

Original Papers

SYNTHESIS OF BaTi₃O₇ IN MOLTEN SALTSVLADIMÍR DANĚK^a, ANDREA TURCÁROVÁ^b, ŽELMÍRA LUBYOVÁ^a^a Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava^b Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava

Received 9. 12. 1992

BaTi₃O₇ is formed in the BaTiO₃ + TiO₂ mixtures by the solid state reaction 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 BaTi₃O₇ 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 BaTi₃O₇ crystals. The activation energy of the BaTi₃O₇ 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 BaSO₄ + Na₂CO₃ + TiO₂ and BaCl₂ + Na₂CO₃ + TiO₂ at the temperatures of 700–900 °C to produce BaTi₃O₇ was not successful. The obtained product contained the mixture of BaTiO₃ and Na₂TiO₃.

In the system BaO – TiO₂ there exists a number of double oxides with important electrical and/or magnetic properties [1]. Till now practical use have found BaTiO₃ as ferroelectric dielectrics and BaTi₄O₉ as the basis of linear dielectrics with small temperature dependence of the permittivity [2].

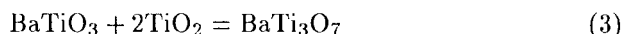
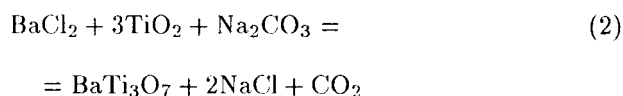
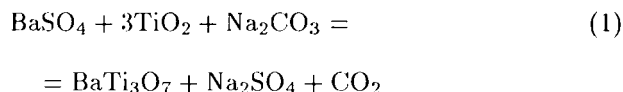
The preparation conditions of different barium – titanium double oxides from the BaCO₃ + TiO₂ mixtures by solid state reactions have been studied in [3]. Pure BaTi₃O₇ originates in the BaCO₃ + TiO₂ mixture with 1:3 mole ratio at the temperatures of 1200–1300 °C and the heating time more than 1 h. The 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 BaTiO₃ crystals in molten alkali metal chlorides medium was studied in [4].

In the present work the experimental conditions for the synthesis of BaTi₃O₇ 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 BaTi₃O₇ 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, BaTiO₃, and titanium oxide according to the equations



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 BaTi₃O₇ synthesis in the solid state reaction (3)

t/h	T/K	α(exp)	α(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 BaTi₃O₇ according to the equations (1) and (2) in the presence of molten sodium chloride was not successful. BaTi₃O₇ does not originate by heating the respective mixtures at the temperatures of 700–900°C. Beside alkali metal chlorides only BaTiO₃ was determined in the samples by X-ray phase analysis. The surplus TiO₂ reacts most probably with the present sodium salts (Na₂CO₃, Na₂SO₄, NaCl) forming the double oxide Na₂TiO₃, which evidently does not react with BaTiO₃ and is not suitable for the further synthesis to BaTi₃O₇. Due to very fine dispersion Na₂TiO₃ 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 BaTi₃O₇ 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 TiO₂ to the BaTi₃O₇ double oxide was determined using the semiquantitative X-ray analysis. The intensity of the 0.210 nm diffraction line for BaTi₃O₇ was measured.

From the results it follows that the formation of the barium – titanium double oxide BaTi₃O₇ starts already at the temperature of 800°C. The BaTi₃O₇ 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 BaTiO₃ to BaTi₃O₇ 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 insufficient homogeneity 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 BaTi₃O₇

Table II

Experimental and calculated conversion degree in the BaTi₃O₇ synthesis according to reaction (3) in the presence of liquid phase

t/h	T/K	α(exp)	α(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

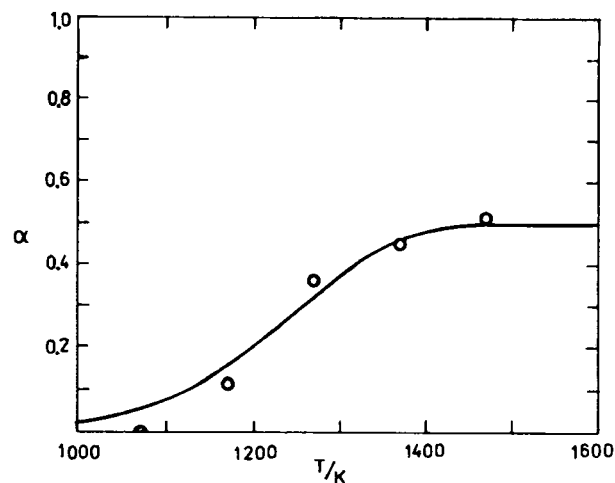


Fig. 1. Dependence of the conversion degree on the temperature for the exposure time of 2 h in the preparation of BaTi₃O₇ by solid state reaction. ○ - experimental, — - according to eqn. (4)

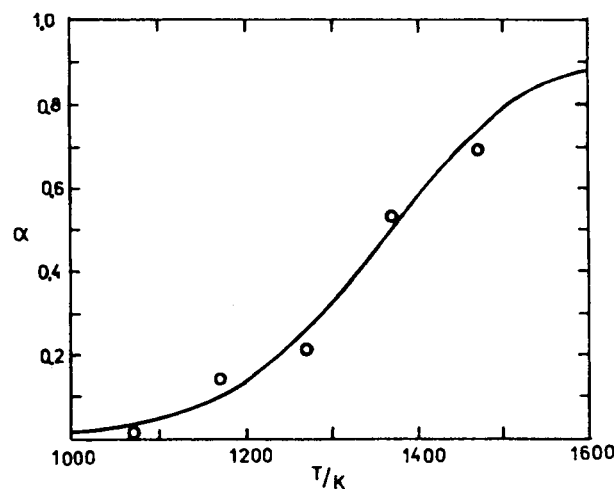


Fig. 2. Dependence of the conversion degree on the temperature for the exposure time of 2 h in the preparation of BaTi₃O₇ by liquid state reaction. ○ - experimental, — - according to eqn. (4)

layer on the BaTiO₃ 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 BaTi₃O₇ was calculated according to the equation

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

where $A' = A \cdot t^n$, 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 $\alpha(\max)$ is the calculated limiting conversion degree.

Equation (4) describes the experimentally determined course of the TiO₂ conversion to the barium-titanium double oxide BaTi₃O₇ very well for $n = 1$ and for the value of the activation energy of the BaTi₃O₇ 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 BaTi₃O₇ 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		
$\alpha(\max) = 0.5$ $\Delta E = 130$ kJ/mol $n = 1$			$\alpha(\max) = 0.9$ $\Delta E = 130$ 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_3O_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_3O_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_3O_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_3O_7 from the $\text{BaSO}_4 + \text{Na}_2\text{CO}_3 + \text{TiO}_2$ or $\text{BaCl}_2 + \text{Na}_2\text{CO}_3 + \text{TiO}_2$ mixtures was not successful. BaTiO_3 and most probably Na_2TiO_3 are formed by heating of these mixtures.

References

- [1] Negas T., Roth R. S., Parker H. S. and Minor D.: J. Solid State Chem. 9, 300 (1974).
- [2] Hlaváč J.: "Fundamentals of the Silicate Technology" (Základy technologie silikátů), SNTL, Prague 1981.
- [3] Rase D. E. and Roy R.: J. Amer. Ceram. Soc. 38, 102 (1955).
- [4] Lubyová Ž. and Daněk V.: J. Mater. Sci., in press.
- [5] Kapur P. C.: J. Amer. Ceram. Soc. 56, 79 (1973).

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

Submitted in English by the authors

SYNTÉZA BaTi_3O_7 V ROZTAVENÝCH SOLIACH

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Príprava BaTi_3O_7 izotermickým zohrevom zmesi $\text{BaSO}_4 + \text{Na}_2\text{CO}_3 + \text{TiO}_2$ a $\text{BaCl}_2 + \text{Na}_2\text{CO}_3 + \text{TiO}_2$ pri teplote 700–900 °C nebola úspešná. Získaný produkt obsahuje zmes BaTiO_3 a Na_2TiO_3 . BaTi_3O_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_3O_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 zohrevu. Vplyv času tepelnej expozície nie je dôležitý, ale pôsobí na priemernú veľkosť kryštálov BaTi_3O_7 . Aktivačná energia tvorby BaTi_3O_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 expozičný čas 2 hodiny pri syntéze BaTi_3O_7 reakciou v tuhej fáze. ○ – experiment, — – podľa rovnice (4)

Obr. 2. Závislosť stupňa konverzie od teploty pre expozičný čas 2 hodiny pri syntéze BaTi_3O_7 reakciou v tavenine. ○ – experiment, — – podľa rovnice (4)

Obr. 3. Mikrofotografie leštených priečných 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 priečných rezov vzoriek pripravených pri teplote 1200 °C reakciou v tavenine. 330 × zväčš. a) čas expozície 2 h, b) čas expozície 4 h