

SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF AN ADVANCED BaO-MgO-Al₂O₃-SiO₂ SYSTEM AS AN ATTRACTIVE PROTECTIVE-COATING MATERIAL

SINTEZA IN FIZIKALNO-KEMIJSKE LASTNOSTI NAPREDNEGA BaO-MgO-Al₂O₃-SiO₂ SISTEMA KOT MATERIALA ZA NAPREDNE ZAŠČITNE PREVLEKE

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One way to increase the turbine efficiency and reduce pollutant emissions would be to work in harsh environments with high temperatures and corrosion environments. Therefore, it is essential to develop new materials that are able to withstand environmental and mechanical conditions. Such coatings are usually a combination of ceramic layers that can better counteract aggressive environments and protect the substrate. Over many years, many ceramic systems have been developed and studied as thermal and ecological barriers. However, the costs and stability of such materials still require research and improvement to decrease the price of production costs, while maintaining the best protective properties. Barium osumilite (BaMg₂Al₆Si₉O₃₀) has many attractive physical and chemical properties that make it most suitable for high-temperature utilities. The main aim of this article is to present a detailed description of a laboratory preparation of Ba-osumilite, including the multistep solid-state reaction after the mechanical activation by high-energy milling and physicochemical characterization of the resulting material, focusing on the microstructure and thermal properties. The thermal-expansion coefficient and microstructure, monitored in view of the changes to the crystallinity, are observed during the heating up to 1200 °C in an Anton Paar HTK 2000 high-temperature chamber.

Keywords: Ba-osumilite, solid-state synthesis, high-energy milling, heat treatment, thermal-expansion coefficient

Eden od načinov povečanja učinkovitosti delovanja turbin in zmanjšanja emisij onesnaževalcev okolja je njihovo obratovanje v težkih pogojih; to je pri visokih temperaturah in v korozivnem okolju. Zato je ključno razvijanje novih materialov, ki so sposobni kljubovati takšnemu okolju ob istočasni visoki mehanski obremenitvi. To so običajno keramične prevleke izdelane v več plasteh, ki lahko kljubujejo agresivnemu okolju in zaščitijo podlago (turbinske lopatice). V preteklih letih so raziskovalci študirali in razvili vrsto keramičnih sistemov, uporabnih kot termične in ekološke bariere. Vendar pa sta tako cena kot stabilnost teh materialov dokaj neugodna in zato je še vedno potreba po raziskavah in razvoju novih ter izboljšanju obstoječih materialov s stališča zmanjšanja njihovih stroškov izdelave in doseganja najboljše zaščite. Barijev osumilit (BaMg₂Al₆Si₉O₃₀) ima mnoge privlačne fizikalne in kemijske lastnosti, ki ga uvrščajo med najbolj primerne materiale po sestavi za visoko temperaturno uporabo. V tem članku avtorji predstavljajo natančen opis laboratorijske priprave Ba-osumilita z večstopenjsko reaktivno sintezo v trdnem stanju po mehanski aktivaciji z visoko energijskim mletjem. Sledila je fizikalno-kemijska karakterizacija izdelanega materiala s poudarkom na mikrostrukturi in termičnih lastnostih. Koeficient toplotnega širjenja in mikrostrukture, ki so jih opazovali s stališča sprememb kristaliničnosti, so analizirali med segrevanjem do 1200 °C v Anton Paar HTK 2000 visoko temperaturni komori.

Ključne besede: Ba-osumilit, reaktivna sinteza v trdnem stanju, visoko energijsko mletje, toplotna obdelava, koeficient toplotnega širjenja

1 INTRODUCTION

During the last decades, barium-magnesium-aluminosilicate (BMAS) has been one of the most promising glass-ceramic systems due to the mechanical and thermal properties that make it suitable for metal-matrix composites such as fiber reinforcements and high-temperature structural applications such as refractory and environmental barriers due to its low thermal-expansion coefficient.¹

The thermal stability of BMAS depends on the crystalline phases that are created during the devitrification of this glass ceramic. Thus, BMAS can include a single phase or a mixture of diverse metastable crystalline phases during the devitrification process, i.e., celsian (BaO·Al₂O₃·2SiO₂, monoclinic), hexacelsian (BaO·Al₂O₃·2SiO₂, hexagonal) and Ba-osumilite (BaO·2MgO·3Al₂O₃·9SiO₂, hexagonal). All these phases are usually present in a eutectic mixture with α/β -cordierite (2MgO·2Al₂O₃·5SiO₂, hexagonal/orthorhombic), depending on the chemical route, source and post-processing of the BMAS material.^{2,3}

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The crystallization behaviour of a BMAS system has been studied for the production of different phases via various synthesis routes like sol-gel, melting of initial oxides, solid-state reaction and others.^{1,3-5} Despite all the effort, a multiple phase system is usually obtained and the resulting phases can change after a post-heating treatment. Therefore, the formation of stoichiometric phases is not an easy task, especially in the case of stoichiometric Ba-osumilite because it is thermally instable and tends to transform into a mixture of the rest of the BMAS crystalline phases.^{2,6} This thermal instability provides a better comprehension of the thermal behaviour of the BMAS glass-ceramics and stimulates the interest in the research of its stabilization process, justified by the fact that Ba-osumilite exhibits a high melting point (1370 °C) and a low thermal-expansion coefficient ($\alpha = 2.8 \times 10^{-6} \text{ K}^{-1}$ in the 20–500 °C range).⁶

The present article is devoted to the high-temperature solid-state synthesis of Ba-osumilite after the mechanical activation caused by high-energy milling and to the characteristics of the microstructure in terms of the crystallite size and thermal expansion after heating from room temperature up to 1200 °C.

2 EXPERIMENTAL PART

For the synthesis of Ba-osumilite, a mechanical activation process with a high-temperature solid-state reaction was used. Barium oxide (BaO, p.a. purity, Merck, Germany), silica oxide (SiO₂, p.a. purity, Lach-Ner, Czech Republic), aluminium oxide (Al₂O₃, p.a. purity, Lach-Ner, Czech Republic) and magnesium oxide (MgO, p.a. purity, Lach-Ner, Czech Republic) as the basic precursors were dosed according to the stoichiometric ratio for the formation of Ba-osumilite, 2MgO·BaO·3Al₂O₃·9SiO₂. The semi-wet approach for the raw-material mixture preparation was used. At first, barium oxide and silica oxide in a molar ratio of 1:9 mol were weighed on a laboratory scale with an accuracy of $\pm 0.01 \text{ g}$ and pre-milled/pre-homogenized in a planetary mill (PULVERISSETTE 6, Fritsch, Germany). The volume of the used steel-milling bowl was 0.5 dm³ and it was filled with 25 steel grinding balls with 20 mm in diameter. Pre-milling of the raw-material mixture was carried out for 60 s at a speed of 350 min⁻¹. The raw-material mixture was used to create a water-based slurry (1:1 wt./wt.) for the mechanical activation by high-energy milling (Simoloyer CM01, Zoz GmbH, Germany). Stainless-steel balls with 4.76 mm in diameter were used. The milling time was 30 min at a speed of 800 min⁻¹. The mechanically activated raw-material mixture was dried in a laboratory dryer (BINDER C170, Czech Republic) at 110 °C for 24 h. Nodules of 10–15 mm in diameter were formed naturally during the drying. The nodules in an amount of 694.14 g were directly dosed to platinum crucibles to react at a temperature of 1150 °C for 8 h inside a high-temperature furnace with superkanthal heating elements (2017S,

CLASIC, Czech Republic). The heating rate was 8 °C/min. The product (BaSi₉O₁₉) in an amount of 694.14 g was slowly cooled down to room temperature for 24 h. The product in the form of a block was crushed into powder in a vibratory-disc mill (RS 200, Retsch, Germany) at 900 min⁻¹ for 20 s.

After the first solid-state reaction, 3 mol of aluminum oxide was added to 1 mol of the BaSi₉O₁₉ product and again mechanically activated so that the slurry was subjected to the same process and parameters as in the previous step. The second solid-state reaction was carried out at 1200 °C for 8 h inside the high-temperature furnace again. The obtained product was crushed into powder in the vibratory-disc mill at 700 min⁻¹ for 20 s and milled in the planetary mill at 350 min⁻¹ for 120 s.

After this milling process, 2 mol of magnesium oxide was added to 1 mol of the BaAl₆Si₉O₂₈ product and mechanically activated, following the same parameters in the high-energy mill (Simoloyer CM01, Zoz GmbH, Germany). The third solid-state reaction was carried out at 1300 °C for 8 h inside the high-temperature furnace and then slowly cooled down to room temperature. The final powder was adjusted with milling in the vibratory and planetary mill for the analysis with an XRD apparatus.

The XRD analysis was performed with a multifunctional diffractometer (XRD, Empyrean, PANalytical B.V., Netherlands) with a Cu anode and K α as the radiation source, $\lambda = 1.540598$ for K α_1 , an accelerating voltage of 45 kV, beam current of 40 mA, diffraction angle 2θ in a range from 5° to 90° with a step scan of 0.01°. The ICSD (released in 2012) was used for the qualitative analysis of diffraction patterns. Quantification was performed with the Rietveld method. For analysing the crystal-lattice evolution in the powder during the heat treatment, diffractometer PANalytical Empyrean with a high-temperature chamber with a platinum heating strip (HTK 2000N, Anton Paar GmbH, Austria) was used. The Ba-osumilite sample was heated from 25 °C to 1200 °C with a ramp of 30 °C/min and dwell time of 2 min. XRD measurements were taken every 100 °C. The collected data were evaluated using the HighScore Plus software (3.0e, PANalytical B.V., Netherlands) for the Rietveld refinement without an internal standard.

Based on the in-situ XRD analyses, the crystallite size and linear thermal-expansion coefficient of the cell parameters (a , b and c) were calculated. The calculation of the crystallite size was based on the measurement of FWHM (full width of half maximum) and the Scherrer equation⁷ with the Warren correction⁸:

$$L = \frac{K \cdot \lambda}{\cos \theta} \cdot \frac{1}{\beta} = \frac{K \cdot \lambda}{\cos \theta} \cdot \frac{1}{\sqrt{B^2 - b^2}} \quad (1)$$

L is the crystallite size, K is the Scherrer constant (the value of 0.89 was used), λ is the K α_1 wavelength of the X-ray radiation, θ is the diffraction angle, B is FWHM (full width of half maximum) and b is FWHM of the

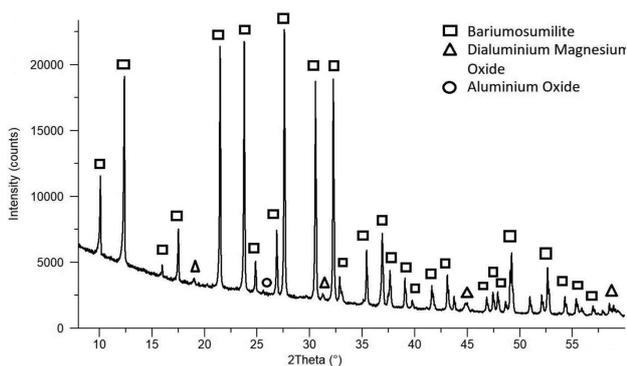


Figure 1: X-ray diffraction patterns of Ba-OSumilite

size/strain standard used (lanthanum hexaboride). The other factors affecting the accuracy of this evaluation method, such as the strain, were neglected because the aim of this experiment was to assess the trend of the crystallite-size development during the heating up.

The linear thermal-expansion coefficient was based on the thermal expansion where coefficient alpha was calculated. The linear thermal-expansion coefficient of the cell parameters (*a*, *b* and *c*) were obtained from the following equation:

$$\alpha_L = \frac{1}{L} \cdot \frac{dL}{dT} \quad (2)$$

L is the particular-length measurement and *dL/dT* is the rate of change of that linear dimension per unit change in temperature.

3 RESULTS

The XRD patterns of the prepared material are shown in Figure 1. For a better illustration of the crystal-structure development, a 3D graph for the Ba-OSumilite main diffraction line determined with Miller indices "hkl" 002 was created and is shown in Figure 2.

The major phase identified in the XRD patterns is Ba-OSumilite (ICSD 79843). The XRD patterns show the presence of two other phases: dialuminium magnesium

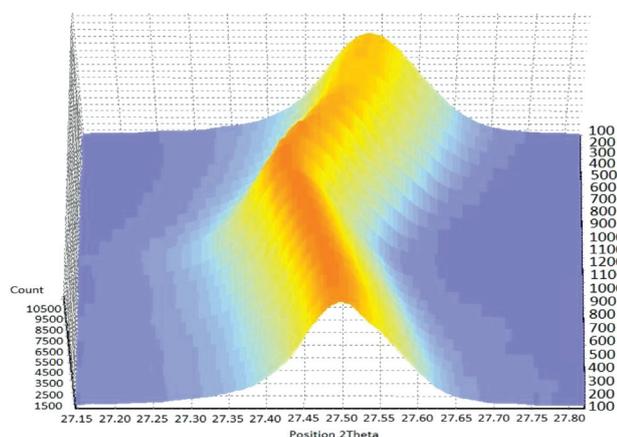


Figure 2: 3D graph of the crystal structure development

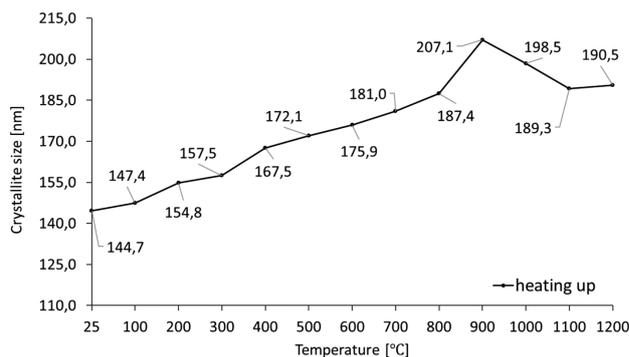


Figure 3: Effect of heat treatment on the crystallite size

oxide (ICSD 24766) and aluminium oxide (ICSD 75560). All the identified phases were quantified. The amount of the residual oxides is approximately 5 %. In terms of purity, for an in-situ HTK experiment, where the mineral structure is studied, 95 % purity of Ba-OSumilite is sufficient.

Based on these results, the HighScore Plus software using the Rietveld refinement was used to calculate the crystallinity growth and the result is shown in Figure 3.

During the heating, the crystallite size increases proportionally up to 800 °C where it reaches the value of 187 nm. As the temperature increases, there is a change in the crystallite-growth trend. The crystallite size reaches 200 nm at 900 °C and then decreases.

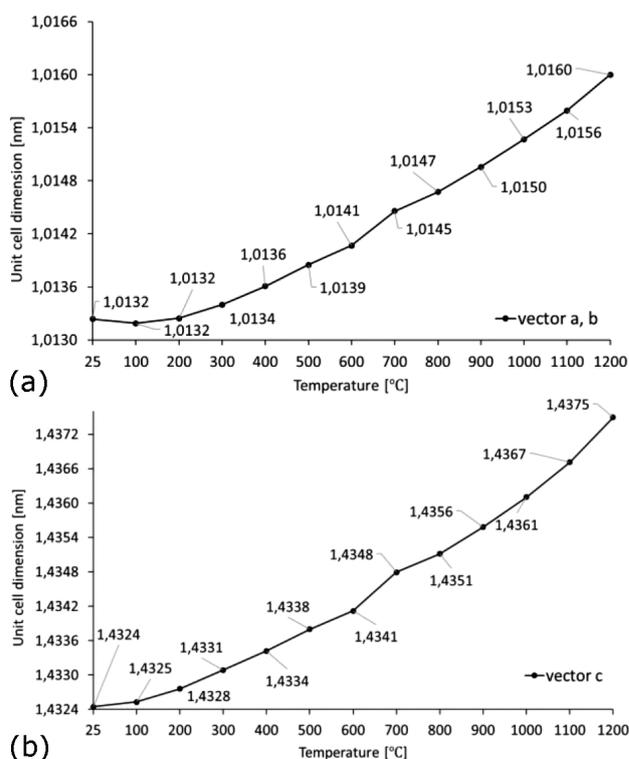


Figure 4: a) Effect of heat treatment on cell parameters *a*, *b*, b) effect of heat treatment on cell parameter *c*

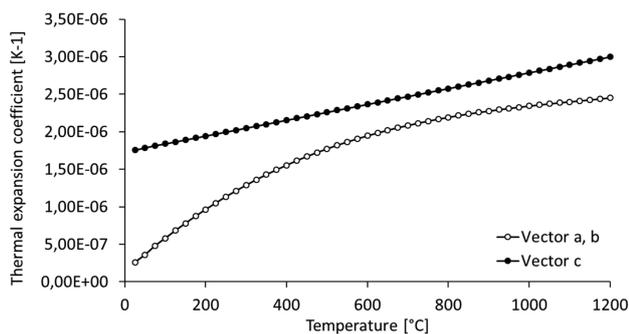


Figure 5: Thermal-expansion curve of Ba-osumilite for vectors *a*, *b* and *c*

Similar to the crystallite size, the cell parameters characterized by vectors *a*, *b* and *c* increase proportionally during the heating.

The thermal-expansion coefficient evaluated for individual vectors is shown in **Figure 5**.

The thermal-expansion coefficient for vector *c* increases proportionally to the maximum value of $3.0 \cdot 10^{-6} \text{ K}^{-1}$ at 1200 °C. The change in the growth trend of the thermal-expansion coefficient for vectors *a* and *b* is visible compared with vector *c*. While the thermal-expansion coefficient for vector *c* increases proportionally with the increasing temperature, the coefficient for vectors *a* and *b* is hyperbolic, reaching a maximum of only $2.5 \cdot 10^{-6} \text{ K}^{-1}$.

4 DISCUSSION

This paper deals with the barium magnesium aluminium silicate as an attractive coating material. The article is divided into two main sections, dealing with the laboratory preparation of Ba-osumilite and an investigation of the physicochemical properties of the obtained material during the heat treatment.

The formation of the stoichiometric phase of Ba-osumilite is quite complicated because it is a thermally instable material, which tends to transform into a mixture of the rest of the BMAS crystalline phases. The composition of the raw-material mixture and the heat-treatment parameters are the most influential factors that determine the final-phase composition of the material. Another important factor is the mechanical activation by high-energy milling, which was used for the preparation of Ba-osumilite. The high-energy ball milling is an effective solid-state method for the production of powders with attractive properties. During high-energy ball milling, friction and high-energy kinetic collisions are the main processes, under which the powder particles are repeatedly subjected to deformation. Especially at the beginning of milling, friction and fracturing are the dominant processes that result in a particle-size reduction.^{9,10}

Mechanochemical activation is engaged in physicochemical changes in substances in all states of aggrega-

tion due to mechanical energy.¹¹ The advantages of this technology include a reduction in the reaction temperature of the material, an increase in the reactivity of the material, shorter milling times (reduced energy demands) and a reduction in the number of technological steps.¹² Using high-energy milling, Ba-osumilite was successfully prepared. It can be stated that high-energy milling facilitated a better material formation through the formation of active surfaces that could support the formation of Ba-osumilite within the multistep solid-state reaction.

The objective of the first part of the study was fully fulfilled because the Ba-osumilite phase without any other crystalline phases such as celsian or hexacelsian was prepared. To achieve higher purity (> 95 %), further mechanochemical activation and the fourth step of the solid-state reaction are suggested. However, for the main purpose of this experiment, a 95-% purity of the Ba-osumilite without any other BMAS phases was sufficient.

Based on these results, the second part of the experiment was completed. The Scherrer method was used to assess the effect of the heating process on the development of the crystal structure. It can be stated that the crystallite grew proportionally until the size of approximately 188 nm was achieved. The values around 200 nm were disregarded because the method was no longer applicable at this level.

Vectors *a*, *b* and *c* exhibit similar crystallinity and grow proportionally with the increasing heating temperature.

According to the available literature, the thermal-expansion coefficient of Ba-osumilite is $2.7 \cdot 10^{-6} \text{ K}^{-1}$ obtained in a temperature range of 20–900 °C. The results presented in this paper correspond to this fact where at 900 °C the thermal-expansion coefficient for vector *c* is $2.68 \cdot 10^{-6} \text{ K}^{-1}$ and for vectors *a* and *b*, it is $2.28 \cdot 10^{-6} \text{ K}^{-1}$. With the temperature increasing to 1200 °C, there was only a slight increase in the thermal-expansion coefficient. Despite the high temperature of 1200 °C, to which the material was subjected in the high-temperature chamber, the coefficient of thermal expansion is very low. This implies that this excellent thermal property makes the material suitable for use in metal-matrix composites as a fiber reinforcement and in high-temperature structural applications as refractory and environmental barriers.

5 CONCLUSIONS

The aim of this article was to describe a process of a laboratory preparation of Ba-osumilite using a multistep solid-state reaction after the mechanical activation by high-energy milling and characterize the microstructure and thermal properties during the heating up to 1200 °C.

Through a simple method based on the mechanical activation by high-energy milling in combination with a multistep solid-state reaction, we successfully prepared Ba-osumilite.

The crystallite size increased proportionally with the increasing temperature.

The thermal-expansion coefficient for the *c*-lattice parameter exhibited linear behaviour and reached $3.0 \cdot 10^{-6} \text{ K}^{-1}$ at 1200 °C.

The glass-ceramic with the composition and thermal properties presented in this paper can be used as the substrate material for thermal and environmental barriers.

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