye-Waller factors, σ, etc.; the qualitative information is, however, best represented by the Fourier transform (FT) of the k^3 weighted normalised EX-

Figure 2: The Ta L$_3$-edge EXAFS Debye-Waller factors for LiTaO$_3$ as a function of milling time.

AFS and these will be mostly used in this short paper. The data for three samples are shown in Figure 1. There is an attenuation of the EXAFS at high k leading to a reduction in the peaks in the corresponding Fourier transform, particularly the Ta-Ta correlation at 3.8 Å. We have analysed the effect in two ways; as a change in the Debye-Waller factor due to disorder and as the effect of an amorphous content. A full analysis with FEFF allowing all the key parameters to float gave very good fits to the spectra. The parameters that changed significantly with milling time were the Debye-Waller factors, σ, for the Ta-O, Ta-O and Ta-Ta correlations at 1.9, 2.0 and 3.8 Å, respectively. These are plotted in Figure 2 in the form of σ^2 versus milling time. It can be seen that for all the correlations σ^2 almost doubles after only 30 minutes milling. This suggests that even this relatively brief milling causes a distortion of the local structure around the Ta ions. After 30 minutes the Ta-O Debye-Waller factors show only a gradual change whereas the Ta-Ta correlation, which is significantly larger, continues to increase steeply with milling time. An explanation of these effects is that milling after 30 minutes causes little changes to the local Ta-O octahedra but the relative arrangement of the octahedra continues to change. This would be expected given that the strong Coulomb interaction between Ta^{5+} and O^{2-} will maintain a relatively rigid local structure. This explanation is also consistent with the shape of the ^{7}Li NMR quadrupolar powder patterns observed for a sample milled for 30 min, see ref. [20]. After 30 min of milling most of the local electric field gradients in the direct neighbourhood of the Li nuclei are still comparable to those in unmilled, coarse-grained LiTaO$_3$ [20].

An alternative, but not contradictory, approach is to assume the attenuation of the EXAFS is due to the ball-milling generating amorphous material, as in the analysis of the EXAFS of ZrO$_2$ [15]. This would be mainly reflected in the peak height of the Ta-Ta shell in the Fourier transform. Assuming that the commercial powder prior to milling is 100% crystalline

Table 1		
Milling Time/Hour	**Estimated Amorphous Content**	
	LiTaO$_3$	**Li$_2$TiO$_3$**
0	0%	0%
0.5	~ 25%	
1	~ 41%	
4	~ 44%	
8	~ 55%	~25%
16	~ 60%	

then the height of the Ta-Ta peak in the Fourier transform is representative of a sample with no amorphous content. Hence the relative height of this peak in the milled samples can be used to estimate the degree of crystallinity, i.e. the amorphous content. The results of this rather crude, but useful, analysis are shown in Table 1. This analysis also reveals that milling for as little as 30 minutes drastically affects the sample and generated ~25 % amorphous material.

3.2 Li_2TiO_3 XAS measurements

We have fewer data for this system but they follow the same pattern as those for $LiTaO_3$. The EXAFS results are shown in Figure 3. Again, ball-milling attenuates the EXAFS and there is a decrease in the height of the Ti-Ti peak in the Fourier transform. The same analysis used for $LiTaO_3$ suggests the ball-milled sample contains 25% amorphous material.
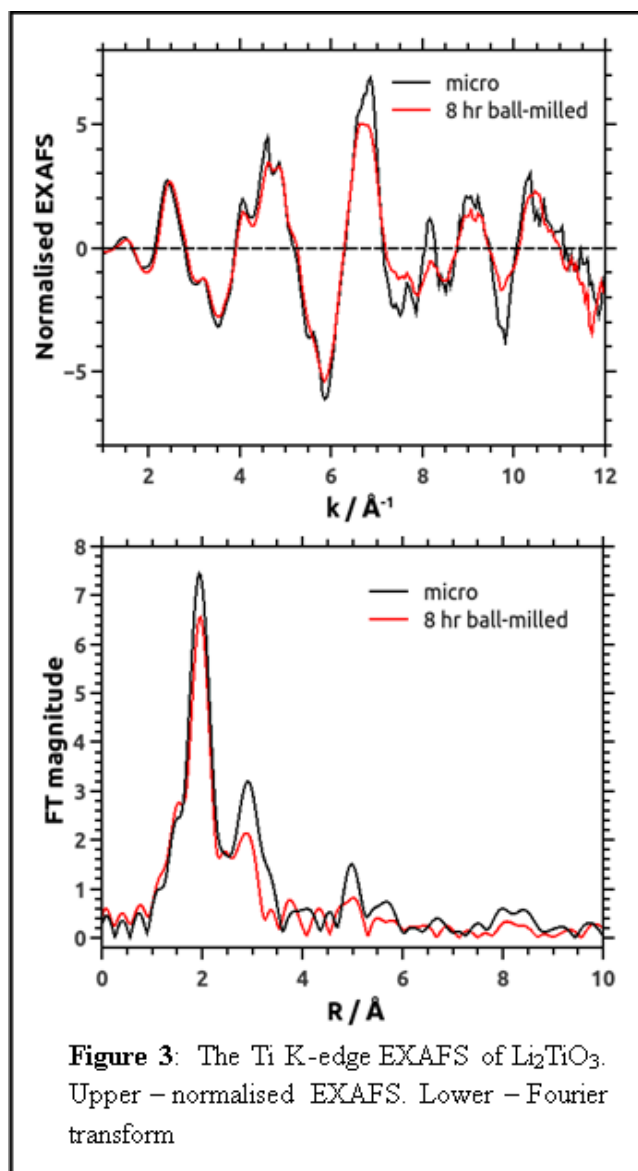
It would be unwise to assume that the apparent quantitative differences between the titanate and tantalate after 8 hours ball-milling are meaningful. Other factors, such as the relative hardness of the tow materials, would need to be considered.

Figure 3: The Ti K-edge EXAFS of Li_2TiO_3. Upper − normalised EXAFS. Lower − Fourier transform

4. Conclusions

There are clear similarities between the current XAS results for $LiTaO_3$ and Li_2TiO_3 and the data for $LiNbO_3$ reported in earlier papers [17, 18]. Hence, a reasonable general explanation of the results for these two systems is that ball-milling is creating nanoparticles that have a crystalline core with an amorphous shell.

The more extensive study of $LiTaO_3$ is particularly interesting as it shows that ball-milling for only 30 minutes dramatically attenuates the EXAFS spectrum, indicating a highly disordered sample. This parallels the conductivity measurements of a sample ball-milled for 30 minutes where the magnitude is four orders higher than that for an un-milled sample [20]. However, the conductivity studies revealed some subtle dependence of the microstructure on the time of ball-milling. The longer the milling time the more difficult it is to recover crystallinity by thermal annealing.

Finally, it is interesting to compare the results for the current systems and other oxides with similar data for binary fluorides. XAS studies of ball-milled binary fluorides, like CaF_2

and BaF$_2$ show virtually no attenuation of the EXAFS spectra, suggesting a very small, if any, amorphous content [25]. The difference is presumably a reflection of the greater strength of metal-fluorine bonds compared to metal-oxygen bonds.

Acknowledgements

References

[1]   Tuller H 2000 Solid State Ionics 131 143

[2]   Indris S, Heitjans P, Roman H E and Bunde A 2000 Phys. Rev.Lett. 84 2889

[3]   Guo X, Tan C and Yuan R-Z 1995 J. Eur. Ceram. Soc. 15 25

[4]   Heitjans P and Indris S 2003 J. Phys.: Condens. Matter 15 1257

[5]   Chadwick A V and Savin S L P 2009 Solid State Electrochemistry I, ed. V V Kharton (Weinheim: VCH-Wiley) p 79

[6]   Chadwick A V and Savin S L P 2010 Low Dimensional Solids, ed. D W Bruce, D O'Hare and R I Walton (Chichester: Weinheim: Wiley) p 1

[7]   Aydin H, Korte C and Janek J 2013 Sci. Technol. Adv. Mater. 14 035007

[8]   Gerstl M, Frömling T, Schintlmeister A, Hutter H and Fleig J 2011 Solid State Ionics 184 23

[9]   Schichtel N; Korte C, Hesse, D, Zakharov N, Butz B, Gerthsen D and Janek J 2010 Phys. Chem. Chem. Phys. 12 14596

[10]   Fecht H J 1995 Nanostruct. Mater. 6 33

[11]   Koch C C 1997 Nanostruct. Mater. 9 13

[12]   Cukrov L M, Tsuzuki T and McCormick P G 2001 Scr. Mater. 44 1787

[13]   Indris S, Bork D and Heitjans P 2000 J. Mater. Synth. Process. 8 245

[14]   Scholz G, Stosser R, Klein J, Silly G, Buzaré J Y, Laligant Y and Ziemer B, 2002 J. Phys.: Condens. Matter 14 2101

[15]   Chadwick A V, Pooley M J, Rammutla K E, Savin S L P and Rougier A 2003 J. Phys.: Condens. Matter 15 431

[16]   Bork D and Heitjans P, 2001 J. Phys. Chem. B 105 9162

[17]   Heitjans P, Masoud M, Feldhoff A, Wilkening M, 2006 Faraday Discuss. 134 67

[18]   Pooley M J and Chadwick A V, 2003 Rad. Eff. Def. Solids 158 197

[19]   Tarascon J-M and Armand M, 2001 Nature 414 359

[20]   Wilkening M, Epp V, Feldhoff A and Heitjans P, 2008 J. Phys. Chem. C 112 9291

[21]   Ruprecht B, Wilkening M, Uecker R and Heitjans P, 2012 PCCP 14 11974

[22[Brandstätter H, Wohlmuth D, Bottke P, Pregartner V and Wilkening M, 2015 Z. Phys. Chem. 229 1363

[23]   Dent A J, et al 2013 Journal of Physics: Conference Series 430 0120231

[24]　Ravel B and Newville M 2005 J. Synchrot. Radiat. 12 537

[25]　Chadwick A V, Düvel A, Heitjans P, Pickup D M, Ramos S, Sayle D C and Sayle T X T, 2015 IOP Conf. Series-Mat. Sci. and Eng. 80 #012005