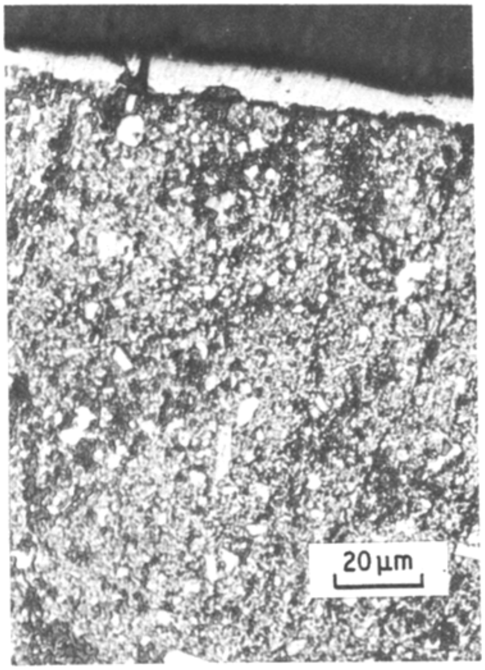

Figure 2 Cross-section of the boron electrode treated in N_2 (unetched).

References

1. M. SOKOŁOWSKI, A. SOKOŁOWSKA, A. RUSEK, A. MICHALSKI and J. GLIJER, *J. Mater. Sci.* **14** (1979) 841.
2. A. RUSEK, M. SOKOŁOWSKI, A. SOKOŁOWSKA, A. MICHALSKI, Z. ROMANOWSKI and B. GOKIELI, IV Krajowa Konferencja Naukowo-Techniczna, Częstochowa, 1979r.
3. M. SOKOŁOWSKI, *J. Cryst. Growth* **46** (1979) 136.
4. J. S. GILLESPIE, Jr, *J. Amer. Chem. Soc.* **88** (1966) 2423.
5. S. S. BACANOV, G. E. BŁOCHINA and A. A. DERIBAS, *Z. Struktur, Chim.* **6** (1965) 227.
6. T. AKASHI, A. SAWOHA, S. SAITO and M. ARAHI, *Jap. J. Appl. Phys.* **15** (1976) 891.

Received 27 October
and accepted 2 December 1980

A. RUSEK
M. SOKOŁOWSKI
A. SOKOŁOWSKA
Institute of Materials Science,
Warsaw Technical University,
Warsaw 02-524 ul.
Narbutta 85,
Poland

Formation of Li_2TiO_3 solid solutions by $4Li^+ \rightleftharpoons Ti^{4+}$ substitution

During a study of the phase diagram Li_2O–TiO_2 [1], it was found that at high temperatures Li_2TiO_3 forms a wide range of solid solutions between 44 and 66 mol% TiO_2. These solid solutions have a disordered rock salt structure based on the high temperature polymorph of Li_2TiO_3. Li_2TiO_3 itself undergoes an order–disorder phase transition at 1213° C [2]. Some structural features of these solid solutions are discussed further in this note since they appear to form by an unusual replacement mechanism which involves monovalent and tetravalent cations.

Direct conformation of mechanisms of solid solution formation normally requires accurate measurements of densities over a range of compositions. It was not possible to measure the density of most of the high Li_2TiO_3 solid solutions present because they cannot be stabilized to room temperature; instead; they decompose and/or transform to low Li_2TiO_3, even on rapid quenching from high temperatures. Consideration of the high Li_2TiO_3 structure, however, reveals that there is only one likely solid solution mechanism. Assuming an oxide array (face centred cubic or cubic close packed) that is essentially unchanged with composition, the overall solid solution mechanism may be written as

$$4Li^+ \rightleftharpoons Ti^{4+}. \tag{1}$$

For the lithia-rich solid solutions, this involves the formation of interstitial lithium ions, probably on tetrahedral sites and for the titania-rich solutions, the formation of cation vacancies on the octahedral sites.

The formula of the lithia-rich solid solutions may be written as

$$Li_{2+x}(\mathrm{oct})\,Li_{3x}(\mathrm{tet})\,Ti_{1-x}(\mathrm{oct})O_3 \qquad 0 < x \leqslant 0.08. \tag{2}$$

The only sites that are available in the rock salt structure for the extra $3xLi^+$ are tetrahedral sites and at the solid solution limit ($x = 0.08$) 4% of these tetrahedral sites must be occupied by Li^+.

0022–2461/81/072023–03$02.30/0

The formula of the titania-rich solid solutions may be written as

$$\mathrm{Li}_{2-4x}(\mathrm{oct})\,\mathrm{Ti}_{1+x}(\mathrm{oct})\,\mathrm{V}_{3x}(\mathrm{oct})\mathrm{O}_3 \qquad 0 < x \leqslant 0.19, \tag{3}$$

in which V(oct) refers to an octahedral cation vacancy. At the solid solution limit ($x = 0.19$) therefore, 19% of the octahedral sites are vacant.

The alternative to the above mechanisms in which the oxide array stays constant, is a mechanism in which the total number of cations remains constant (since the cations are disordered, it does not seem valid to consider mechanisms in which either the Li^+ content or the Ti^{4+} content remains constant). This mechanism would necessitate the creation of oxide ion vacancies in the lithia-rich solid solutions and oxide ion interstitials in the titania-rich solid solutions. While the former is a distinct possibility, there appears to be little likelihood of the latter occurring: it is not possible to have a significant concentration of oxide ion interstitials in a structure that contains close packed oxide ions. This mechanism is therefore rejected.

It is unusual to find solutions in which monovalent and tetravalent ions replace each other, although there appears to be no good theoretical reasons why this should not occur provided that (1) local electroneutrality is maintained fairly well and (2) the two cations have similar bonding requirements and are of similar size. In octahedral co-ordination to oxygen, Li^+ and Ti^{4+} appear to be of fairly similar size: typical bond distances are Ti–O, 1.98 Å and Li–O, 2.16 Å [3]. Variations in local electroneutrality must certainly occur in the $\mathrm{Li_2TiO_3}$ solid solutions, but the cations should be able to reorganize themselves so as to minimize such effects. Thus, in the lithia-rich solid solutions the oxide ions that are co-ordinated to substitutional Li^+ ions must carry a considerable net negative charge. This charge may be balanced if the interstitial Li^+ ions are located in tetrahedral sites that are adjacent to these oxide ions. In this way, defect complexes formed by association of substitutional and interstitial Li^+ ions may perhaps occur. Similarly, in the titania-rich solid solutions, the oxide ions that are associated with the substitutional Ti^{4+} ions must carry a considerable net positive charge and this may be at least partially reduced if the cation vacancies are also associated with these same oxide ions.

An explanation of the large variation with composition in the rate of the high → low phase transition in $\mathrm{Li_2TiO_3}$ solid solutions may now be given, based on the above mechanism of solid solution formation. In $\mathrm{Li_2TiO_3}$ and the titania-rich solid solutions, the transition takes place extremely rapidly and cannot be prevented from occurring by quenching [1]. In lithia-rich solid solutions containing $\gtrsim 52\%$ $\mathrm{Li_2O}$, however, the disordered, high temperature solid solutions may be readily preserved to room temperature and they transform to the low temperature structure only quite slowly on annealing at high temperature [1].

In order to undergo the high → low transition, Li^+ and Ti^{4+} ions must reorganize themselves over the octahedral sites and clearly, this process is assisted greatly if there are already some octahedral sites vacant. In the titania-rich solutions, cation vacancies occur as a consequence of the solid solution mechanism and hence, the transition takes place rapidly. In the lithia-rich solid solutions, vacancies arise only through the thermal creation of defects, i.e. by the formation of Schottky and Frenkel defects at high temperatures. The number of such defects is likely to be small and is further reduced by the presence of a large number of interstitial Li^+ ions on tetrahedral sites, since interstitial Li^+ ions and cation vacancies will tend to annihilate each other. Thus, the destruction of Frenkel defects by recombination may be written as

$$\mathrm{Li}^+(\mathrm{tet}) + \mathrm{V}(\mathrm{oct}) \rightarrow \mathrm{Li}^+/\mathrm{V}(\mathrm{oct}). \tag{4}$$

In stoichiometric $\mathrm{Li_2TiO_3}$, a thermal equilibrium concentration of vacancies will be established by, for instance, the reverse of the above equation. In lithia-rich solid solutions, however, the large concentration of interstitial Li^+ ions will cause a great reduction in the concentration of vacancies. Hence the sluggishness of the transition in the lithia-rich solid solutions may be qualitatively explained.

References

1. G. IZQUIERDO and A. R. WEST, *Mater. Res. Bull.* **15** (1980) 1655.
2. M. CASTELLANOS and A. R. WEST, *J. Mater. Sci.* **14** (1979) 450.

3. International Tables for X-ray Crystallography, edited by K. Lonsdale, Vol. III (Kynoch Press, Birmingham, 1962).

Received 30 October
and accepted 2 December 1980

A. R. WEST
University of Aberdeen,
Department of Chemistry,
Meston Walk, Old Aberdeen,
Scotland

Compressive strength and glass transition temperature

An empirical relation between the compressive strength and the glass transition temperature of materials composed of mainly first-row elements of the periodic table is presented. This relation indicates that flexible-chain polymers have an intrinsically low strength in axial compression, which probably disqualifies them as a reinforcement fibre in composite materials that are subjected to bending vibrations.

For an effective development of a new material it is important to have some foreknowledge of the ultimate properties that may be attained.

In the case of extended polymer chains the maximum tensile modulus is determined by the force–displacement curve of two adjacent atoms in the chain and by the cross-sectional area of the chain [1]. Moduli calculated in this way closely approach the observed values [2]. For extended linear chains (flexible as well as rigid-rod) made up of first-row atoms the theoretical modulus lies between 180 and 250 GPa. In that case the tensile curve shows elastic and brittle behaviour.

The limit for the tensile strength of a brittle, elastic solid can be derived from the force–displacement curve between two atoms. Accordingly, the theoretical strength σ_t is estimated to be [3]

$$\sigma_t \approx \frac{E}{10} \qquad (1)$$

where E is the tensile modulus. Applying Equation 1 a theoretical upper limit for the strength of about 25 GPa is derived for linear polymers. Experimentally, the fractural stress is of the order of 10 to 100 times less than σ_t.

A third important property is the strength in axial compression; commonly designated as the compressive stress at which yielding occurs. In many constructions the materials are subjected to compressive stress as in the case of bending vibrations. The phenomena which usually accompany compressive yielding of polymers are the well-known observations of kink and slip bands. These macro-distortions are large-scale manifestations resulting from the buckling of chains. In places where buckling takes place the chains are forced to adopt a very different conformation which may extend over a large part of the chain.

Below the glass transition or softening temperature, T_g, a polymer has glassy properties, above this temperature it has rubber-like properties and and near the melting point flow behaviour prevails. In the molecular interpretation of the glass–rubber transition of polymers this relaxation is associated with the onset of large-scale segmental motions in the chain. These motions are in fact large conformational changes at certain atoms in the main chain.

The amount of work required to bring about these conformational changes at compressive yielding may also be derived from the thermal energy, which becomes sufficiently large at the temperature T_g. Accordingly, such changes appear spontaneously in the material above T_g. Assuming elastic behaviour up to compressive yielding, for the compressive strength

$$\sigma_c = (2E_cW)^{1/2} \qquad (2)$$

can be written where W is the work per unit volume needed for yielding and E_c is the axially compressive modulus. The apparently common origin of phenomena such as compressive yielding and glass-transition, relating to chain flexibility and intermolecular interactions, suggests a correlation between σ_c and T_g.

In the compilation given in Table I materials have also been included which are actually three-dimensional networks in the amorphous or crystalline state. Here, however, they are regarded as three-dimensional polymers. The softening temperature cannot be properly defined for every

0022–2461/81/072025–04$02.40/0