Original Papers

SYNTHESIS OF $BaTi_3O_7$ IN MOLTEN SALTS

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$BaTi_3O_7$ is formed in the $BaTiO_3 + TiO_2$ mixtures by the solid state reactin as well as in the molten salts medium in the temperature and time intervals of 800–1200° C and 1–4 h, respectively. In the presence of liquid phase the $BaTi_3O_7$ formation rate is higher than that in the solid state. While in the solid state reaction the maximum conversion degree was ca 50%, in the presence of the flux the conversion degree attains ca 70% at the temperature of 1470 K. The conversion degree is favourably influenced also by the increasing temperature of the isothermal heating. The reaction time is not influenced by the reaction time in the range from 1 to 4 h, however, it affects the average size of the $BaTi_3O_7$ crystals. The activation energy of the $BaTi_3O_7$ formation has the value $\Delta E = 130$ kJ/mol for the reaction in the liquid as well as in the solid state. The isothermal heating of the stoichiometric mixtures $BaSO_4 + Na_2CO_3 + TiO_2$ and $BaCl_2 + Na_2CO_3 + TiO_2$ at the temperatures of 700–900° C to produce $BaTi_3O_7$ was not successful. The obtained product contained the mixture of $BaTiO_3$ and Na_2TiO_3.

In the system $BaO - TiO_2$ there exists a number of double oxides with important electrical and/or magnetic properties [1]. Till now practical use have found $BaTiO_3$ as ferroelectric dielectrics and $BaTi_4O_9$ as the basis of linear dielectrics with small temperature dependence of the permitivity [2].
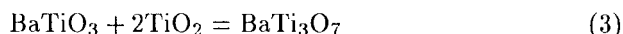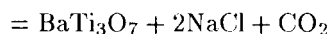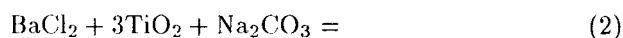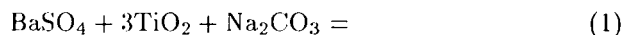
The preparation conditions of different barium – titanium double oxides from the $BaCO_3 + TiO_2$ mixtures by solid state reactions have been studied in [3]. Pure $BaTi_3O_7$ originates in the $BaCO_3 + TiO_2$ mixture with 1:3 mole ratio at the temperatures of 1200–1300°C and the heating time more than 1 h. The preparation of different barium – titanium double oxides with other stoichiometry than 1:1 by precipitation from molten salts was not described in the literature till now. The synthesis of equiaxed and rod – like $BaTiO_3$ crystals in molten alkali metal chlorides medium was studied in [4].

In the present work the experimental conditions for the synthesis of $BaTi_3O_7$ were therefore studied. The main stress was layed upon the possibility to lower the temperature and time of the thermal heating by application of the molten alkali metal chlorides as reaction medium.

EXPERIMENTAL

The synthesis of $BaTi_3O_7$ was attempted from the mixture of barium sulphate, or barium chloride, sodium carbonate and titanium oxide as well as from the mixture of barium titanate, $BaTiO_3$, and titanium oxide according to the equations

$$BaSO_4 + 3TiO_2 + Na_2CO_3 = \qquad (1)$$
$$= BaTi_3O_7 + Na_2SO_4 + CO_2$$

$$BaCl_2 + 3TiO_2 + Na_2CO_3 = \qquad (2)$$
$$= BaTi_3O_7 + 2NaCl + CO_2$$

$$BaTiO_3 + 2TiO_2 = BaTi_3O_7 \qquad (3)$$

The alkali metal chlorides were used as flux: the NaCl + KCl equimolar mixture at 700°C, potassium chloride at 800 °C and sodium chloride in the temperature range of 900–1200 °C. All reactants used were of reagent grade, Lachema Brno.

The starting stoichiometric mixtures containing 20 mass % of flux were homogenized for 24 h. Pellets of 8 mm in diameter and ca 0.6 g in mass were pressed from the mixtures for the measurements. The pellets were heated in the furnace at the temperatures of 800, 900, 1000, 1100 and 1200°C for 1, 2, 3 and 4 h. After the thermal exposure the composition of the samples was determined using the X-ray phase analysis and the X-ray microanalysis. The microstructure evolution was followed on the microphotographs of the polished cross-sections of the samples.

Table I

Experimental and calculated conversion degree in the
$BaTi_3O_7$ synthesis in the solid state reaction (3)

t/h	T/K	$\alpha(exp)$	$\alpha(calc)$
1	1070	0.00	0.03
	1170	0.10	0.10
	1270	0.26	0.24
	1370	0.40	0.40
	1470	0.36	0.48
2	1070	0.00	0.05
	1170	0.11	0.15
	1270	0.36	0.32
	1370	0.45	0.46
	1470	0.51	0.50
3	1070	0.00	0.04
	1170	0.12	0.13
	1270	0.28	0.29
	1370	0.49	0.44
	1470	0.49	0.50
4	1070	0.07	0.06
	1170	0.14	0.17
	1270	0.35	0.34
	1370	0.50	0.47
	1470	0.54	0.50

RESULTS AND DISCUSSION

The preparation of $BaTi_3O_7$ according to the equations (1) and (2) in the presence of molten sodium chloride was not successful. $BaTi_3O_7$ does not originate by heating the respective mixtures at the temperatures of 700–900°C. Beside alkali metal chlorides only $BaTiO_3$ was determined in the samples by X-ray phase analysis. The surplus TiO_2 reacts most probably with the present sodium salts (Na_2CO_3, Na_2SO_4, NaCl) forming the double oxide Na_2TiO_3, which evidently does not react with $BaTiO_3$ and is not suitable for the further synthesis to $BaTi_3O_7$. Due to very fine dispersion Na_2TiO_3 possessed low diffraction ability and might not be determined by X-ray phase analysis. The same experience was obtained in our previous work [4].

The experimentally determined conversion degrees for the exposure temperatures and times followed are summarized for the solid state reaction and the liquid state reaction in Table I and II respectively.

The reaction conditions and the kinetics of formation of $BaTi_3O_7$ according to the equation (3) were studied in the solid state as well as in the presence of

flux. The synthesis was carried out at the temperatures of 800–1200 °C and the heating times of 1–4 h.

The conversion degree of TiO_2 to the $BaTi_3O_7$ double oxide was determined using the semiquantitative X-ray analysis. The intensity of the 0.210 nm diffraction line for $BaTi_3O_7$ was measured.

From the results it follows that the formation of the barium – titanium double oxide $BaTi_3O_7$ starts already at the temperature of 800°C. The $BaTi_3O_7$ content increases with increasing temperature. The formation rate in the solid state reaction is lower than in the molten salts medium. From the experiments it follows that the conversion of $BaTiO_3$ to $BaTi_3O_7$ does not terminate at 1470 K, but limits to a certain value. The limiting conversion degree is for the liquid state reaction higher than that for the solid state reaction. This observation is probably due to the unsufficient homogenity of the starting mixtures, when in some areas one of the reactants is absent. For the total conversion the transport of the absenting reactant through the solid state is necessary, for which favourable conditions are not created. On the other hand the formation of the compact $BaTi_3O_7$

Table II

Experimental and calculated conversion degree in the
$BaTi_3O_7$ synthesis according to reation (3) in the
presence of liquid phase

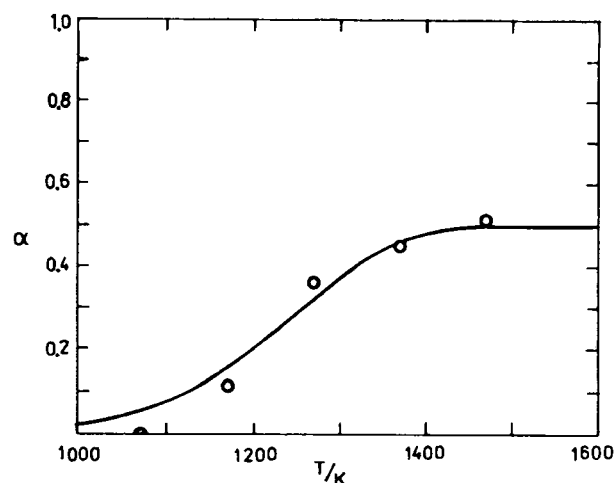| t/h	T/K	$\alpha(exp)$	$\alpha(calc)$
1	1070	0.00	0.02
	1170	0.12	0.06
	1270	0.13	0.16
	1370	0.33	0.34
	1470	0.62	0.58
2	1070	0.01	0.03
	1170	0.14	0.10
	1270	0.21	0.25
	1370	0.53	0.49
	1470	0.69	0.74
3	1070	0.01	0.03
	1170	0.14	0.10
	1270	0.23	0.27
	1370	0.57	0.51
	1470	0.69	0.75
4	1070	0.07	0.03
	1170	0.14	0.10
	1270	0.23	0.25
	1370	0.59	0.50
	1470	0.64	0.75

Fig. 1. Dependence of the conversion degree on the temperature for the exposure time of 2 h in the preparation of $BaTi_3O_7$ by solid state reaction. O - experimental, — - according to eqn. (4)
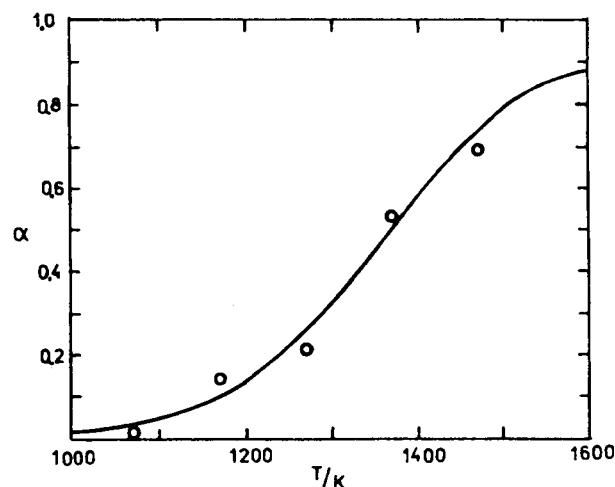

Fig. 2. Dependence of the conversion degree on the temperature for the exposure time of 2 h in the preparation of $BaTi_3O_7$ by liquid state reaction. O - experimental, — - according to eqn. (4)

layer on the $BaTiO_3$ grains surface may also hinder the continuation of the reaction. The presence of the liquid phase lowers substantially this effects by improvement of the mass transport through the liquid phase. This explanation supports the microstructure evolution of the investigated samples. However, under the experimental conditions used the maximum conversion degree attained in the liquid phase reaction does not exceed the value of 0.7 at 1470 K.

On the basis of the experimentally determined conversion degree (see Table I and II) and using the pro-

cedure described in [5, 6] the activation energy of the formation of $BaTi_3O_7$ was calculated according to the equation

$$\alpha = \{1 - \exp[A'.\exp(-\Delta E/RT)]\}.\alpha(\text{max}) \qquad (4)$$

where $A' = A.t^n$, t is the time, n depends on the reaction mechanism, the nucleation rate and the geometric factors, A is the frequency factor in the Arrhenius equation, ΔE is the activation energy of the reaction and α (max) is the calculated limiting conversion degree.

Equation (4) describes the experimentally determined course of the TiO_2 conversion to the barium-titanium double oxide $BaTi_3O_7$ very well for $n = 1$ and for the value of the activation energy of the $BaTi_3O_7$ formation $\Delta E = 130$ kJ/mol valid both for the solid as well as the liquid state reaction. A good agreement of the experimental and calculated values of the conversion degrees is evident from the data given in Tables I and II. The measured and calculated dependences of the conversion degree on the temperature for the exposition time of 2 h are shown for illustration for the solid and liquid state reaction in Fig. 1 and 2, respectively. The values of the constants used at the conversion degree calculation as well as the standard deviations of the approximations are given in Table III.

The formation of $BaTi_3O_7$ and evolution of its microstructure was followed also in the microphotographs of the polished cross-sections of the samples (cf. Fig. 3a, b and 4a, b). In accordance with the results given in Table I and II the favourable influence of the increasing temperature and the presence of flux

Table III

The values of the constants used in equation (4) for the calculation of the conversion degree and the standard deviations of approximation in the temperature interval of 800–1200°C

solid state reaction			liquid state reaction		
$\alpha(\text{max}) = 0.5$ $\Delta E = 130$ kJ/mol $n = 1$			$\alpha(\text{max}) = 0.9$ $\Delta E = 130$ kJ/mol $n = 1$		
t/h	A'	s.d.	t/h	A'	s.d.
1	40	0.058	1	12	0.036
2	32	0.034	2	10	0.039
3	18	0.030	3	6.9	0.046
4	18	0.026	4	5.1	0.068

as well as the non-important influence of the heating time on the conversion degree is evident from the microphotographs (cf. Fig. 3a, b and 4a, b). When the amount and the size of the BaTi$_3$O$_7$ crystals in the sample attain such value that they touch mutually, the sintering under formation of a dense ceramic material takes place (see Fig. 4b).

CONCLUSIONS

BaTi$_3$O$_7$ is formed from the stoichiometric mixtures of BaTiO$_3$ and TiO$_2$ in the temperature range of 800–1200 °C. The favourable influence of the presence of the liquid phase on the conversion degree was confirmed. The conversion degree attained depends on the temperature and the heating time. The maximum conversion degree in the solid state reaction is ca 50% at 1470 K while in the liquid state reaction it attains ca 90% at the same temperature. The substantial increase of the conversion degree in the presence of flux is ascribed to the improved transport properties of the liquid phase and the removal of the surface hindrances.

The activation energy of the BaTi$_3$O$_7$ formation has the value $\Delta E = 130$ kJ/mol for the reaction in the solid as well as in the liquid state.

The synthesis of BaTi$_3$O$_7$ from the BaSO$_4$ + Na$_2$CO$_3$ + TiO$_2$ or BaCl$_2$ + Na$_2$CO$_3$ + TiO$_2$ mixtures was not successful. BaTiO$_3$ and most probably Na$_2$TiO$_3$ are formed by heating of these mixtures.

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SYNTÉZA BaTi$_3$O$_7$ V ROZTAVENÝCH SOLIACH

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Príprava BaTi$_3$O$_7$ izotermickým záhrevom zmesí BaSO$_4$ + Na$_2$CO$_3$ + TiO$_2$ a BaCl$_2$ + Na$_2$CO$_3$ + TiO$_2$ pri teplote 700–900 °C nebola úspešná. Získaný produkt obsahuje zmes BaTiO$_3$ a Na$_2$TiO$_3$. BaTi$_3$O$_7$ sa pripravil zo zmesi BaTiO$_3$ a TiO$_2$ reakciou v prostredí roztavených solí pri teplote 800–1200 °C v časových intervaloch 1–4 h.

Rýchlosť tvorby BaTi$_3$O$_7$ je v prítomnosti kvapalnej fázy vyššia ako v tuhej fáze. Kým pri reakcii v tuhej fáze je maximálny stupeň konverzie cca 50%, v prítomnosti kvapalnej fázy dosahuje stupeň konverzie pri teplote 1470 K cca 70%. Stupeň konverzie je priaznivo ovplyvnený zvýšením teploty izotermického záhrevu. Vplyv času tepelnej expozície nie je dôležitý, ale pôsobí na priemernú veľkosť kryštálov BaTi$_3$O$_7$. Aktivačná energia tvorby BaTi$_3$O$_7$ je rovnaká pre reakciu v kvapalnej fáze i pre reakciu v tuhej fáze a má hodnotu $\Delta E = 130$ kJ/mol.

Obr. 1. Závislosť stupňa konverzie od teploty pre epozičný čas 2 hodiny pri syntéze BaTi$_3$O$_7$ reakciou v tuhej fáze. O – experiment, —— – podľa rovnice (4)
Obr. 2. Závislosť stupňa konverzie od teploty pre expozičný čas 2 hodiny pri syntéze BaTi$_3$O$_7$ reakciou v tavenine. O – experiment, —— – podľa rovnice (4)
Obr. 3. Mikrofotografie leštených priečnych rezov vzoriek pripravených pri teplote 1200° C reakciou v tuhej fáze. 330 × zväčš. a) čas expozície 2 h, b) čas expozície 4 h
Obr. 4. Mikrofotografie leštených priečnych rezov vzoriek pripravených pri teplote 1200° C reakciou v tavenine. 330 × zväčš. a) čas expozície 2 h, b) čas expozície 4 h
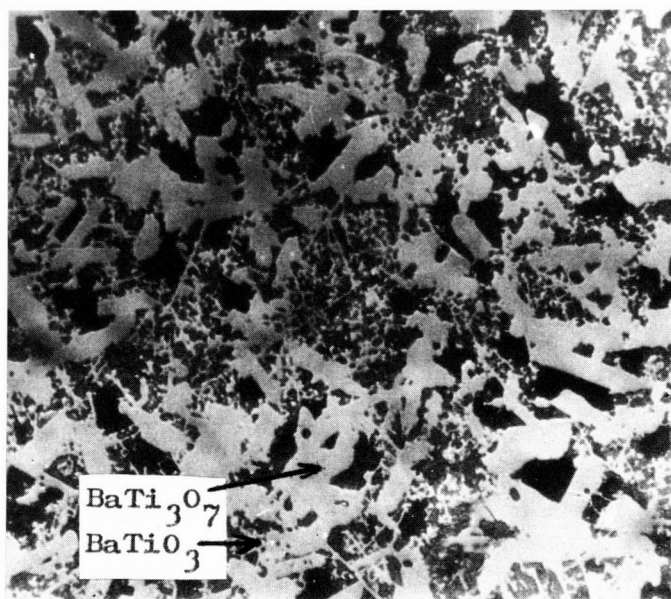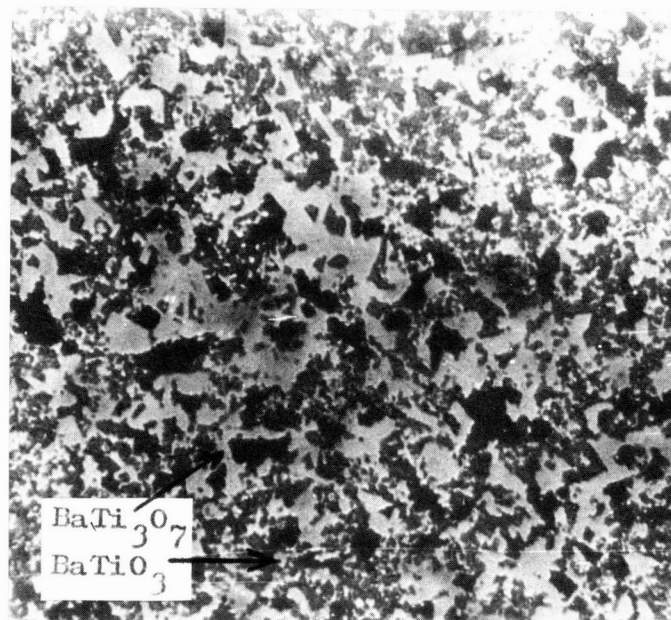
Fig. 3. Microphotographs of the polished cross-section of samples prepared at the temperature of 1200° C by the solid state reaction. 330 × a) heating time 2 h, b) heating time 4 h

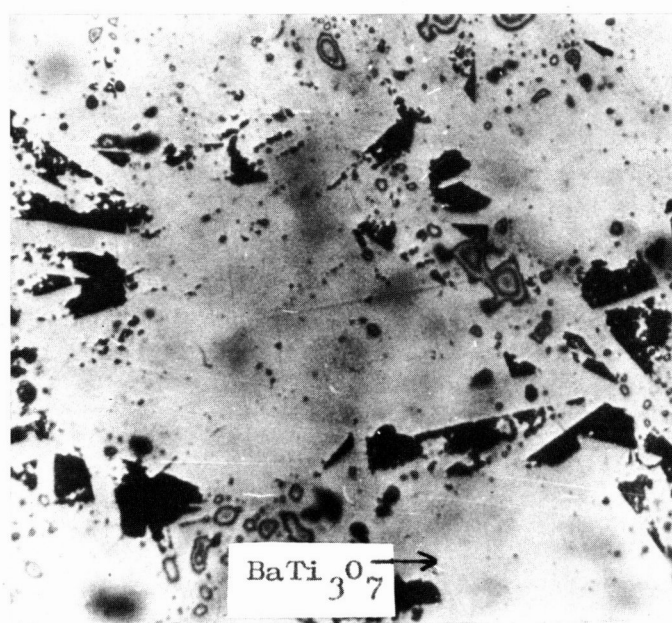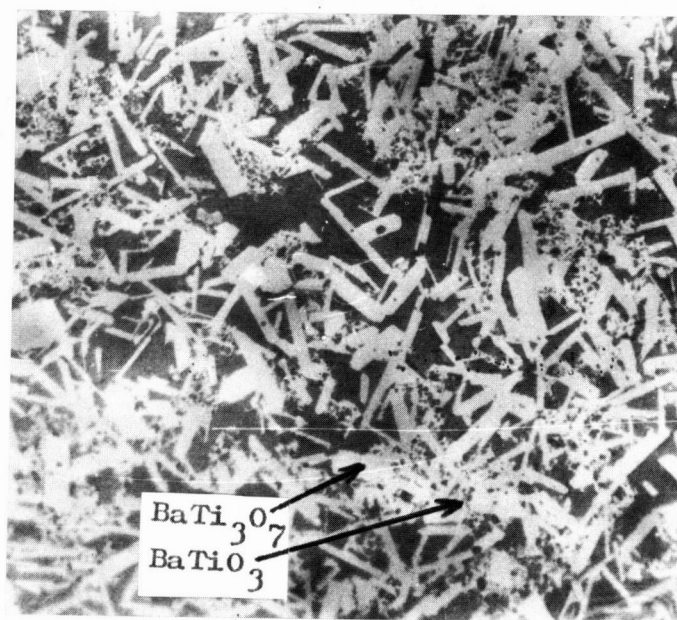*Fig. 4. Microphotographs of the polished cross-section of samples prepared at the temperature of 1200° C by the liquid state rection. 330 × a) heating time 2 h, b) heating time 4 h*