Acknowledgements

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A note on the preparation of the high transition temperature superconductor lithium titanate

Superconductivity in $LiTi_2O_4$ was first reported by Johnston *et al.* [1] who also recognized this material as belonging to the cubic spinel group of compounds. These compounds are currently of much interest because they appear to be examples of a ternary system in which the superconducting property depends upon the strong coupling mechanism [2, 3]. Such materials are frequently difficult to prepare and our recent experience with $LiTi_2O_4$ indicates that this spinel is no exception, but that a single phased compound can be obtained provided certain conditions are satisfied. It is the purpose of this paper to describe circumstances which seem to provide these conditions and to briefly report the crystal structure and superconducting transition characteristics of the best material prepared by our method.

In the experiments carried out by Johnston *et al.* samples were produced by arc-melting Li_2CO_3, TiO_2 and Ti metal together, by sintering mixtures of $Li_2Ti_2O_5$ and Ti_2O_3 under a helium or argon atmosphere and by reduction of pre-reacted mixtures of Li_2CO_3 and TiO_2 with hydrogen. None of their procedures, however, produced single-phased material, some of the samples with highest superconducting transition temperatures apparently containing as much as 20% of unreacted $Li_2Ti_2O_5$ or other impurity.

In the present work therefore, efforts were directed towards a more detailed investigation of the best conditions for the following simple reactions:

(1) $Li_2CO_3 + 4TiO_2 + H_2\text{(gas)} = 2LiTi_2O_4 + CO_2\uparrow + H_2O\uparrow$

(2) $2LiH + 4TiO_2 + H_2\text{(gas)} = 2LiTi_2O_4 + 2H_2\uparrow$

The starting materials in each case were A.R. grade chemicals and the parameters investigated were sintering temperature and time at this temperature. For simplicity, all samples were mixed so as to yield a nominally stoichiometric product, hydraulically pressed to form a thin cylindrical pellet, and fired only once. However, subsequent investigation suggests that, unlike some other oxide spinels, repeated firing effects little improvement in either purity or stoichiometry. In all cases the firing run was arranged so that samples rose rapidly to the sintering temperature, were maintained at that temperature for a predetermined time, and then were furnace cooled. A continuous flow of hydrogen gas over the samples, held in a silica tube, was maintained throughout this programme.

In the experiments concerned with the effect

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of temperature, samples were sintered for 24 h at a temperature fixed within the range 750 to 950° C. After each run, the product was examined by X-ray powder diffractometry and the diffraction pattern analysed to derive information on the structural parameters of the spinel phase and level of impurity. The results found with either Reaction 1 or Reaction 2 were very similar. In both cases, the production of the spinel phase depended critically upon sintering temperature, the purest material being invariably obtained with this temperature close to 860° C. A change of less than 30° C, for example, either above or below 860° C, led to an appreciable increase in the intensity of the diffraction lines corresponding to impurity phases. However, the material obtained with Reaction 2 was always of poorer quality (i.e. higher impurity level) than that given under the same sintering conditions using Reaction 1. LiH is, of course, slightly hygroscopic, and it may be that this difference is connected with adding a proper quantity of the TiO_2 (anatase) or with the quality of the commercially available material. In contrast, we find that, with careful optimization of the sintering temperature, impurity diffraction lines can be eliminated using Reaction 1.

The time at the sintering temperature was also found to be significant, for although samples consisting primarily of spinel phase could be produced in as little as 6 h, the impurity level in these circumstances was always very high. With our pellet size (approximate dimensions: 1 cm diameter × 1 mm thick) best results for spinel phase purity and superconducting transition temperature were obtained with a sintering time in excess of 48 h. As this seems likely to be connected with the diffusion of hydrogen into a given sample, these observations are tentatively interpreted as a measure of the time necessary to provide hydrogen saturation.

Finally, it is worth remarking that, given an optimum sintering temperature and adequate time at that temperature, all samples prepared according to Reaction 1 showed a weight loss which was within experimental error of that expected theoretically.

X-ray diffraction studies of the best material produced in this investigation indicates that $LiTi_2O_4$ crystallizes with a cation distribution which closely conforms to the normal spinel arrangement, i.e. with the space group Fd3m (International Tables for Crystallography, Volume 1), only Li occupies the positions 8(a) and only Ti occupies positions 16(d). The intensity data is then fitted best with an oxygen position parameter $u = 0.3874$. This value is lightly lower than that observed by Johnston [4] while our unit cell parameter $a_0 = 8.408$ Å, is slightly higher. The superconducting transition in this sample was observed both from measurements of the resistivity and from the heat capacity. Some of the latter measurements are displayed as a graph in Fig. 1 and show an onset transition temperature, T_c, of 12.8 K. This is lower than the best results of Johnston *et al.* [1] and Johnston [4] but our transition is much sharper. Thus the mean transition temperature of 12.40 K, which we observe, is higher than any previously reported for this compound (Table I).

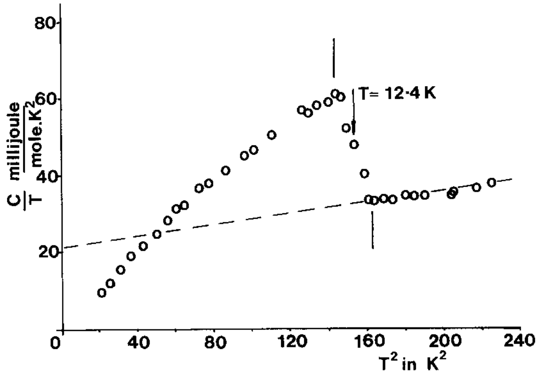

Figure 1 Low temperature heat capacity data for $LiTi_2O_4$ prepared by hydrogen reduction at 860° C.

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TABLE I Transition temperatures, T_c, reported for superconducting lithium titanate

Reference	% impurity phases	T_c (K)	ΔT_c (K)
Johnston *et al.* [1]	~ 20	10.95 (onset T_c = 13.7 K)	4.2
Johnston [4]	not given	10–12	–
McCallum *et al.* [5]	not given	11.7	1.2
Shelton *et al.* [6]	(~ 10)	11.2	> 0.1
	(~ 15)	11.26	0.04
Present work	0	12.40	0.46

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The grain-boundary sliding component in high-temperature fatigue

Recent measurements of grain-boundary sliding (GBS) during high-temperature fatigue of Magnox Al80 [1], α-iron [2], copper and α-zirconium [3] have shown that the rates of GBS can be up to three orders of magnitude greater than those rates reported for monotonic (creep) stress. The rates of GBS in fatigue are consistent with observations which indicate the importance of GBS in high-temperature fatigue failure [1–5, 7]. However, although the rate of GBS has been measured in high-temperature fatigue, there have been no attempts to assess the contribution of GBS strain to the total strain as has been done so extensively for high-temperature creep [6].

For creep conditions, the strain contribution of GBS (ϵ_{gb}) is generally observed to be proportional to the total strain (ϵ_t), i.e. $\epsilon_t = \epsilon_{gb}/\lambda$, where the value of λ tends to increase with increasing temperature and decreasing stress [6]. Values of λ (conventionally expressed as percentages) up to ~ 90% which have been reported show that the GBS strain can make a major contribution to the total creep strain under low-stress high-temperature conditions. If a similar expression for λ applies to fatigue as that in creep, substantial values of λ might be expected because of the low stresses and high temperatures used in many tests. The present communication reports estimates of λ derived from measurements of GBS in Magnox Al80 [1], α-zirconium and copper [3] which were subjected to low-strain high-temperature fatigue.

For fatigue conditions, the estimates of λ are based on the ratio of the average measured GBS strain per cycle ($\bar{\epsilon}_{gb}$) to the total strain per cycle ($\bar{\epsilon}_t$) i.e. $\bar{\lambda} = \bar{\epsilon}_{gb}/\bar{\epsilon}_t$. The expression $\bar{\epsilon}_{gb} = K\bar{s}/d$ was used to calculate $\bar{\epsilon}_{gb}$, where $\bar{s}$ is the average GBS per cycle (μm cycle^{-1}), d is the average grain size

TABLE I Estimates of $\bar{\lambda}$ for cyclic stress conditions

Material	Frequency (Hz)	T (° C)	$\bar{\epsilon}_t$ (σ, MPa)	d (μm)	$\bar{s}$ (μm cycle^{-1})	$\bar{\epsilon}_{gb}$ (μm cycle^{-1})	$\bar{\lambda}$ (%)
Magnox Al80 [1]	60	430	4.4×10^{-5} (2.4)	3048	1.4×10^{-7}	4.5×10^{-11}	0.0001
			1.4×10^{-4} (4.1)	3048	7.5×10^{-7}	2.5×10^{-10}	0.0002
			2.4×10^{-4} (4.4)	3048	1.1×10^{-6}	3.7×10^{-10}	0.002
			3.2×10^{-4} (5.8)	3048	2.0×10^{-5}	6.5×10^{-9}	0.002
			1.6×10^{-4} (5.8)	864	7.2×10^{-7}	8.3×10^{-10}	0.005
α-zirconium [3]	15.6	700	8×10^{-3}	102	2.9×10^{-4}	2.9×10^{-6}	0.04
Copper [3]	15.6	400	8×10^{-3}	113	2.3×10^{-4}	2.0×10^{-6}	0.03
		500	8×10^{-3}	113	5.0×10^{-4}	4.4×10^{-6}	0.06
		550	8×10^{-3}	113	6.1×10^{-4}	5.4×10^{-6}	0.07
α-iron [2]	0.125	700	2×10^{-2}	75	7.8×10^{-3}	1.0×10^{-4}	0.50

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