Original Papers

REACTION MECHANISM AND KINETICS OF $SrTiO_3$ CRYSTAL GROWTH IN MOLTEN ALKALI METAL CHLORIDES MEDIUM

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The reaction mechanism of strontium titanium oxide $SrTiO_3$ formation and the kinetics of its crystal growth from the molten mixture of alkali metal chlorides in the temperature range of 700–900° C and the exposition time of 1 to 30 min were studied.

During the synthesis of $SrTiO_3$ from the molten mixture of $SrSO_4$ + Na_2CO_3 + TiO_2 + KCl + NaCl the sodium titanium oxide, Na_2TiO_3, arises in the first step. Above 500° C strontium carbonate is formed temporarily as well. The double oxide Na_2TiO_3 reacts with strontium sulphate and strontium carbonate forming the double oxide $SrTiO_3$.

In the investigated temperature interval and the exposition times the average diameter of the synthetized $SrTiO_3$ crystals was in the range of 0.08–0.19 μm. It was found that the $SrTiO_3$ crystal growth at the temperatures of 800 and 900° C and in the time interval of 1 min up to 4 h is controlled by the diffusion of Sr and Ti through the liquid phase.

INTRODUCTION

The double oxide $SrTiO_3$ is an alternative construction material for electrolyte matrix and electrodes for molten carbonate fuel cells [1, 2]. Besides, it is also a suitable support for high temperature ceramic superconductors [3]. Fine dispersed $SrTiO_3$ powders may by prepared with advantage by precipitation in the molten salts media [4]. In the present work the reaction mechanism of the $SrTiO_3$ formation in the molten alkali metal chloride mixture in terms of the temperature and time of heating as well as the kinetics of the crystal growth were studied. On the basis of the statistical analysis of the time dependences of the average crystal diameters the probable control mechanism of the isothermal crystal growth of $SrTiO_3$ and by means of the procedure described in [5] also the activation energy of its formation were determined.

EXPERIMENTAL

The double oxide $SrTiO_3$ was prepared by the reaction of titanium oxide with strontium sulphate and sodium carbonate in the medium of molten alkali metal chlorides according to the eqn.

$$SrSO_4(l) + TiO_2(s) + Na_2CO_3(l) = \quad (1)$$
$$= SrTiO_3(s) + Na_2SO_4(l) + CO_2(g)$$

NaCl at the temperature of 900°C, KCl at 800°C and the equimolar mixture NaCl + KCl at 700°C were used as flux. A similar set of samples without flux were investigated for comparison. The preparation procedure is desribed in detail in [5].

The composition of samples was determined by means of the X-ray powder diffraction phase analysis. The morphology and the size of the crystals of the powdered products were studied using a scanning electron microprobe JEOL X5C. The average diameter of crystals was determined in the microphotographs by direct measurement of the individual crystal size in a set of minimum 100 crystals. For the reaction mechanism study the thermogravimetric analysis was used as well.

RESULTS AND DISCUSSION

A. Reaction mechanism of the $SrTiO_3$ precipitation

The thermogravimetric analysis was carried out with the aim to determine the weight loss in the investigated mixtures $SrCO_3$ + TiO_2, $SrSO_4$ + Na_2CO_3 + TiO_2 and $SrSO_4$ + Na_2CO_3 + TiO_2 + NaCl + KCl due to the CO_2 evolution during the reaction (1). The results of the thermogravimetric analysis of the investigated samples in terms of the temperature are given in Table I. It is obvious that from among the three investigated mixtures the most intensive $SrTiO_3$ formation occurs in the $SrSO_4$ + Na_2CO_3 + TiO_2 + NaCl + KCl mixture whereas the slowest formation takes place in the $SrCO_3$ + TiO_2 one. While in the

Table I

Temperature dependence of the relative weight loss (in mass %) related to the CO_2 evolution at the $SrTiO_3$ formation

Θ/°C	Mass % of CO_2 loss in the mixtures		
	$SrCO_3 + TiO_2$	$SrSO_4 + TiO_2 + Na_2CO_3$	$SrSO_4 + TiO_2 + Na_2CO_3 + NaCl + KCl$
300	5.7	4.5	–
400	6.7	6.2	–
500	7.7	9.1	3.1
600	9.3	13.6	77.5
700	11.2	22.3	82.4
800	17.6	42.1	91.5
900	38.2	87.4	92.1
980	64.1	99.1	99.3

Table II

Phase composition of mixtures heated for 30 min at temperatures of 300 to 980°C. The phase ordering corresponds approximately to its relative content

Mixture	Θ/°C	Phase composition
$SrCO_3 + TiO_2$	300	$SrCO_3$, TiO_2
	500	$SrCO_3$, TiO_2
	600	$SrCO_3$, TiO_2
	700	$SrCO_3$, TiO_2, $SrTiO_3$
	800	$SrCO_3$, TiO_2, $SrTiO_3$
	900	$SrTiO_3$, $SrCO_3$, TiO_2
	980	$SrTiO_3$, $SrCO_3$, TiO_2
$SrSO_4 + TiO_2 + Na_2CO_3$	300	$SrSO_4$, Na_2CO_3, TiO_2
	500	$SrSO_4$, Na_2CO_3, TiO_2
	600	$SrSO_4$, TiO_2, Na_2CO_3, $SrCO_3$, Na_2SO_4
	700	$SrTiO_3$, TiO_2, $SrSO_4$, $SrCO_3$, Na_2SO_4
	800	$SrTiO_3$, $SrSO_4$, Na_2SO_4, TiO_2, $SrCO_3$
	900	$SrTiO_3$, Na_2SO_4
	980	$SrTiO_3$, Na_2SO_4
$SrSO_4 + TiO_2 + Na_2CO_3 + NaCl + KCl$	300	KCl, NaCl, $SrSO_4$, TiO_2, Na_2CO_3
	500	KCl, NaCl, $SrTiO_3$, TiO_2
	600	$SrTiO_3$, TiO_2*
	700	$SrTiO_3$*
	800	$SrTiO_3$*
	900	$SrTiO_3$*
	980	$SrTiO_3$*

*the flux components were not followed

former mixture the reaction starts at 400°C and ends practically at 980°C, in the latter one the reaction begins at 600°C and at 980°C is still not over.

The phase composition of the investigated three mixtures heated at the temperatures of 300 to 980°C for 30 min was determined by means of the X-ray powder diffraction analysis. From the results of analysis, summarized in Table II, it follows that at temperatures above 500°C an exchange reaction

$$SrSO_4 + Na_2CO_3 \rightleftharpoons SrCO_3 + Na_2SO_4 \qquad (2)$$

$$\Delta G_r^0(800\ K) = -43.9\ kJ/mol$$

takes place. The conversion degree of TiO_2 to the double oxide $SrTiO_3$ was estimated using a semiquantitative X-ray analysis. The intensities of the diffraction peaks at 0.276, 0.225 and 0.159 nm for $SrTiO_3$ and at 0.352 nm for TiO_2 were measured. In Fig. 1–3 the dependences of the conversion degrees, α, on the temperature for all three investigated mixtures are shown and compared with the theoretical curve calculated according to the eqn. [5].

$$\alpha = 1 - \exp[A' \exp(-E/RT)] \qquad (3)$$

where $A' = At^n$, t is time, n is a function of the reaction mechanism, of the nucleation rate and of the steric factor, A is the frequency factor in the Arrhenius equation, and E is the activation energy. From Figs. 1–3 it follows that eqn. (3) describes very well the experimentally determined course of the TiO_2 conversion to the double oxide $SrTiO_3$ for n = 1 and for following values of the activation energy: $E(SrTiO_3)$ = 100 kJ/mol for the $SrCO_3$ + TiO_2 mixture, $E(SrTiO_3)$ = 70 kJ/mol for the $SrSO_4$ + Na_2CO_3 + TiO_2 mixture and $E(SrTiO_3)$ = 100 kJ/mol for the $SrSO_4$ + Na_2CO_3 + TiO_2 + NaCl + KCl mixture.

From the results of the thermogravimetric analysis, of the semiquantitative X-ray diffraction analysis as well as from the reaction Gibbs energy values for individual possible reaction schemes the following conclusions may be deduced:

- The formation of $SrTiO_3$ from the mixture of strontium sulphate, sodium carbonate and titanium oxide realizes across Na_2TiO_3 as an intermediate product. Na_2TiO_3 arises in this mixture already at low temperatures [5] and reacts in the next step with strontium sulphate and strontium carbonate, respectively,

$$Na_2TiO_3 + SrSO_4 \rightleftharpoons SrTiO_3 + Na_2SO_4 \qquad (4)$$

$$\Delta G_r^0(700\ K) = -76.0\ kJ/mol$$

$$Na_2TiO_3 + SrCO_3 \rightleftharpoons SrTiO_3 + Na_2CO_3 \qquad (5)$$

$$\Delta G_r^0(700\ K) = -33.3\ kJ/mol$$

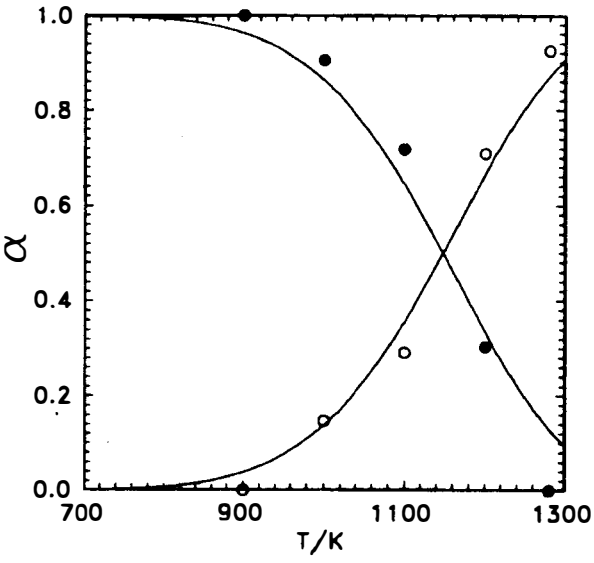

Fig. 1. Dependence of the conversion degree on the temperature for the mixture $SrCO_3$ + TiO_2 at constant time 30 min. ● - TiO_2; ○ - $SrTiO_3$; ——— according to eqn. (3) for A' = 13,7 and E = 100 kJ/mol.

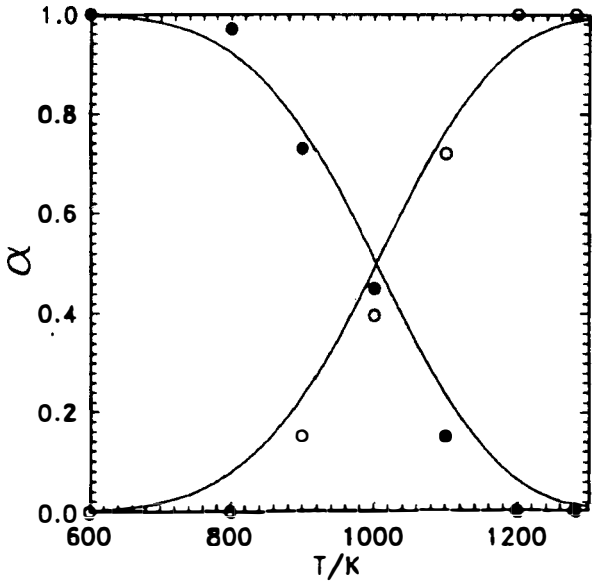

Fig. 2. Dependence of the conversion degree on the temperature for the mixture $SrSO_4$ + TiO_2 + Na_2CO_3 at constant time 30 min. ● - TiO_2; ○ - $SrTiO_3$; ——— according to eqn. (3) for A' = 1,7 and E = 70 kJ/mol.

- Alkali metal chlorides, which are added to the mixtures as a flux, exhibit favourable influence to the $SrTiO_3$ formation due to the improvement of the diffusion conditions. As mentioned in [5], the

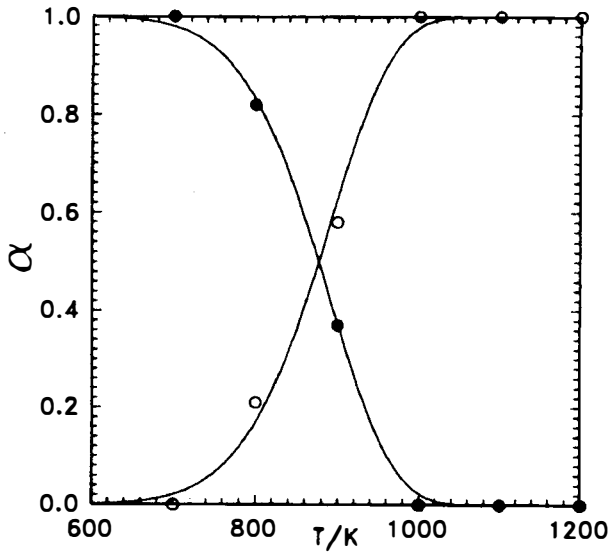

Fig. 3. Dependence of the conversion degree on the temperature for the mixture $SrSO_4$ + TiO_2 + Na_2CO_3 + KCl + NaCl at constant time 30 min. ● – TiO_2; ○ – $SrTiO_3$; ——— according to eqn. (3) for A' = 350 and E = 100 kJ/mol.

Table III

Average diameters of $SrTiO_3$ crystals prepared from the mixture $SrSO_4$ + TiO_2 + Na_2CO_3 + NaCl + KCl at temperatures of 700, 800 and 900°C

700°C		800°C		900°C	
t/s	$\bar{d}/\mu m$	t/s	$\bar{d}/\mu m$	t/s	$\bar{d}/\mu m$
139	0.102	64	0.087	120	0.083
317	0.096	136	0.097	300	0.055
450	0.068	302	0.084	300	0.101
630	0.098	605	0.107	585	0.148
1815	0.149	1250	0.153	585	0.101
		1250	0.168	585	0.161
				1190	0.155
				1190	0.179
				1190	0.170
				1935	0.147
				1935	0.194
				1935	0.135
				3600	0.189*
				7200	0.256*
				10800	0.281*
				14400	0.343*

*taken from [4]

surplus of alkali metal chlorides in the Na_2CO_3 + TiO_2 mixture shifts the reaction equilibrium to the side of the Na_2TiO_3 formation and supports so the $SrTiO_3$ formation according to eqns. (4) and (5).

B. Kinetics of the $SrTiO_3$ crystal growth

Microphotographs of the $SrTiO_3$ crystals prepared at temperatures of 700, 800 and 900°C in the medium of molten alkali metal chlorides according to eqn. (1) in the starting and final stage of crystallization are shown in Figs. 4a–4f for illustration. The favourable influence of the temperature and the time on the $SrTiO_3$ crystal growth is obvious. The average values of the crystal diameters of $SrTiO_3$ for the exposition time of 1 min to 4 h at the temperature of 900°C and for times of 1 to 30 min at temperatures of 800 and 700°C are given in Table III. With respect to the low number of experimental data and the narrow time interval at the temperature of 700°C only the values obtained at temperatures of 800 and 900°C were used for the determination of the rate controling process. The dependences of the cube of the average crystal diameter of $SrTiO_3$ on the exposure time at temperatures of 800 and 900°C are shown in Figs. 5 and 6. Using the regression analysis the third power equations

$$\frac{\bar{d}^3(800)}{\mu m^3} = 2.5 \times 10^{-6} t/s \qquad (6)$$

$$\frac{\bar{d}^3(900)}{\mu m^3} = 2.7 \times 10^{-6} t/s \qquad (7)$$

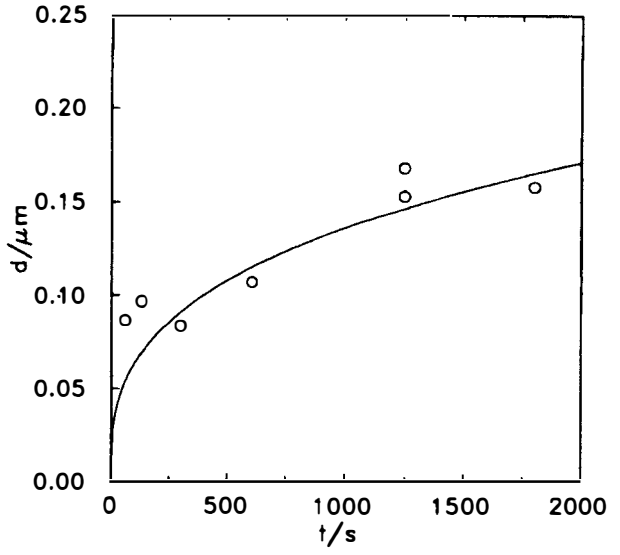

Fig. 5. Dependence of the average diameter of $SrTiO_3$ crystals on the heating time at the temperature of 800° C. ○ – experimental; ——— according to eqn. (6).

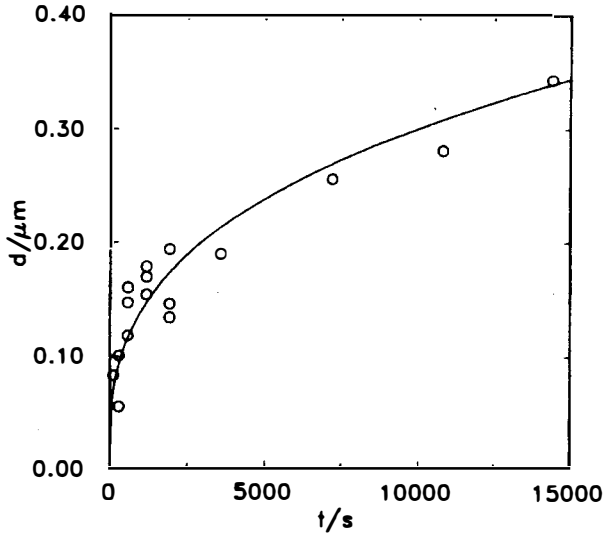

Fig. 6. Dependence of the average diameter of $SrTiO_3$ crystals on the heating time at the temperature of 900° C. o – experimental; ———— according to eqn. (7).

shows an unambiguous linear character. The standard deviations of the measured values from the regression function were $s(800) = 0.003\ \mu m^3$ and $s(900) = 0.002\ \mu m^3$. It may be therefore concluded that the $SrTiO_3$ crystal growth in the medium of alkali metal chlorides in the temperature interval of 800–900°C and in the time interval of 1 min to 4 h is controled by the diffusion of Sr and Ti in the liquid phase.

References

[1] Lovering, D. G.: *Molten Salt Technology*, Plenum Press, New York, London 1982.

[2] Lessing, P. A., Miller, G. R. and Yamada, H.: J. Electrochem. Soc. *133*, 1537 (1986).

[3] Gao, W., Li, S. C., Rudman, D. A., Yurek, G. J. and Vander-Sander, J. B.: Appl. Phys. Lett. *55*, 2227 (1989)

[4] Smutná, Ľ., Daněk, V. and Matiašovský, K.: Ceramics – Silikáty *34*, 49 (1990).

[5] Lubyová, Ž. and Daněk, V.: Ceramics – Silikáty, *36*, 21 (1992).

REAKČNÝ MECHANIZMUS A KINETIKA RASTU KRYŠTÁLOV $SrTiO_3$ V PROSTREDÍ ROZTAVENÝCH CHLORIDOV ALKALICKÝCH KOVOV

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Študoval sa reakčný mechanizmus vzniku a kinetika rastu kryštálov $SrTiO_3$ v prostredí roztavených chloridov alkalických kovov v teplotnej oblasti 700–900° C a pri časoch záhrevu od 1 do 30 min.

Pri syntéze zo zmesi $SrSO_4 + Na_2CO_3 + TiO_2 + KCl + NaCl$ vzniká najprv podvojný oxid sodno-titaničitý, Na_2TiO_3. Nad teplotou 500° C prechodne vzniká tiež uhličitan strontnatý. Podvojný oxid Na_2TiO_3 reaguje so síranom a uhličitanom strontnatým za tvorby podvojného oxidu $SrTiO_3$.

V sledovanej teplotnej oblasti a expozičnej dobe vznikaly kryštály $SrTiO_3$ poriadku 0,08–0,19 μm. Zistilo sa, že rýchlosť rastu kryštálov $SrTiO_3$ je pri teplotách 800 a 900° C a v časovom intervale od 1 min do 4 h riadená difúziou Sr a Ti cez kvapalnú fázu.

Obr. 1. Závislosť stupňa konverzie od teploty pre zmes $SrCO_3 + TiO_2$ pri konštantnom čase 30 min. ● – TiO_2; o – $SrTiO_3$; ———— podľa rovnice (3) pre A' = 13,7 a E = 100 kJ/mol.

Obr. 2. Závislosť stupňa konverzie od teploty pre zmes $SrSO_4 + TiO_2 + Na_2CO_3$ pri konštantnom čase 30 min. ● – TiO_2; o – $SrTiO_3$; ———— podľa rovnice (3) pre A' = 1,7 a E = 70 kJ/mol.

Obr. 3. Závislosť stupňa konverzie od teploty pre zmes $SrSO_4 + TiO_2 + Na_2CO_3 + KCl + NaCl$ pri konštantnom čase 30 min. ● – TiO_2; o – $SrTiO_3$; ———— podľa rovnice (3) pre A' = 350 a E = 100 kJ/mol.

Obr. 4. Mikrofotografie kryštálov $SrTiO_3$ pripravených v prostredí roztavených chloridov alkalických kovov podľa rovnice (1) pri rôznych teplotách v počiatočných a konečných fázach kryštalizácie. a – 700° C a 139 s, b – 700° C a 1815 s, c – 800° C a 64 s, d – 800° C a 1800 s, e – 900° C a 120 s, f – 900° C a 1935 s.

Obr. 5. Závislosť stredného priemeru kryštálov $SrTiO_3$ od doby záhrevu pri teplote 800° C. o – experiment; ———— podľa rovnice (6).

Obr. 6. Závislosť stredného priemeru kryštálov $SrTiO_3$ od doby záhrevu pri teplote 900° C. o – experiment; ———— podľa rovnice (7).

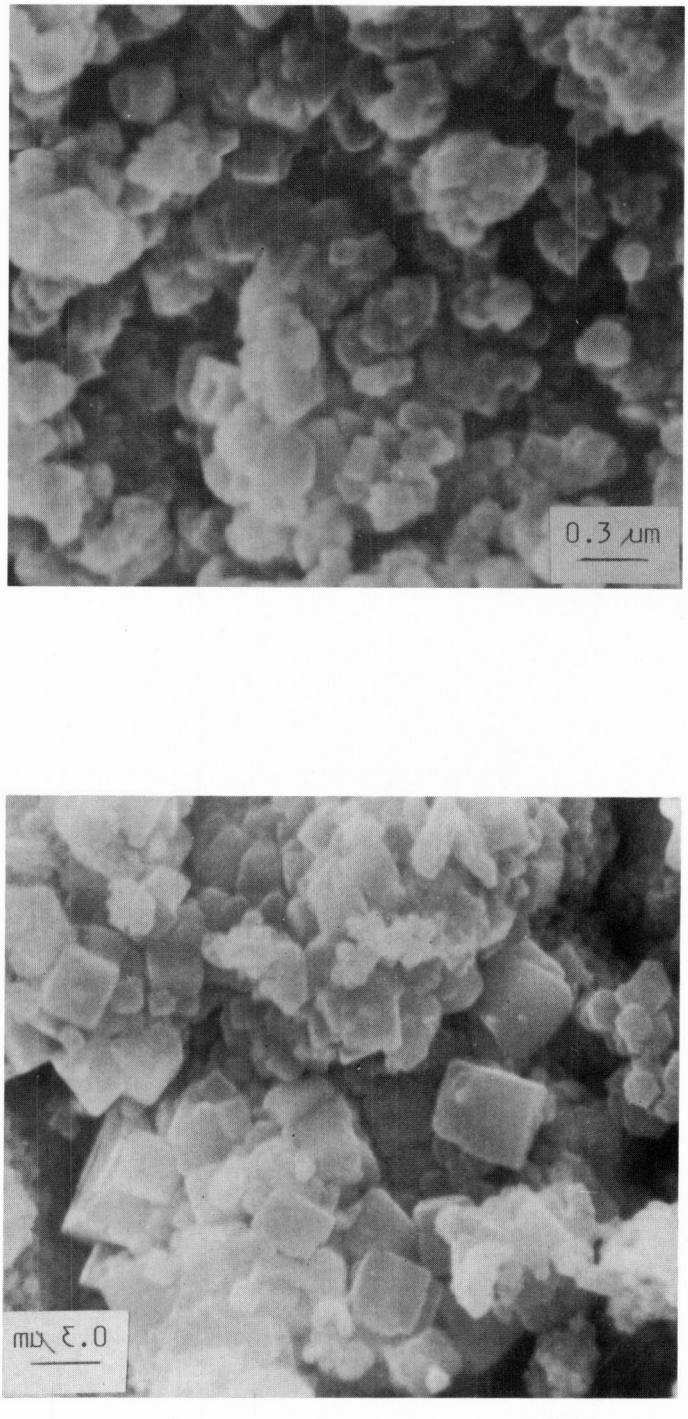
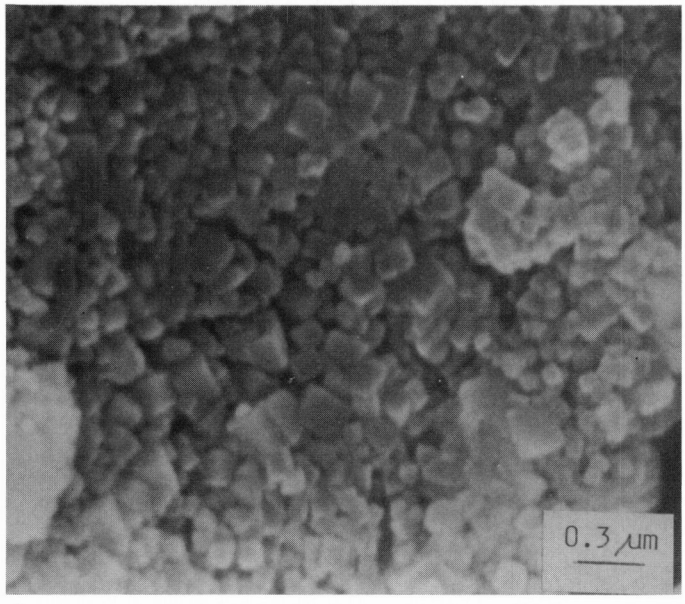
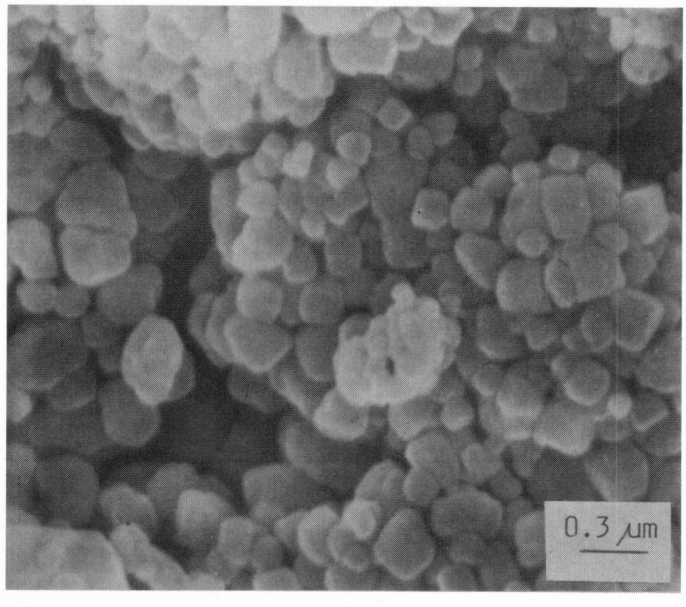
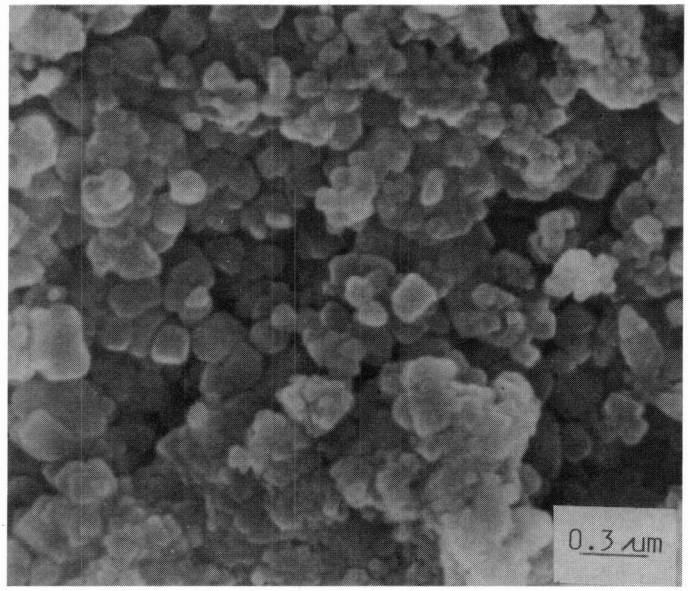


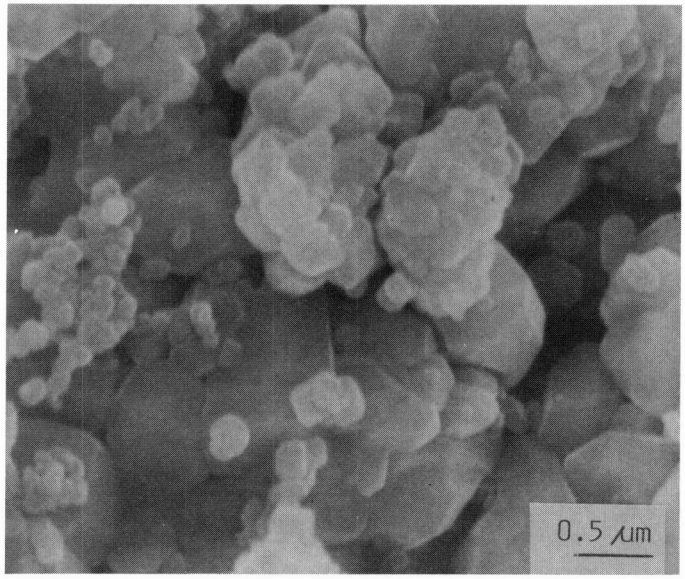
Fig. 4. Microphotographs of the $SrTiO_3$ crystals prepared in the medium of molten alkali metal chlorides according to eqn. (1) at different temperatures in the starting and final stage of crystallization. a – 700° C and 139 s, b – 700° C and 1815 s





c – 800° C and 64 s, d – 800° C and 1800 s





e – 900° C and 120 s, f – 900° C and 1935 s