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Effect of Mechanical Activation on Kinetic Features of $BaZrO_3$ Formation

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Abstract—Barium zirconate $BaZrO_3$ has been prepared via heating of equimolar mixture of $BaCO_3$ with ZrO_2 at 900–1050°C with and without preliminary mechanical activation of the reactants. Degree of $BaZrO_3$ formation has been analyzed using basic equations of kinetics of solid-phase reactions in comparison with analogous synthesis of strontium and calcium zirconates. The relative efficiency of mechanical activation in the zirconates synthesis follows the Ca > Sr ≈ Ba series.

Keywords: barium zirconate, synthesis, mechanical activation, kinetics

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This study extends the earlier published reports on synthesis of alkaline earth metals zirconates using mechanical activation [1, 2]. In particular, we studied the effect of preliminary mechanical activation on kinetic features of $BaZrO_3$ formation during heating of a mixture of $BaCO_3$ and ZrO_2 in comparison with analogous processes of strontium and calcium zirconates preparation.

In earlier reports on $BaZrO_3$ synthesis via annealing of a mixture of barium carbonate and zirconium dioxide without mechanical activation the kinetics studies were limited [3, 4]. The syntheses were performed via pressing the reactants mixture, the major goal being the study of the physico-technical properties of ceramics based on barium zirconate. The completeness of $BaZrO_3$ synthesis required the $BaCO_3$/ZrO_2 mixture annealing during several hours at temperature no lower than 1200°C [3, 4]. Additionally, zirconium dioxide and barium carbonate practically did not react at joint mechanical treatment in a planetary mill during 30 min [5]. It was noticed that mechanical activation of $BaCO_3$ and ZrO_2 allowed decreasing the temperature of $BaZrO_3$ formation, but kinetics of barium zirconate synthesis under conditions of mechanical activation were not investigated [6].

Heating of a mixture of $BaCO_3$ and ZrO_2 without mechanical activation was not accompanied with formation of any intermediates or solid solutions; instead, barium zirconate was directly formed according to Eq. (1) [3, 4, 7].

$$BaCO_3 + ZrO_2 = BaZrO_3 + CO_2. \quad (1)$$

For comparison, the analogous synthesis of calcium zirconate was preceded by complete thermolysis of $CaCO_3$ [8], whereas strontium zirconate was formed via the two pathways [Eqs. (2), (3)] [2].

$$SrCO_3 + ZrO_2 = SrZrO_3 + CO_2, \quad (2)$$

$$SrO + ZrO_2 = SrZrO_3. \quad (3)$$

SrO was formed via thermal degradation of strontium carbonate, the thermolysis being somewhat faster than the zirconate formation [2]. Those results were in agreement with the experimentally determined stability of the carbonates, increasing in the $CaCO_3$ < $SrCO_3$ < $BaCO_3$ series, as well as with temperature dependences of the standard Gibbs energy $\Delta_r G^0$ of decomposition of $CaCO_3$ [2], $SrCO_3$, and $BaCO_3$ (Fig. 1).

Figure 1 displays the $\Delta_r G^0$ values of reactions (1) and (2) as functions of temperature, as calculated using the available reference data [9]; according to the calculation results, the reactions were thermodynamically allowed above 560°C [Eq. (1)] and above 620°C [Eq. (2)]. The $\Delta_r G^0$ values of reactions of strontium and barium zirconates from the corresponding car-

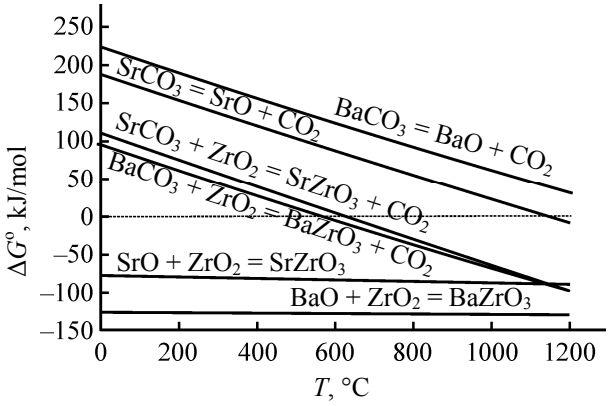

Fig. 1. Gibbs energy of reactions of formation of strontium and barium zirconates and of decomposition of $SrCO_3$ and $BaCO_3$ [9].

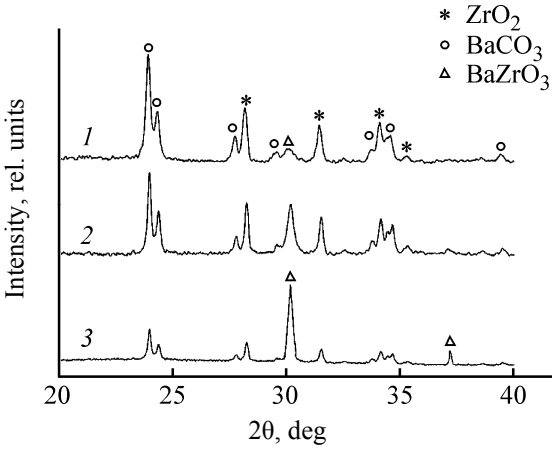

Fig. 2. X-ray diffraction patterns of the mixture of $BaCO_3$ and ZrO_2 annealed (*1*) during 4 h at 950°C, (*2*) during 3 h at 1000°C, and (*3*) during 3 h at 1050°C.

bonates were very close (Fig. 1). In contrast to reactions (1) and (2), syntheses of strontium [reaction (3)] and barium [reaction (4)] zirconates were thermodynamically allowed over a wide temperature range.

$$BaO + ZrO_2 = BaZrO_3. \quad (4)$$

Formation of barium zirconate from the oxides according to Eq. (4) was by 40–50 kJ/mol more favorable than the analogous synthesis of strontium zirconnate via Eq. (3) (Fig. 1). As the situation was the opposite for the carbonates decomposition, the reactions (1) and (2) turned out to be almost equally favorable (Fig. 1).

Figure 2 shows X-ray diffraction patterns of the mixture of zirconium dioxide and barium carbonate annealed at 950–1050°C without mechanical activation. The results revealed the presence of the initial reactants and the $BaZrO_3$ product in the mixtures thus confirming the occurrence of reaction (1), in accordance with the results reported in [3, 4, 7].

Experimentally determined degree of $BaZrO_3$ formation (expressed hereinafter as a fraction of unity) as a function of the annealing duration at 950, 1000, and 1050°C without mechanical activation is shown in Fig. 3. Similarly to the case of strontium zirconate reported in [2], kinetic analysis of $BaZrO_3$ synthesis was complicated. Even though formation of $BaZrO_3$ occurred via a single pathway (in contrast to the synthesis of $SrZrO_3$), it was affected by the two polymorphic transformations of $BaCO_3$ taking place at 800–830 and 970–1000°C due to the Hedvall effect [3, 4, 7]. On top of that, the formation of $BaZrO_3$ and $SrZrO_3$ (in contrast to the synthesis of $CaZrO_3$) occurred via a two-way diffusion of zirconium ions and those of the bivalent metal; modeling of such process is a complicated task [7]. In view of the above, our kinetic analysis of $BaZrO_3$ synthesis was not strict, and the calculated rate constants should not be regarded as quantitative parameters of the reaction mechanism.

Processing of the experimental data on degree of $BaZrO_3$ formation was attempted using the parabolic product growth, the shrinking sphere, the Avrami–Erofeev, the Jander's, the Ginstling–Brounstein's and the Zhuravlev–Lesokhin–Tempelman models [10] demonstrated that the model of shrinking sphere [Eq. (5)] provided the best fit (Fig. 3).

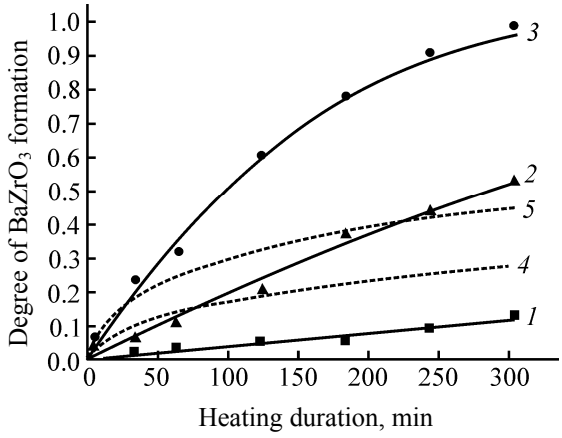

Fig. 3. (Markers) experimental and (lines) calculated degree of $BaZrO_3$ formation upon heating of $BaCO_3$ mixture with ZrO_2 at 950, (*2*) 1000, and (*3*) 1050°C without mechanical activation. (Dashed lines) show the degree of $SrZrO_3$ formation upon heating of $SrCO_3$ mixture with ZrO_2 at (*4*) 950 and (*5*) 1050°C without mechanical activation [2].

Rate constants of $BaZrO_3$ formation (k) as calculated from equation of the parabolic growth[a]

Duration of mechanical activation, min	T, °C	k, min^{-1}	R
0	950	$(1.34\pm0.08) \times 10^{-4}$[a]	0.9709
	1000	$(7.15\pm0.24) \times 10^{-4}$[a]	0.9940
	1050	$(2.17\pm0.07) \times 10^{-3}$[a]	0.9975
0	950	$(3.17\pm0.56) \times 10^{-5}$	0.9319
	1000	$(6.70\pm1.13) \times 10^{-4}$	0.9430
	1050	$(3.05\pm0.22) \times 10^{-3}$	0.9866
2	900	$(9.39\pm1.40) \times 10^{-5}$	0.8978
	950	$(2.65\pm0.28) \times 10^{-4}$	0.9598
	1000	$(1.59\pm0.15) \times 10^{-3}$	0.9777
6	900	$(1.33\pm0.16) \times 10^{-4}$	0.9363
	950	$(4.28\pm0.45) \times 10^{-4}$	0.9606
	1000	$(2.27\pm0.17) \times 10^{-3}$	0.9845
10	900	$(2.11\pm0.35) \times 10^{-4}$	0.8760
	950	$(7.01\pm0.51) \times 10^{-4}$	0.9817
	1000	$(3.04\pm0.16) \times 10^{-3}$	0.9923

[a] Rate constants of $BaZrO_3$ formation without mechanical activation were calculated using equation of the shrinking sphere.

$$1 - (1 - \alpha)^{1/3} = k_1\tau. \quad (5)$$

Here α is the degree of $BaZrO_3$ formation, τ is the duration of isothermal annealing, and k_1 is the reaction rate constant.

The parabolic product growth model [Eq. (6)] provided somewhat poorer fit.

$$\alpha^2 = k_2\tau. \quad (6)$$

The table shows the reaction rate constants calculated by minimization of the $\Sigma(\alpha^{exp} - \alpha^{calc})^2$ sum using the nonlinear least-squares method for both equations along with the corresponding correlation coefficients. The tabulated errors are root-mean-square deviations.

The calculated values of $\alpha(BaZrO_3)$ shown in Fig. 3 correspond to the shrinking sphere equation. The data on $SrZrO_3$ formation via heating of a mixture of $SrCO_3$ and ZrO_2 at 950 and 1050°C without mechanical activation [2] are shown in the same figure for the sake of comparison. Synthesis of strontium zirconate was faster than that of barium zirconate at 950°C, whereas at 1050°C the situation was the opposite.

Formation of strontium and barium zirconates occurred at a high rate over a relatively narrow temperature range [4]. The factors accelerating the interaction were the Hedvall effect (due to polymorphic transformations of $SrCO_3$ and $BaCO_3$) and the significantly larger (more than twice) molar volumes of the zirconates as compared to that of ZrO_2, the latter factor resulting in chipping of the reaction product from the zirconia grains [4]. Hence, the reaction rate was determined by surface diffusion rather than three-dimensional diffusion.

The reason for previously not noticed inversion of the relative rates of $SrZrO_3$ and $BaZrO_3$ formation at 950–1050°C was likely as follows. Firstly, a polymorphic transition of rhombic $SrCO_3$ form into hexagonal one occurs at 920–950°C [3, 4, 7]; due to the Hedvall effect that should enhance strontium carbonate reactivity and accelerate the synthesis in the stated temperature range. Moreover, theformation of $SrZrO_3$ at 950°C can partially occur via reaction (3) [2] because at this temperature reaction (3) was by 25 kJ/mol more favorable than reaction (1) (Fig. 1). At 1050°C $SrZrO_3$ is formed mainly via reaction (3) [2] which is less favorable than reaction (1) at this temperature (Fig. 1). Secondly, the formation of $BaZrO_3$ at 1050°C can be faster than that of $SrZrO_3$ because ZrO_2 reacts with barium oxide freshly formed via the carbonate decomposition and thus extremely reactive. On the other hand, strontium carbonate is practically decom-posed under the similar conditions [2], and reactivity of strontium oxide is reduced due to ageing.

X-ray diffraction study of the $BaCO_3$ mixture with ZrO_2 mechanically activated during 2–10 min revealed that the reagents peaks were weakened and broadened, but no new phase was formed. Chemical analysis showed that the degree of conversion via reaction (1) was very low under high-energy mechanical treatment in a planetary mill. In particular, degree of formation of $BaZrO_3$ was 0.2% (2 min treatment), 0.4% (6 min), and 0.8% (10 min), in accordance with the data of [5]. Experimentally determined values of $\alpha(BaZrO_3)$ for the mechanically activated mixtures subsequently annealed at 900, 950, and 1000°C are given in Figs. 4 and 5. The results processing demonstrated that the best fit was attained when using the equation of parabolic product growth [Eq. (6)]. The calculated reaction rate constants are collected in the Table, and the simulated kinetic curves are plotted in Figs. 4 and 5.

Kinetic curves of $SrZrO_3$ formation during annealing of mechanically activated (10 min) mixture of $SrCO_3$ with ZrO_2 at 950 and 1000°C [2] are shown

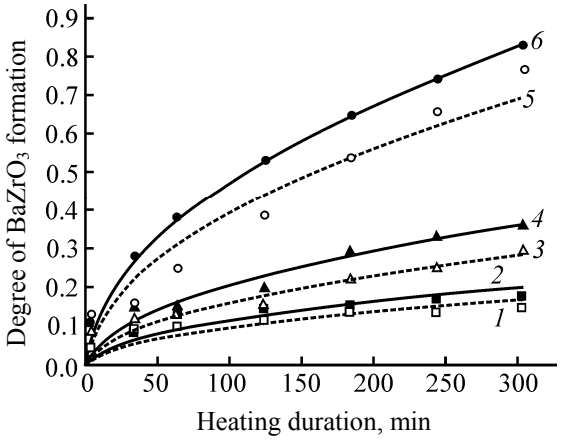

Fig. 4. (Markers) experimental and (lines) calculated degree of $BaZrO_3$ formation upon heating of mechanically activated $BaCO_3$ mixture with ZrO_2 at (*1*, *2*) 900, (*3*, *4*) 950, and (*5*, *6*) 1000°C. Duration of mechanical activation: (*1*, *3*, *5*) 2 and (*2*, *4*, *6*) 6 min.

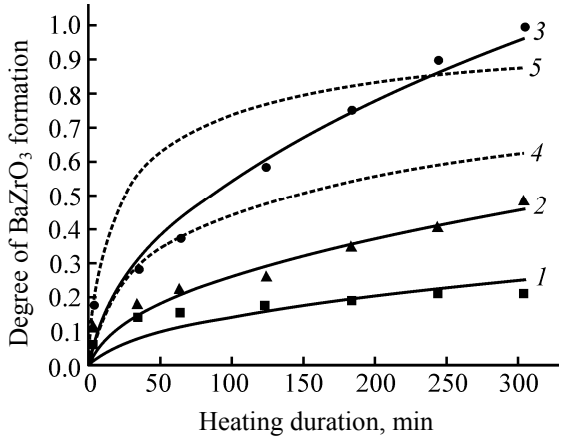

Fig. 5. (Markers) experimental and (lines) calculated degree of $BaZrO_3$ formation upon heating of mechanically activated (10 min) $BaCO_3$ mixture with ZrO_2 at (*1*) 900, (*2*) 950, and (*3*) 1000°C. (Dashed lines) show the degree of $SrZrO_3$ formation upon heating of mechanically activated (10 min) $SrCO_3$ mixture with ZrO_2 at (*4*) 950 and (*5*) 1000°C [2].

in Fig. 5 for the sake of comparison. The notable difference of kinetic curves of formation of $SrZrO_3$ and $BaZrO_3$ was observed both in the case of untreated (Fig. 3) and the mechanically activated (Fig. 5) mixtures. It was earlier demonstrated that kinetics of formation of $SrZrO_3$ from untreated and mechanically activated precursors was best fitted using the diffusion Zhuravlev–Lesokhin–Tempelman model [2], and the same model was successfully applied to describe calcium zirconate synthesis [1, 8]. Noteworthily, kinetics of formation of barium zirconate without mechanical activation was satisfactorily described with the shrinking sphere model (corresponding to the reaction rate limited by the processes at the interphase boundary). In the case of $BaZrO_3$ synthesis from mechanically activated mixtures of $BaCO_3$ with ZrO_2, the best results were achieved when using the parabolic product growth model derived for the planar plates interaction. Even though the kinetic analysis of synthesis of barium and strontium zirconates was rather formal than mechanistic, processing of the experimental data as well as the shape of the kinetic curves (Figs. 3–5) evidenced significantly smaller diffusion impediments in the case of $BaZrO_3$ preparation as compared with formation of $SrZrO_3$. The above mentioned difference of molar volumes of the zirconates and zirconia was likely among the reasons. In the case of barium zirconate the difference was the highest, leading to significant exposure of ZrO_2 grains and, hence, to the accelerated diffusion.

The mechanical activation revealed close acceleration effects on the formation of strontium and barium zirconates. For example, a difference between degrees of formation of $SrZrO_3$ and $BaZrO_3$ was of 0.16 (5 h, 950°C, no mechanical activation) (Fig. 3), whereas the difference was of 0.17 after 10 min mechanical activation, other conditions being the same (Fig. 5). It was earlier demonstrated that the effect of the mechanical activation on the synthesis of calcium zirconate was stronger as compared with the case of strontium zirconate [2]. Hence, the relative efficacy of mechanical activation as a synthetic step followed the Ca > Sr ≈ Ba zirconates series.

The observed decrease of efficacy of mechanical activation in the cases of $SrZrO_3$ and $BaZrO_3$ was likely due to the different synthesis mechanism and the above-mentioned additional accelerating factors operative during the formation of strontium and barium zirconates. Indeed, being initially faster, the formation of $SrZrO_3$ and $BaZrO_3$ experienced weaker effect of the mechanical activation than did the formation of $CaZrO_3$. On top of that, the rate of solid-phase reactions could be affected by the microstructure of mechanically activated powder mixtures, not studied in this work.

Besides accelerating the reaction upon annealing, mechanical activation was superior in that higher degree of dispersion of the reactants and the mixture homogeneity favored formation of the nanosized pro-

duct. Decrease of the annealing temperature and duration possible due to the effect of mechanical activation prevented the enlargement and crystallization of the formed particles, allowing for completeness of the reaction and preservation of the nanostructure of the product. In particular, mechanical activation of the $CaCO_3/ZrO_2$ mixture allowed preparation of calcium calcium zirconate having crystallites of below 50 nm in size [11].

EXPERIMENTAL

The following materials were used: monoclinic zirconium dioxide ("chemically pure" grade, specific surface of 0.74 m^2/g) and barium carbonate ("chemically pure," 1.70 m^2/g).

The initial mixture containing ZrO_2 and $BaCO_3$ in the equimolar ratio was prepared by mixing of the weighed compounds in a FritschPulverisette 2 mechanical mortar during 4 h.

The joint mechanical activation of the reaction mixture was performed in an AGO-2 laboratory centrifugal-planetary mill as described in detail elsewhere [2]. Specific surface of the mixture was of 2.9, 4.6, and 5.1 m^2/g after 2, 6, and 10 min activation, respectively.

The mixture was then heated in a SNOL 6.7/1300 electric furnace in air as described elsewhere [2, 8]. As the formation of barium zirconate and decomposition of barium carbonate occurred simultaneously, the reaction course was monitored following the specimen mass loss; the weighing accuracy was of ±0.0001 g.

X-ray diffraction study was performed using a ShimadzuXRD 6000 diffractometer (CuK_α radiation) at the scanning rate of 2 deg/min. Specific surface was determined via the low-temperature nitrogen adsorption using a Flow-SorbII 2300 analyzer (Micromeritics).

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