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FORMATION MECHANISM, NUCLEATION AND CRYSTALLIZATION OF Li_2TiO_3 FROM FUSED SALTS

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During synthesis of Li_2TiO_3 *from a* $Li_2SO_4 + TiO_2 + Na_2CO_3$ *mixture in the molten alkali metal chloride media* Li_2CO_3 *is formed as the first intermediate product. Beside* Li_2TiO_3 *also* Na_2TiO_3 *is formed at lower temperatures. Above the temperature of 500° C the preferential formation of* Li_2TiO_3 *takes place.*

At temperatures below 800° C and short exposition times (1 and 2 min) the crystals of Li_2TiO_3 *in the size order of 50 – 100 nm are formed and a significant amount of amorphous phase is observed. The* Li_2TiO_3 *crystal growth at the temperatures of 800 and 900° C in the time interval from 1 to 30 min is controlled by the surface reaction, i.e. the dissolution and precipitation of* Li_2TiO_3.

The precipitation of double oxides from the inorganic melts is one of the most progressive technology of the preparation of the starting powders for high technology ceramics. This method allows the substantial lowering of the temperature and shortening of the preparation time in comparison with the classical solid state synthesis, the increasing of the product quality and especially the obtaining of powders of such a chemical and phase composition which preparation is difficult or inpossible by other methods [1 – 3]. The main advantage of the synthesis of mixed oxides in the molten salts media lies in the possibility of controlling the size of the crystals. The particles of a new phase nucleating from the liquid phase grow due to the material supply from the surroundings. The isothermal growth of the new phase particles in the presence of liquid phase (Ostvald rippening) takes place, the rate of which is given both by the temperature and the transport properties of the liquid phase. The size of the new phase may be controlled by suitable choice of the temperature and the time of the isothermal heating.

From the kinetic point of view two cases may be distinquished at the crystal growth in the presence of liquid phase. If the diffusion of the atoms in the melt is the slowest process then the diffusion controlled crystal growth takes place. If the dissolution and precipitation of atoms at the crystal surface is the slowest process then the crystal growth is controlled by chemical reaction. The exact matematical derivation of the equations for both cases was given by Lifshitz and Slyozov [4], Greenwood [5] and Wagner [6] for the growth of spherical particles in the liquid in which they are soluble.

For the diffusion controlled crystal growth Lifshitz and Slyzov [4] and Wagner [6] obtained

$$r^3 - r_0^3 = \frac{8\gamma c_0 D V^2}{9RT} t = k_d t \qquad (1)$$

where γ is the interfacial tension at the crystal-melt boundary, c_0 is the solubility of the solid phase in the melt, D is the diffusion coefficient of the solid phase in the melt, V is the molar volume of the solid phase, r_0 is the initial average radius of the particles and r is the average particle radius in time t. Greenwood [5] derived a similar equation for the growth of crystals of the double average diameter of all crystals. The Greenwood's solution differs from the eqn. (1) in the numerical coefficient (6 against 8/9).

In the case of the reaction controlled crystal growth the slowest process is the dissolution and precipitation of the solid phase atoms. For the time dependence of the average radius of all crystals Wagner [6] obtained

$$r^2 - r_0^2 = \frac{k_p \Delta c \gamma V^2}{RT} t = k_r t \qquad (2)$$

where k_p is the trasference constant, Δc is the supersaturation of the solid phase atoms at the solid-liquid boundary, γ is the interfacial tension, V is the molar volume of the solid phase, r_0 is the initial average crystal radius and r is the average crystal radius in the time t. Comparing eqn. (1) and (2) it follows that the crystal growth rate controlled by diffusion is substantially lower than the crystal growth rate controlled by chemical reaction.

In this paper, formation mechanism, morphology and crystal growth of Li_2TiO_3 in the molten micture containing different reactants was studied as a function of temperature and time. From the analysis of the time dependences of the average crystal size a tentative control process of the Li_2TiO_3 crystal growth was determined.

Li_2TiO_3 crystallizes in the monoclinic system with a space group C' 2/c and is considered as an alternating construction material for the molten carbonate fuell cells.

EXPERIMENTAL

The mixed oxide Li_2TiO_3 was prepared by the reaction of titanium oxide, lithium sulphate and sodi-

um carbonate in the medium of molten alkali metal chlorides according to the eqn.

$$Li_2SO_4(l) + TiO_2(s) + Na_2CO_3(l) = Li_2TiO_3(s) + Na_2SO_4(l) + CO_2(g). \quad (3)$$

The twofold amount of NaCl, KCl and equimolar mixture NaCl + KCl at temperatures of 900, 800 and 700°C, respectively, was used as a flux. The total mass of reactants was 1 g. The platinum crucible with the mixture suspended on a ceramic holder with a Pt-PtRh10 thermocouple was inserted into a tempered furnace. Due to the low mass the temperature of the sample attained relatively soon the desired temperature. The exposure time was counted from the moment of the melting of the sample up to the pull up from the furnace. The exposure times were in the range 1 – 30 min. After the thermal exposure and cooling the mixture was dissoluted in a hot distilled water. The insoluble remainder was filtered, washed with a distilled water and dried at 120°C.

The composition of the samples was determined by means of the X-ray diffraction analysis. The morphology and size of the crystals were studied using a JEOL X5C scanning electrone microscope. The average crystal diameters were determined on the microphotographs by direct measurement of more then 100 individual crystals.

The mechanism and the kinetics of the reaction was studied by means of the thermogravimetric method, recording the sample weight loss due to the CO_2 escape. The obtained results were compared with the course of reaction performed without the flux at the temperatures of 300, 500, 700 and 900°C after the 30 min exposure using a X-ray diffraction analysis.

Table I

Phase composition and the diffraction ability of samples prepared according to eqn. (3). The sequence of individual phases corresponds to their relative content in the sample

θ/°C	t/s	present phases	diffr. ability
700	70	Li_2CO_3, TiO_2, Li_2TiO_3, Na_2TiO_3	good
	120	Li_2TiO_3, Li_2CO_3, TiO_2, Na_2TiO_3	weak
	300	Li_2TiO_3, Li_2CO_3, TiO_2	weak
	600	Li_2TiO_3, Li_2CO_3, TiO_2	weak
	1200	Li_2TiO_3	weak
	1800	Li_2TiO_3	weak
800	70	Li_2TiO_3, Li_2CO_3, TiO_2, Na_2TiO_3	weak
	120	Li_2TiO_3, Li_2CO_3, TiO_2	weak
	300	Li_2TiO_3	good
	600	Li_2TiO_3	good
	1200	Li_2TiO_3	good
	1800	Li_2TiO_3	good
900	70	Li_2TiO_3, Li_2CO_3, Na_2TiO_3	good
	120	Li_2TiO_3, Li_2CO_3, Na_2TiO_3	good
	300	Li_2TiO_3, Li_2CO_3, Na_2TiO_3	good
	600	Li_2TiO_3	good
	1200	Li_2TiO_3	good
	1800	Li_2TiO_3	good

RESULTS AND DISCUSSION

A. Reaction mechanism of Li_2TiO_3 precipitation

The results of the X-ray powder analysis of the samples heated at desired temperatures and times are given in Table I. From the table it follows that after a short exposure time the samples contained beside the reaction product, Li_2TiO_3, still TiO_2 and the products of secondary reactions, Li_2CO_3 and Na_2TiO_3. The phase sequence in Table I corresponds to their relative content in the sample. The Li_2CO_3 is formed in the mixture already at low temperatures by the exchange reaction

$$Li_2SO_4 + Na_2CO_3 \rightleftharpoons Li_2CO_3 + Na_2SO_4 \quad (4)$$

$$\Delta G^\circ(600\ K) = -27.6\ kJ/mol.$$

Obviously, in the presence of sodium carbonate originates temporarily in the first stages also Na_2TiO_3. Its formation is supported also by the surplus of sodium ions coming from the NaCl containing flux (cf. Table I, 700 and 900°C). The results of the thermogravimetric measurements of the 1 : 1 molar ratio Li_2CO_3 + TiO_2 and Na_2CO_3 + TiO_2 mixtures are shown in Fig. 1 as a dependence of the relative weight loss of the starting mixture on temperature at a constant heating rate. It is obvious that the formation of Li_2TiO_3 is at lower temperatures less intensive than the formation of Na_2TiO_3. At temperatures above 500°C, however, the reaction of Li_2TiO_3 formation is faster and terminates also at lower temperature (ca 900°C).

The conversion degree of titanium oxide to the respective double oxide was estimated also on the basis of the semiquantitative X-ray analysis of the above mentioned mixtures heated during 30 min at the temperatures of 300, 500, 700 and 900°C. The intensities of the 0.222 nm, 0.207 nm and 0.352 nm diffraction

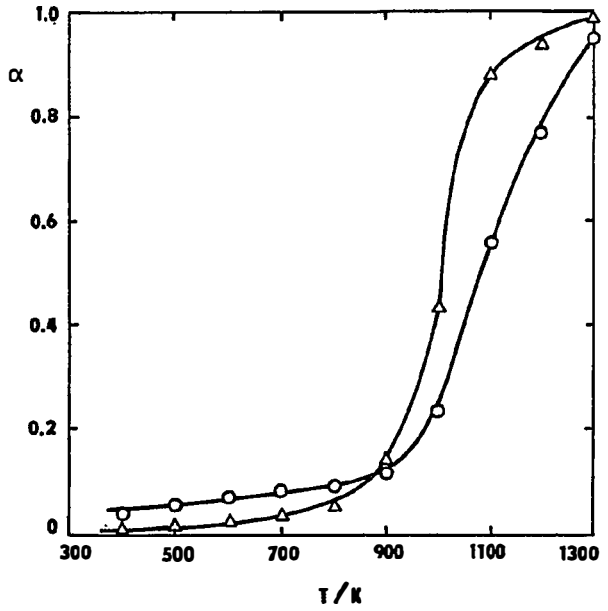

Fig. 1. The relative weight loss of the starting mixture at heating rate 10° C/min. (Mass of the sample 250 mg). Δ – $Li_2CO_3 + TiO_2$, o – $Na_2CO_3 + TiO_2$.

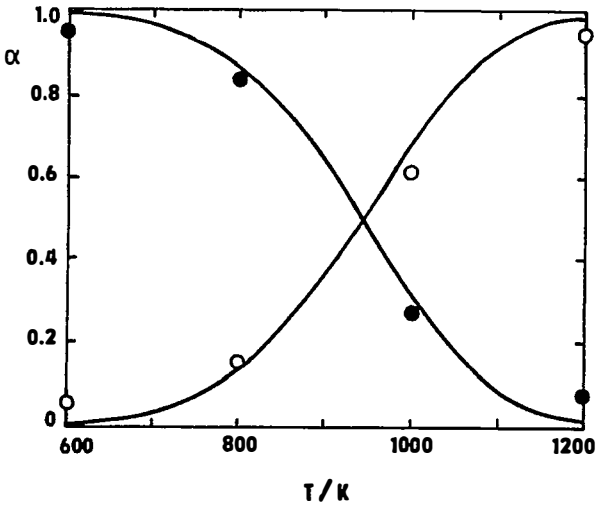

Fig. 2. The dependence of the conversion degree on the temperature for the mixture $Li_2CO_3 + TiO_2$ *at constant time.* ● – TiO_2, o – Li_2TiO_3 *experimental points,* ——— *theoretical course according to eqn. (7) for* $A' = 2.9$ *and* $E = 70$ *kJ/mol.*

lines for Na_2TiO_3, Li_2TiO_3 and TiO_2, respectively, were followed. The relative concentration error was 10%.

For the conversion degree of TiO_2 to a double oxide, α ,the following general kinetic equation is valid [7,8]

$$\alpha = 1 - \exp(Kt^n) , \tag{5}$$

where K is the rate constant, t is the time and n is a function of the reaction mechanism, the nucleation rate as well as the geometrical factors. The temperature dependence of the rate constant can be described by means of the Arrhenius eqn.

$$K = A\exp(-E/RT) , \tag{6}$$

where E is the activation energy of the reaction. Assuming that the reaction runs at all temperatures with the same mechanism and for the case of the constant time t, we get substituting eqn. (6) into the eqn. (5)

$$\alpha = 1 - \exp[A' \exp(-E/RT)] , \tag{7}$$

where $A' = At^n$. Equation (7) describes the course of TiO_2 conversion to the respective double oxide very well for $n = 1$. The dependences of the conversion degree α on the temperature are shown in Figs. 2 and 3 and compared with the theoretical course calculated according to eqn. (7). For the activation energies of the reactions

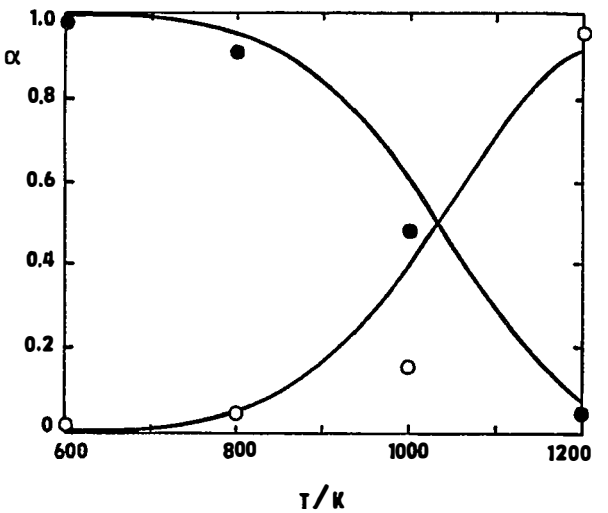

Fig. 3. The dependence of the conversion degree on the temperature for the mixture $Na_2CO_3 + TiO_2$ *at constant time.* ● – TiO_2, o – Na_2TiO_3 *experimental points,* ——— *theoretical course according to eqn. (7) for* $A' = 4.3$ *and* $E = 80$ *kJ/mol.*

$$Me_2CO_3 + TiO_2 = Me_2TiO_3 + CO_2 \tag{8}$$

(Me = Li, Na)

the values $E(Li_2TiO_3) = 70$ kJ/mol and $E(Na_2TiO_3) = 80$ kJ/mol were accepted. These values are in a good accordance with the mean values of the reaction enthalpies of formation of the respective mixed oxide

Table II

Average crystal diameters of Li_2TiO_3 prepared at the temperatures of 800 and 900°C

t/s	d/μm	
	800°C	900°C
70	0.11	0.19
120	-	0.24
300	0.10	0.24
600	0.14	0.32
1200	0.18	0.39
1800	0.24	0.57
3600+	-	1.27
7200+	-	1.34

+ results given in [11]

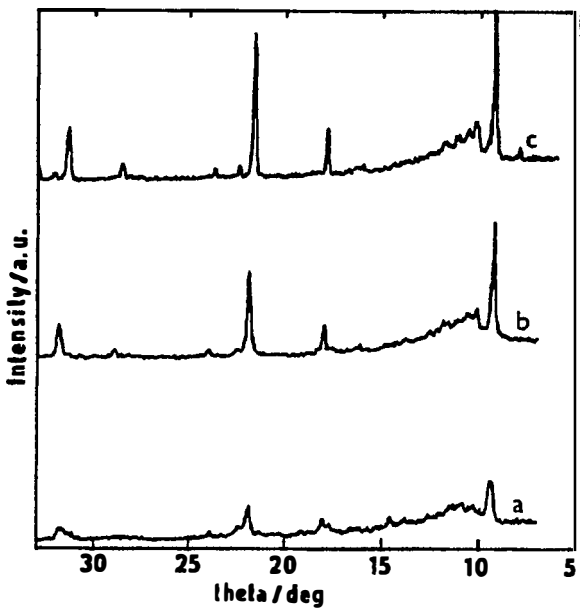

Fig. 10. Diffraction patern of the powdered Li_2TiO_3. *Conditions of preparation: a) 800° C, 120 s. b) 800° C, 1200 s., c) 900° C, 1200 s.*

in the given temperature interval $\Delta_f H(Li_2TiO_3)$ = 79 kJ/mol and $\Delta_f H(Na_2TiO_3)$ = 89 kJ/mol [9, 10].

B. Crystallization kinetics of Li_2TiO_3

The values of the average Li_2TiO_3 crystal diameters for the individual exposure times at the temperatures of 800 and 900°C are given in Table II. The average diameters of crystals prepared at 700°C have not been determined, because of their nondistinct habitus also at the 30 000-fold magnification (the higher magnification was not possible). The microphotographs of the Li_2TiO_3 crystals prepared at the individual temperatures in the initial and final crystallization stage are shown in Figs. 4 – 9 for illustration. From the figures it follows that the crystal growth is strongly influenced by temperature. The diffraction patterns of the samples prepared at 700°C and also at 800°C for short times show a significant amount of amorphous phase, which refer to a considerable portion of surfaces against the crystal volume (cf. Fig. 10). As follows from the respective microphotographs the particles in such cases were in the range of 50 – 100 nm. The diffraction ability of such powders was very weak. Well developed Li_2TiO_3 crystals with a good diffraction ability originate until the temperature of 900°C.

The regression analysis of data given in Table II shows, that the crystal growth of Li_2TiO_3 may be described by eqns.

$$\frac{d^2(800)}{\mu m^2/s} = 3.02 \times 10^{-5} t \quad (s = 0.006\ \mu m^2) \qquad (9)$$

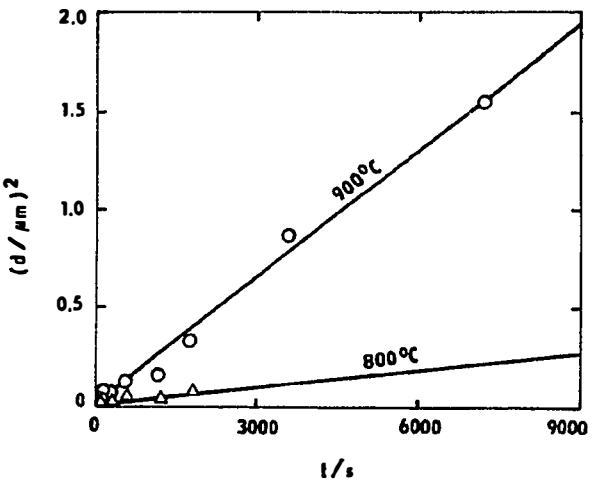

Fig. 11. The dependence of the square of the average crystal diameter of Li_2TiO_3 *on the exposure time.* Δ – *800° C,* o – *900° C.*

$$\frac{d^2(900)}{\mu m^2/s} = 2.18 \times 10^{-4} t \quad (s = 0.06\ \mu m^2) \qquad (10)$$

and is therefore controlled by the surface reaction. The dependence of the square of the average crystal diameters on the exposure time at the temperatures of 800 and 900°C are shown in Fig. 11. These dependences have an unambiquous linear character, the absolute term, d_0^2, was on the 0.95 confidence level statistically nonimportant. In the regression analysis

were included also the average crystal diameter data for 1 and 2 h, given in [11]. The dependence of the cube of the average crystal diameters on the exposure time at both temperatures was a second, resp. third power one.

CONSLUSION

During the synthesis of Li_2TiO_3 from the $Li_2SO_4 + Na_2CO_3 + TiO_2$ mixture in the medium of molten alkali metal chlorides Li_2TiO_3 originates as the first intermediate phase. Beside it, at lower temperatures also Na_2TiO_3 occurs. Above the temperature of 500°C, Li_2TiO_3 is formed preferentially.

At temperatures bellow 800°C and shorter exposure times Li_2TiO_3 crystals with a size order of 50 – 100 nm containing a significant amount of amorphous phase were observed. The crystal growth of Li_2TiO_3 at temperatures of 800 and 900°C is controlled by surface reaction, i.e. by dissolution and precipitation of Li_2TiO_3.

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MECHANIZMUS TVORBY, NUKLEÁCIA A KRYŠTALIZÁCIA Li_2TiO_3 Z ROZTAVENÝCH SOLÍ

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Uskutočnilo sa štúdium mechanizmu tvorby a kinetiky kryštalizácie Li_2TiO_3 v taveninových zmesiach obsahujúcich rôzne reaktanty, ako funkcie teploty a doby záhrevu. Pri syntéze Li_2TiO_3 zo zmesi $Li_2SO_4 + TiO_2 + Na_2CO_3$ v prostredí roztavených chloridov alkalických kovov vzniká ako prvý medziprodukt Li_2CO_3. Popri Li_2TiO_3 sa pri nižších teplotách tvorí aj Na_2TiO_3. Pri teplotách nad 500°C dochádza k prednostnej tvorbe Li_2TiO_3 (pozri tabulku I).

Pri teplotách pod 800°C a krátkych expozičných dobách (1 a 2 min) vznikajú kryštály Li_2TiO_3 s veľkosťou 50 – 100 nm a pozorovala sa prítomnosť signifikantného podielu amorfnej fázy. Rast kryštálov Li_2TiO_3 pri teplotách 800 a 900°C v časovom intervale 1 až 30 min je riadený povrchovou reakciou, t.j. rozpúšťaním a precipitáciou Li_2TiO_3 (pozri obrázok 11).

Obr. 1. Relatívna strata hmotnosti východiskovej zmesi pri rýchlosti záhrevu 10° C/min. (Hmotnost vzorky 250 mg). Δ – $Li_2CO_3 + TiO_2$, o – $Na_2CO_3 + TiO_2$.

Obr. 2. Závislosť stupňa konverzie od teploty pre zmes $Li_2CO_3 + TiO_2$ *pri konštantnom čase.* ● – TiO_2, o – Li_2TiO_3 *experimentálne body,* ——— *teoretický priebeh podľa rovnice (7) pre* $A' = 2.9$ *a* $E = 70$ *kJ/mol.*

Obr. 3. Závislosť stupňa konverzie od teploty pre zmes $Na_2CO_3 + TiO_2$ *pri konštantnom čase.* ● – TiO_2, o – Na_2TiO_3 *experimentálne body,* ——— *teoretický priebeh podľa rovnice (7) pre* $A' = 4.3$ *a* $E = 80$ *kJ/mol.*

Obr. 4. Kryštály Li_2TiO_3 *pripravené pri 700° C za 300 s.*

Obr. 5. Kryštály Li_2TiO_3 *pripravené pri 700° C za 1800 s.*

Obr. 6. Kryštály Li_2TiO_3 *pripravené pri 800° C za 300 s.*

Obr. 7. Kryštály Li_2TiO_3 *pripravené pri 800° C za 1200 s.*

Obr. 8. Kryštály Li_2TiO_3 *pripravené pri 900° C za 300 s.*

Obr. 9. Kryštály Li_2TiO_3 *pripravené pri 900° C za 1200 s.*

Obr. 10. Difrakčný záznam práškového Li_2TiO_3. *Podmienky prípravy: a) 800° C, 120 s. b) 800° C, 1200 s., c) 900° C, 1200 s.*

Obr. 11. Závislosť druhej mocniny stredného priemeru kryštálov Li_2TiO_3 *od času expozície.* Δ – *800° C,* o – *900° C.*

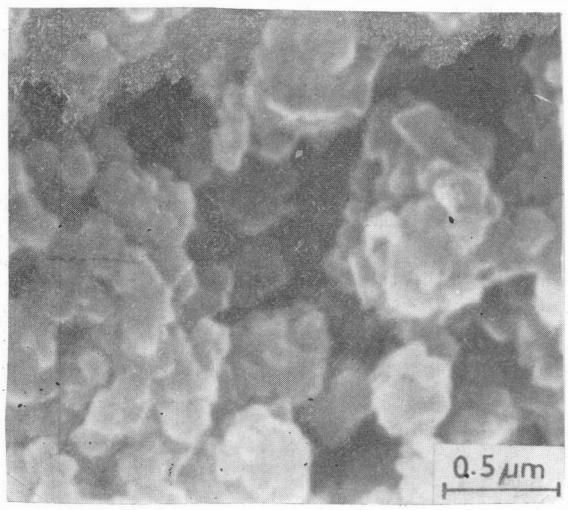

Fig. 4. Li_2TiO_3 *crystals prepared at 700° C for 300 s.*

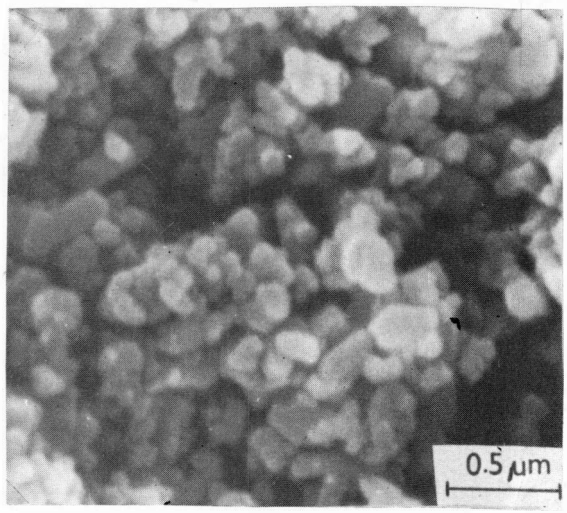

Fig. 6. Li_2TiO_3 *crystals prepared at 800° C for 300 s.*

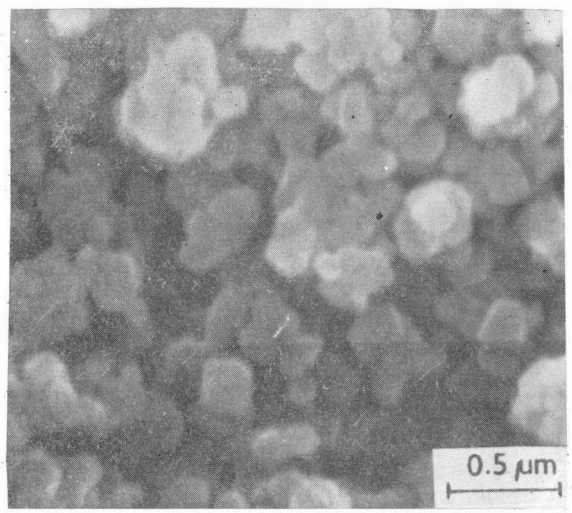

Fig. 5. Li_2TiO_3 *crystals prepared at 700° C for 1800 s.*

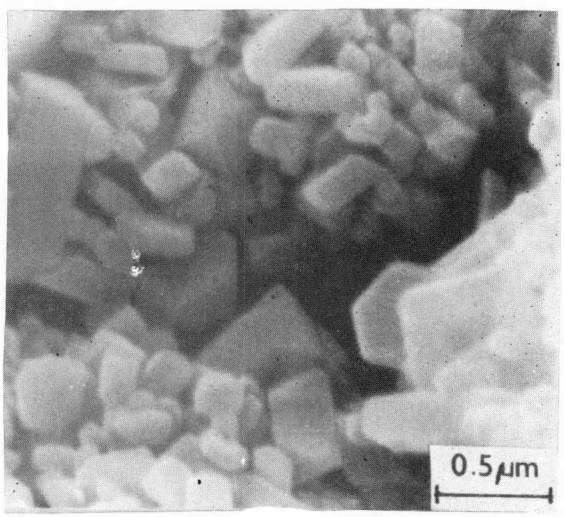

Fig. 7. Li_2TiO_3 *crystals prepared at 800° C for 1200 s.*

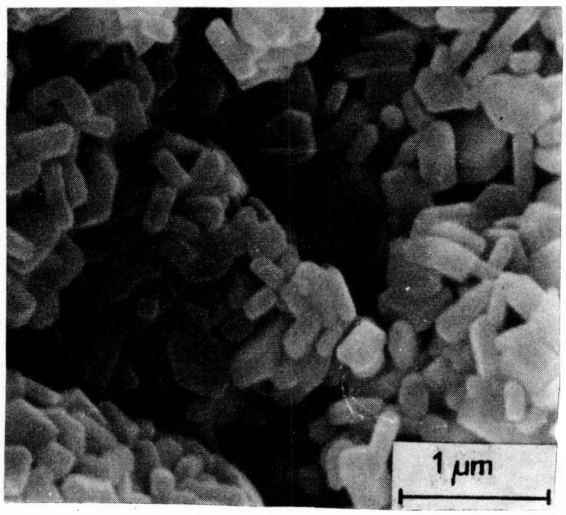

Fig. 8. Li_2TiO_3 *crystals prepared at 900° C for 300 s.*

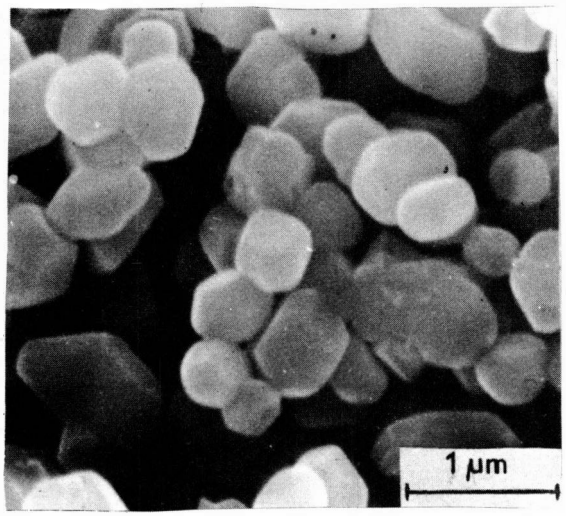

Fig. 9. Li_2TiO_3 *crystals prepared at 900° C for 1200 s.*