Use of recycled glass fiber-epoxy resin as additive for mullite ceramics

Emese Kurovics ▪ Institute of Energy, Ceramics and Polymer Technology, University of Miskolc ▪ emese.mesterne@uni-miskolc.hu

Habtamu Mnichl ▪ Institute of Energy, Ceramics and Polymer Technology, University of Miskolc ▪ habteched@gmail.com

Monika Tokár ▪ Institute of Metallurgy, Metal Forming and Nanotechnology, University of Miskolc ▪ monika.tokar@uni-miskolc.hu

Érkezett: 2025. 06. 18. ▪ Received: 18. 06. 2025. ▪ https://doi.org/10.14382/epitoanyag-jsbcm.2025.8

Emese KUROVICS
received her PhD degree in 2022 from the University of Miskolc, where she is currently working as a research fellow at the Institute of Energy, Ceramics and Polymer Technology. She is the author or co-author of more than 70 scientific articles and a member of the Scientific Society of the Silicate Industry.

Habtamu MNICHL
is currently participating in the AMIR Master's Double Degree Program at the University of Miskolc and the Universidad Politécnica de Madrid. His areas of specialization include materials engineering and the circular economy.

Monika TOKÁR
is currently working as an assistant lecturer at the Institute of Metallurgy, Metal Forming, and Nanotechnology at the University of Miskolc. She is the author or co-author of more than 60 scientific publications.

Abstract

The use of recycled materials in ceramic production is becoming increasingly important in the development of more sustainable and cost-effective materials. This study focuses on the use of recycled glass fiber-reinforced epoxy resin (GFRE) powder, produced by mechanical grinding, as an additive in mullite-based ceramic systems. The goal is to investigate how the addition of this composite powder affects mullite formation and the physical properties of the fired ceramic specimens. The main aim of the study is to determine whether the recycled GFRE powder can act as a reactive filler that promotes mullite formation at lower temperatures, and whether it has any effect on the porosity or other characteristics of the sintered ceramics. X-ray diffraction (XRD) and scanning electron microscopy (SEM) will be used to analyze the phase composition and microstructure of the samples. Using GFRP waste as a ceramic additive offers a novel way to recycle difficult-to-process composite materials. This approach may contribute to the development of more sustainable ceramic technologies and provide a practical solution for reusing industrial composite waste in high-temperature applications.

Keywords: ceramics, glass fiber, GFRE, mullite, SEM, XRD
Kulcsszavak: kerámiák, üvegszál, GFRE, mullit, SEM, XRD

1. Introduction

Mullite ($3\ Al_2O_3 \cdot 2\ SiO_2$) is a highly desirable ceramic material due to its excellent thermal stability, low thermal conductivity, high refractoriness, and superior mechanical strength at elevated temperatures [1, 2]. These properties make it suitable for demanding applications in the fields of advanced refractories, thermal insulation, and structural ceramics [3]. However, the synthesis of mullite traditionally requires high-purity raw materials and elevated sintering temperatures (typically >1200 °C), which contribute to significant energy consumption and environmental impact [4, 5].

To address these concerns, growing research efforts have focused on incorporating industrial by-products and waste materials into mullite-based ceramics to reduce production costs and improve sustainability [6-10]. Kaolin, a naturally occurring aluminosilicate, and alumina are common starting materials, but recent studies have demonstrated the potential of using silica- or alumina-containing waste – such as fly ash, glass waste, or ceramic sludge – to aid mullite formation and modify the microstructure of the resulting ceramics [11-15]. Glass fiber-reinforced epoxy (GFRE) composite waste, originating from end-of-life composite products, represents a particularly challenging and underutilized material for recycling due to its thermoset nature and mixed inorganic-organic composition [16, 17].

In this context, this study investigates the use of recycled GFRE powder – produced by mechanical grinding of composite waste – as an additive in kaolin-alumina-based ceramic formulations. The primary objective is to evaluate whether the GFRE powder can function as a reactive filler that contributes to mullite formation at lower temperatures, possibly through the release of SiO_2 and fluxing agents during thermal decomposition [18, 19]. In addition, the influence of GFRE on the porosity, microstructure, and phase composition of the sintered ceramics is examined [20].

To characterize the effect of the GFRE addition, X-ray diffraction (XRD) is employed to identify and quantify the crystalline phases formed during firing, while scanning electron microscopy (SEM) provides insights into the morphology and distribution of mullite crystals and the porosity of the ceramic matrix [21-23]. These analyses aim to clarify the relationship between composite waste addition and microstructural evolution, thereby assessing the feasibility of using GFRE as a functional ceramic additive [24].

The integration of GFRE waste into ceramic systems offers a promising strategy for recycling composite materials that are otherwise difficult to process [25]. By valorizing this waste stream within high-temperature ceramic applications, the proposed approach contributes to the advancement of circular economy practices and the development of more sustainable ceramic technologies [26, 27].

2. Materials and methods

Ceramic mixtures were prepared using Nabalox 315 alumina and Sedlecky ml kaolin as alumina- and silica-based raw materials, respectively. The formulations were prepared both with and without the addition of recycled glass fiber-reinforced epoxy (GFRE) powder, as summarized in *Table 1*.

Mixture sign	Sedlecky ml kaolin	Nabalox 315 alumina	Glass fiber-reinforced epoxy resin as additive
I.	76.71	23.29	0
II.	76.71	23.29	2.5
III.	76.71	23.29	5

Table 1 Mixture compositions in wt.%
1. táblázat Keverék összetételek tömegszázalékban

The GFRE additive was obtained by mechanical grinding of composite waste and was sieved to a particle size below 250 µm. Based on loss-on-ignition tests, the GFRE powder was found to contain approximately 58.42 wt.% glass fiber, which is expected to increase the overall SiO_2 content of the ceramic body.

The proportions of alumina and kaolin were adjusted to achieve an Al_2O_3:SiO_2 molar ratio of 3:2 in the fired product, corresponding to the stoichiometric composition of mullite ($3\ Al_2O_3 \cdot 2\ SiO_2$).

Raw materials were mixed and milled for 20 minutes at 200 rpm using a Retsch PM 400 planetary ball mill. The homogenized powders were compacted by uniaxial pressing using a hydraulic press to form test specimens with a diameter of 25 mm.

Heat treatment was carried out in a Nabaltech laboratory electric kiln. Sintering was performed at 1150 °C and 1250 °C for both the reference and GFRE-containing compositions (*Fig. 1*). Additionally, a reference sample (without additive) was sintered at 1400 °C to serve as a benchmark for mullite formation at elevated temperature.

The firing schedule was designed to enable complete burnout of the organic epoxy matrix and to facilitate phase transformation and microstructural development. Following sintering, the samples were analyzed by X-ray diffraction (XRD) to identify crystalline phases and by scanning electron microscopy (SEM) to observe fracture surface morphology and microstructural evolution.

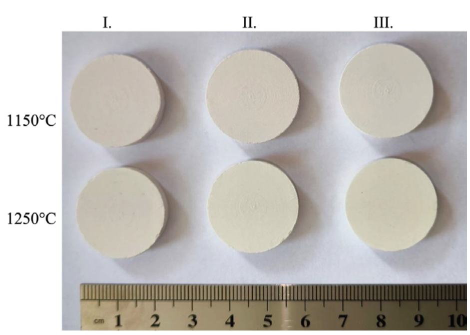


Fig. 1 The sintered test samples
1. ábra A szinterelt próbatestek

3. Results and discussions

Fig. 2 presents the bulk density of the sintered ceramic samples as a function of the heat treatment temperature for both the reference and GFRE-containing compositions. As expected, an increase in sintering temperature led to a corresponding increase in the bulk density of all samples, indicating enhanced sintering activity and the development of a more compact microstructure.

Notably, the addition of GFRE powder consistently reduced the density of the sintered products across all temperatures. This trend appears linear and can be attributed to the partial burnout of the organic epoxy matrix during firing, which increases porosity. The presence of glass fibers may also influence the packing behavior and inhibit full densification. These findings suggest that while GFRE may contribute silica for mullite formation, it simultaneously introduces structural features that limit densification.

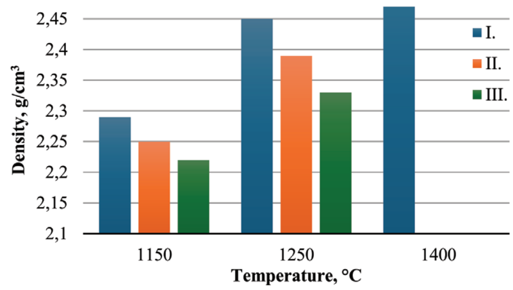


Fig. 2 The density of the sintered ceramic samples
2. ábra A szinterelt próbatestek sűrűsége

The microstructural evolution of the Type I (reference) samples sintered at different temperatures is shown in *Fig. 3*. The SEM images clearly indicate that, as the firing temperature increases, the ceramic particles become more interconnected, reflecting enhanced sintering and grain coalescence.

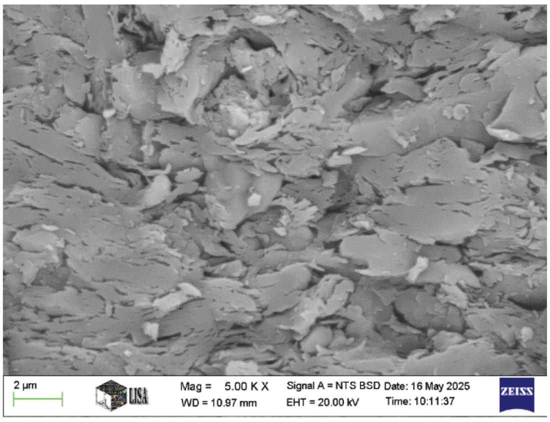
EDS analysis revealed that a portion of the alumina added to the kaolin remained in its original form within the microstructure. This indicates that not all of the alumina participated in the mullitization reaction during the heat treatment, especially at lower temperatures. Unreacted alumina grains were typically observed embedded within the ceramic matrix, distinguishable by their relatively high aluminum content.

At 1400 °C, the formation of mullite became more apparent, and regions exhibiting needle-like mullite crystals could be observed, which are characteristic of advanced mullitization. These elongated features suggest the onset of secondary mullite growth, commonly associated with higher firing temperatures and partial liquid-phase formation.

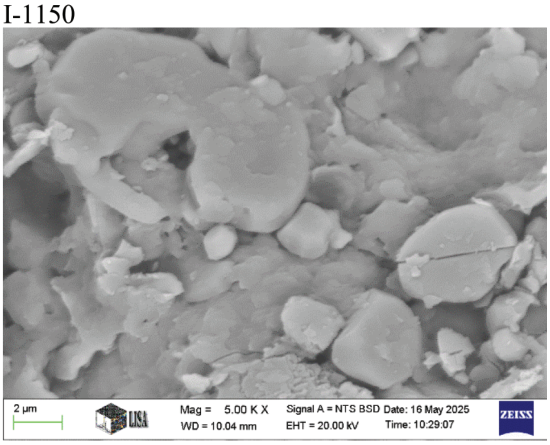
Elemental and oxide compositional analysis showed that the overall chemical composition of the samples remained relatively stable across the firing temperature range, with no significant elemental segregation or loss detected.

The SEM images of the GFRE-containing samples reveal the presence of numerous elongated and irregularly shaped pores, especially at higher firing temperatures (*Fig. 4*). These features are likely the result of thermal decomposition and burnout of the organic epoxy matrix within the GFRE additive. The morphology and distribution of these pores suggest that the combustion of the polymer phase created channels or voids aligned with the original fiber orientation.

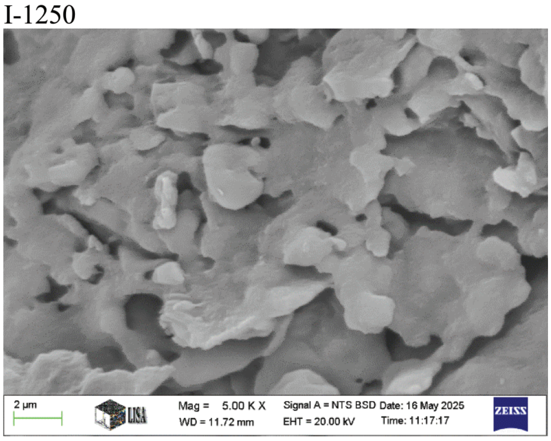
Despite the increased porosity, the ceramic matrix itself appears more homogeneous and continuous compared to the reference samples. This visual impression may indicate a higher proportion of amorphous glassy phase, possibly originating from the partial melting of the glass fibers during sintering. Such an increase in glassy phase content could also enhance viscous flow, promoting local densification and phase integration.



I-1150



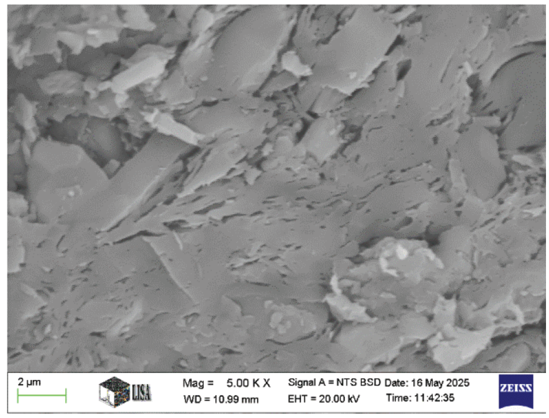
I-1250



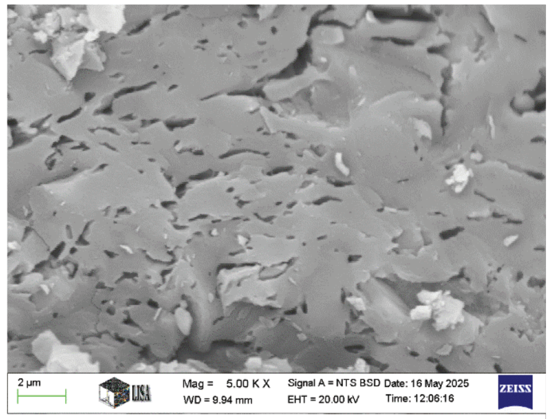
I-1400

Fig. 3 The microstructure of fracture surface of the Type I (reference) samples
3. ábra Az I. típusú (referencia) minták töretfelületének mikroszerkezete

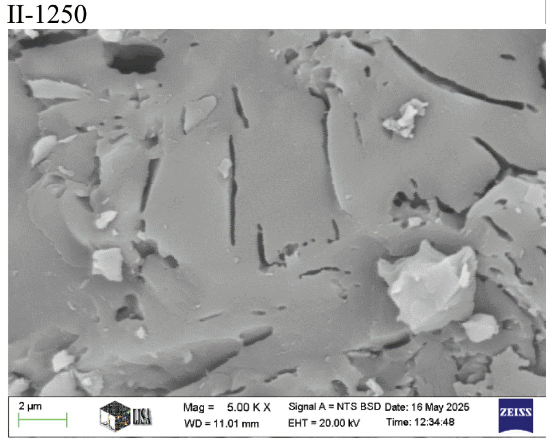
In some of the larger pores – approximately 2 to 2.5 µm in diameter – residual elongated fragments with high SiO_2 content were identified via EDS. These are presumed to be remnants of glass fibers that were only partially decomposed or encapsulated within the ceramic matrix during sintering. Their persistence suggests that some glass fibers may survive firing under certain thermal conditions, potentially contributing to the local SiO_2 content and influencing mullite formation.



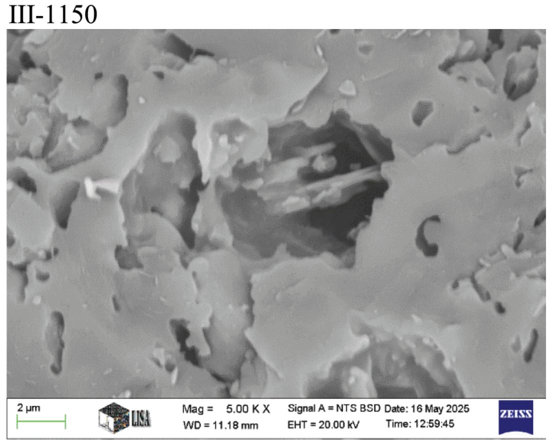
II-1150



II-1250



III-1150



III-1250

Fig. 4 The microstructure of fracture surface of the Type II and III (GFRE-containing) samples
4. ábra Az II. és III. típusú (GFRE tartalmú) minták töretfelületének mikroszerkezete

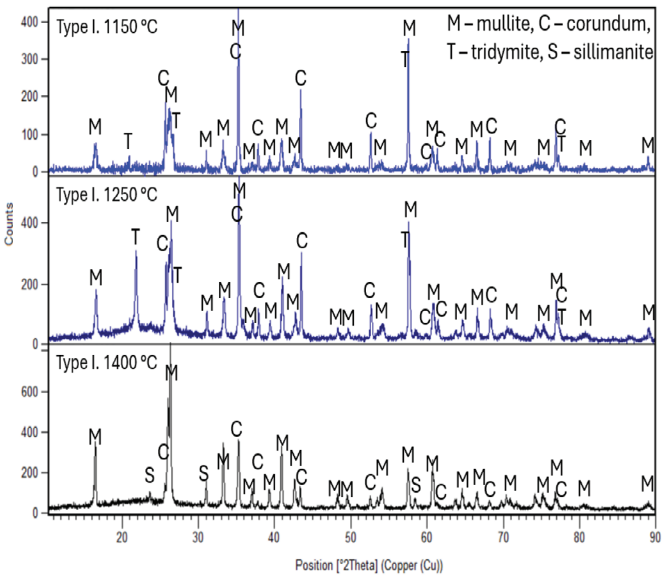


Fig. 5 The XRD pattern of the Type I (reference) samples
5. ábra Az I. típusú (referencia) minták röntgendiffraktogramja

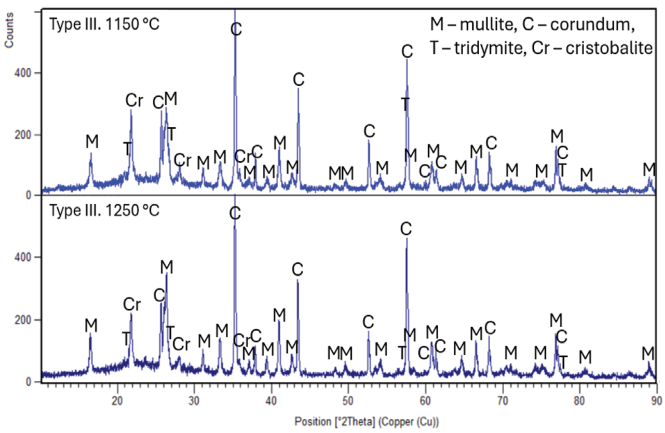


Fig. 6 The XRD pattern of the Type III (GFRE-containing) samples
6. ábra Az II. és III. típusú (GFRE tartalmú) minták röntgendiffraktogramja

Sintering temperature		1150 °C			1250 °C			1400 °C
Type of sample / Mixture sign		I.	II.	III.	I.	II.	III.	I.
Crystalline content, wt.%		41,0	41,8	40,6	58,1	61,3	64,1	74,9
Amorphous content, wt.%		59,0	58,2	59,4	41,9	38,7	35,9	25,1
Crystalline phases, wt.%	Mullite	17,2	24,0	25,0	37,8	36,2	42,3	52,4
	Corundum	14,8	10,6	11,0	16,3	12,3	16,0	11,2
	Tridymite	9,0	3,7	3,8	4,1	7,4	1,3	0,0
	Cristobalite	0,0	2,4	2,5	0,0	6,1	4,5	0,0
	Sillimanite	0,0	0,0	0,0	0,0	0,0	0,0	11,2

Table 2 Phase compositions of the sintered samples
2. táblázat A szinterelt minták fázisösszetétele

The results of the XRD measurements are summarized in *Table 2*, while representative diffractograms are presented in *Fig. 5* and *6*. The effect of sintering temperature on phase composition is clearly observable in all samples.

At 1150 °C, mullite formation had already begun, with a crystalline phase content around 41% in all mixtures. Increasing the sintering temperature to 1250 °C led to a significant rise – by at least 29% – in the total crystalline content across all three compositions, indicating enhanced crystallization and sintering activity.

In general, the GFRE-containing samples (Type II and III) exhibited a higher proportion of crystalline phases compared to the additive-free reference (Type I) at each temperature. This may be due to the glass fiber content of the GFRE additive, which includes amorphous silica that can crystallize upon slow cooling. As a result, cristobalite and tridymite phases appeared specifically in the GFRE-containing ceramics, likely formed from the devitrification of the residual glass.

Mullite was the dominant crystalline phase in all samples, and its quantity increased steadily with temperature. The presence of unreacted corundum (α- Al_2O_3) in each composition suggests that not all of the alumina participated in the mullitization reaction. Part of the alumina likely reacted with the tridymite generated during kaolin dehydration, and with glass-derived silica in the GFRE-containing systems, contributing to mullite formation.

At 1250 °C, mullite content reached 37.8% in the reference and up to 42.3% in GFRE-added mixtures, indicating that this temperature may be optimal for mullite synthesis under the given conditions. At 1400 °C, mullite formation peaked (52.4%), and sillimanite appeared in the reference sample, likely due to phase transitions at elevated temperature.

Overall, these results confirm that GFRE not only supports mullite crystallization but may also enhance overall crystallinity by contributing reactive SiO_2, while also introducing secondary silica phases due to partial devitrification of glass fibers.

4. Conclusions

This study demonstrated the feasibility of using mechanically ground glass fiber-reinforced epoxy (GFRE) waste as an additive in kaolin–alumina-based mullite ceramic systems. The following key conclusions can be drawn:

- The incorporation of GFRE powder led to a consistent decrease in the bulk density of the sintered ceramics due to the formation of elongated pores, originating from the burnout of the organic matrix.
- SEM analysis confirmed the development of a more continuous and interconnected ceramic network in the GFRE-containing samples, likely promoted by the presence of amorphous glassy phases derived from the melted glass fibers.
- XRD results showed that mullite formation occurred in all compositions and increased with sintering temperature. At 1150–1250 °C, GFRE-containing samples exhibited slightly higher mullite content than the additive-free reference, indicating that the recycled additive can serve as a reactive silica source.

- The presence of cristobalite and tridymite in the GFRE samples, as well as unreacted corundum across all compositions, suggests that phase evolution is influenced by both the additive composition and firing conditions.
- An optimal sintering temperature of 1250 °C was identified for promoting mullite formation while balancing porosity and crystallinity.

Overall, the results confirm that recycled GFRE waste can be effectively reused in the production of mullite ceramics, contributing both reactive components and structural modifications. This approach supports sustainable ceramic manufacturing and offers a practical valorization route for difficult-to-recycle composite materials.

Acknowledgement

„Supported by the University Research Scholarship Program of the Ministry for Culture and Innovation from the source of the National Research, Development and Innovation Fund."

References

[1] Romero M, Padilla I, Contreras M, López-Delgado A. Mullite-Based Ceramics from Mining Waste: A Review. Minerals. 2021, 11(3) p.332. https://doi.org/10.3390/min11030332

[2] Behera P.S., Bhattacharyya S. Sintering and microstructural study of mullite prepared from kaolinite and reactive alumina: Effect of MgO and TiO_2, International Journal of Applied Ceramic Technology, 2020, 17(2), pp. 560–572, https://doi.org/10.1111/ijac.13637

[3] Ma J. et al., Low-temperature synthesis of highly porous whisker-structured mullite ceramic from kaolin, Ceramics International, 2018, 44(11), pp. 13320–13327, https://doi.org/10.1016/j.ceramint.2018.04.163

[4] Ptáček P., The kinetics and mechanism of kaolin powder sintering I, Powder Technology, 2012, 232, pp. 24–32, https://doi.org/10.1016/j.powtec.2012.07.060

[5] Chen Y-F., Wang M-C., Hon M-H., Phase transformation and growth of mullite in kaolin ceramics, Journal of the European Ceramic Society, 2004, 24(8), pp. 2389–2397, https://doi.org/10.1016/S0955-2219(03)00631-9

[6] Choo T.F. et al., A review on synthesis of mullite ceramics from industrial wastes, Recycling, 2019 4(3), pp. 39–63, https://doi.org/10.3390/recycling4030039

[7] Foo C.T. et al., Mineralogy and thermal expansion study of mullite-based ceramics synthesized from coal fly ash and aluminum dross industrial wastes, Ceramics International, 2019, 45(5), pp. 7488–7494, https://doi.org/10.1016/j.ceramint.2019.01.041

[8] Alves H.P.A. et al., Preparation of mullite based ceramics from clay–kaolin waste mixtures, Ceramics International, 2016, 42(16), pp. 19086–19090, https://doi.org/10.1016/j.ceramint.2016.09.068

[9] Silva V.J. et al., Porous mullite blocks with compositions containing kaolin and alumina waste, Ceramics International, 2016, 42(12), pp. 15471–15478, https://doi.org/10.1016/j.ceramint.2016.06.199

[10] Kocserha I., Hamza A., Géber R., The effects of red mud on clay compounds, IOP Conference Series: Materials Science and Engineering, 2018, 426, 012026, https://doi.org/10.1088/1757-899X/426/1/012026

[11] Ji H. et al., Effect of La_2O_3 additives on the strength and microstructure of mullite ceramics obtained from coal gangue and γ-Al2O3, Ceramics International, 2013, 39(6), pp. 6841–6846, https://doi.org/10.1016/j.ceramint.2013.02.016

[12] Zhang J. et al., Mechanism of mechanical–chemical synergistic activation for preparation of mullite ceramics from high-alumina coal fly ash, Ceramics International, 2018, 44(3), pp. 3884–3892, https://doi.org/10.1016/j.ceramint.2017.11.178

[13] Sahraoui T., Belhouchet H., Heraiz M., Brihi N. Guermat A., The effects of mechanical activation on the sintering of mullite produced from kaolin and aluminum powder, Ceramics International, 2016, 42(10), pp. 12185–12193, https://doi.org/10.1016/j.ceramint.2016.04.157

[14] Rashad M., Balasubramanian M., Characteristics of porous mullite developed from clay and $AlF_3{\cdot}3H_2O$, Journal of the European Ceramic Society, 2018, 38(11), pp. 3673–3680, https://doi.org/10.1016/j.jeurceramsoc.2018.03.002

[15] Ibrahim J.F.M., Gömze A.L., Koncz-Horvath D., Filep Á., Kocserha I., Preparation, characterization, and physicomechanical properties of glass-ceramic foams based on alkali-activation and sintering of zeolite-poor rock and eggshell, Ceramics International, 2022, 48(18), pp. 25905-25917 https://doi.org/10.1016/j.ceramint.2022.05.267

[16] Guangfa Gao, Yongchi Li, Mechanical Properties of Woven Glass-Fiber Reinforced Polymer Composites, Emerging Materials Research 5(2) http://dx.doi.org/10.1680/jemmr.16.00018

[17] Shubham Utekar, Suriya V K, Neha More, Adarsh Rao, Comprehensive study of recycling of thermosetting polymer composites – Driving force, challenges and methods, Composites Part B: Engineering, 2021, 207, 108596, https://doi.org/10.1016/j.compositesb.2020.108596

[18] Xu M-X. et al., Insights into the pyrolysis mechanisms of epoxy resin polymers based on the combination of experiments and ReaxFF-MD simulation, Chemical Engineering Journal, 2023, 473, 145404, https://doi.org/10.1016/j.cej.2023.145404

[19] López F.A. et al., Recycling of Glass Fibers from Fiberglass Polyester Waste Composite for the Manufacture of Glass-Ceramic Materials, Journal of Environmental Protection, 2012, 03(08) pp.740-747. http://dx.doi.org/10.4236/jep.2012.38088

[20] Ondro J. et al., Kinetic analysis of sinter-crystallization of mullite and cristobalite from kaolinite, Thermochimica Acta, 2019, 678, pp. 30–37, https://doi.org/10.1016/j.tca.2019.178312

[21] Badanoiu A., Influence of Synthesis Route on Composition and Main Properties of Mullite Ceramics Based on Waste, MDPI Materials, 2025, 18(5), pp. 1098–1112, https://doi.org/10.3390/ma18051098

[22] Mohamed L.J. et al., Effect of sintering temperatures on the physical, structural properties and microstructure of mullite-based ceramics, AIMS Materials Science, 2024, 11(2), pp. 243–255, https://doi.org/10.3934/matersci.2024014

[23] Behera P.S., Bhattacharyya S., Effect of different alumina sources on phase formation and densification of single-phase mullite ceramic – Reference clay alumina system, Materials Today Communications, 2021, 26, 101818, https://doi.org/10.1016/j.mtcomm.2020.101818

[24] Aziz A.A., Fabrication and characterization of mullite ceramic hollow fiber membrane from natural occurring ball clay, Applied Clay Science, 2019, 177, pp.51–59, https://doi.org/10.1016/j.clay.2019.05.003

[25] Gonçalves R. M., Martinho A., Oliveira J. P., Recycling of Reinforced Glass Fibers Waste: Current Status, MDPI Materials (Basel), 2022, 15(4), 1596, https://doi.org/10.3390/ma15041596

[26] Li Junfeng, Lin Hong, Li Jianbao, Wu Jiang, Effects of different potassium salts on the formation of mullite as the only crystal phase in kaolinite, Journal of the European Ceramic Society, 2009, 29(14), pp.2929–2938, https://doi.org/10.1016/j.jeurceramsoc.2009.04.032

[27] Chen Y., Effect of quartz and muscovite on mullite formation, Applied Clay Science, 2013, 80–81, pp.176–184, https://doi.org/10.1016/j.clay.2013.04.008

Ref.:

Kurovics, Emese – **Mnichl**, Habtamu – **Tokár**, Monika: *Use of recycled glass fiber–epoxy resin as additive for mullite ceramics*
Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 77, No. 2 (2025), 55–59 p.
https://doi.org/10.14382/epitoanyag-jsbcm.2025.8