



AKADÉMIAI KIADÓ

Pollack Periodica •
An International Journal
for Engineering and
Information Sciences

18 (2023) 1, 119–125

DOI:


[10.1556/606.2022.00641](https://doi.org/10.1556/606.2022.00641)

© 2022 The Author(s)

ORIGINAL RESEARCH
PAPER



Glass-ceramic foams produced from zeolite-poor rock (Tokaj)

Jamal Eldin F. M. Ibrahim^{1*} , Mohammed Tihtih¹,
Emese Kurovics¹, Ethem İlhan Şahin², László A. Gömze¹ and
István Kocserha¹

¹ Institute of Ceramics and Polymer Engineering, University of Miskolc, Miskolc-Egyetemváros, Hungary

² Advanced Technology Research and Application Center, Adana Alparslan Türkeş Science and Technology University, Adana, Turkey

Received: March 28, 2022 • Revised manuscript received: July 15, 2022 • Accepted: August 1, 2022

Published online: December 12, 2022

ABSTRACT

This study evaluated the possibility of producing innovative glass-ceramic foams from zeolite-poor rock (Tokaj, Hungary) using alkali-activation and reactive sintering techniques. The composition and morphology of the samples were studied using X-ray diffraction, X-ray fluorescence, scanning electron microscope, and computed tomography techniques. The influence of various sintering temperatures on glass-ceramic foams was examined. It has been observed that zeolite-poor rock has a self-foaming capability. The heat treatment temperature affects the pore size and distribution as well as the technical characteristics of the obtained samples. The resulting glass-ceramic foams possess moderate thermal conductivity ranging from 0.11 to 0.17 W mK⁻¹ and good compressive strength (1.5–4.4 MPa). The produced samples might be utilized for thermal insulation, which would have both economic and environmental advantages.

KEYWORDS

zeolite-poor rock, ceramic foams, alkali activation, thermal conductivity

1. INTRODUCTION

Global energy consumption is predicted to jump in the upcoming decades due to the rapid growth in population and urbanization [1]. Presently, 80% of the energy consumption is supplied by fossil fuels which have harmful environmental implications like CO₂ emission, global warming, and climate change [2, 3]. Buildings are indeed the highest energy consumer, accounting for around 40% of the overall global energy usage. Most of this energy is used for heating and cooling the building to obtain internal thermal comfort in the buildings [4]. The energy requirement for heating or cooling in the buildings could be lowered by employing the passive thermal insulation method using materials like glass-ceramic foams [5]. Glass-ceramic foams is a heterogeneous system comprising both solid and gas phases. The solid matrix is made of ceramic material, whereas the gas fills the interior pores [6]. They are typically manufactured by fusing tiny powdered ceramics or glass and foaming agents at temperatures ranging from 800 to 1,000 °C [7]. Upon the sintering and when the temperature exceeds the glass transition temperature, the mixture starts to soften, making a viscoelastic material associated with the emission of the gas resulting from the foaming agent. As the heat treatment temperature rises, the viscosity reduces, and the volume of gas grows under the influence of increased internal pressure leading to a high degree of foam-ability [8]. However, when the pressure reaches the critical value, the gas escapes from the pores leading to emerging of neighboring pores in the bulk of the ceramic foams. Therefore, adjusting the sintering parameters (heating rate, sintering temperature, residence time), particle size, and

*Corresponding author.

E-mail: qkojamal@uni-miskolc.hu

the foaming agent is of great importance to achieve the product with the required technical properties [9]. The glass-ceramic foams normally possess fascinating characteristics, including high durability, low thermal conductivity, lightweight, high corrosion resistivity, sound insulation, and flame resistance. All these properties make glass-ceramic foams a recommended choice over other thermal insulation materials like polymeric materials [10–12]. However, manufacturing glass-ceramic foams from primary glass is a highly expensive operation since multiple heating periods are necessary in this case: Firstly, sintering at 1,450–1,500 °C is required to produce primary glass. Secondly, the glass and foaming agent mixture is sintered at 800–900 °C to achieve the desired cellular structure [13, 14]. Therefore, the manufacturing of new eco-friendly glass-ceramic foams that are both highly effective and low-cost is gaining a lot of attention lately. Cost-effective glass-ceramic foams can be obtained by either recycling waste glass or using natural materials, for instance, fly ash, red mud, natural zeolite, and other waste [15–19].

Zeolite-poor rocks are volcanic rocks that comprise a low proportion of zeolite (less than 10%) and additional components like cristobalite, quartz, montmorillonite, and possibly feldspar [20]. However, the low zeolite content of these minerals limits their classical uses. Yet, zeolite-poor rocks are great construction materials that may be utilized to make bricks due to their good mechanical qualities [21–23]. Furthermore, it is a great alternative for making glass-ceramic foam as it is readily available, offers a high silica concentration, and is easy to mine. According to the literature, only a few research explored making glass-ceramic foam exclusively from zeolite rocks. The majority of these researchers, however, employed zeolite-rich rocks, which possess lower silica content [17, 24]. The availability of large zeolite-poor rock resources in Hungary (Tokaj) prompted this study to look into the possibility of using zeolite-poor rocks to make glass-ceramic foams. As far as we can tell, no previous work has been done on the production of glass-ceramic foams using Tokaj zeolite poor-rock. It is highly believed that the results of this paper will have a value-added to the literature.

The goal of this study is to evaluate the possibilities of making glass-ceramic foams entirely from zeolite-poor rock (Tokaj) through alkali-activation and reactive sintering techniques. The alkali-activated samples were sintered at a temperature range of 850–950 °C and examined for their mechanical, physical, and thermal properties. The ability to produce glass-ceramic foams at a lower cost while still meeting quality standards is especially compelling. This might lower manufacturing costs and boost competitiveness.

2. MATERIALS AND METHODOLOGIES

2.1. Characterization methods

Zeolite-poor rock is mined from Tokaj Hill in northeastern Hungary, which is utilized as a basic material for the

manufacturing of glass-ceramic foam. X-Ray Fluorescence (XRF) spectroscopy was used to analyze the chemical constitution. The X-Ray Diffractometer (XRD, Rigaku, Miniflex II, Japan, 150 mA and 40 kV, CuK α radiation with wavelength 1.5418 Å, step size of 0.01°) was utilized to investigate the qualitative and quantitative phases composition of the basic raw material and the manufactured glass ceramic foams at $2\theta = 5\text{--}90^\circ$ and scan speed of $10^\circ \text{ min}^{-1}$. X'Pert HighScore Plus software was employed for the computer-aided phase evaluation. The thermal characteristics of alkali-activated zeolite-poor rock were studied using ThermoGravimetry/Differential Thermal Analysis (TG/DTA), (1750 SETARAM, Sestys evolution) from ambient temperature to 1,200 °C with a heating speed of $5^\circ \text{ C min}^{-1}$ at oxygen environment. The foaming capability of the alkali-activated samples was examined using a heating microscope (Camar Electronica). Scanning Electron Microscopy (SEM, EVO MA10, Carl Zeiss) and Energy Dispersive Analysis X-Ray (EDAX Genesis) were used to investigate the microstructure and elemental content of the fracture surface of the prepared glass-ceramic foams. Moreover, the pore structure of the produced sample was determined using X-ray computed tomography (CT, YXLON FF35, Gemini). The densities of the produced sample were calculated using Archimedes approach. The thermal conductivity is evaluated using a thermal conductivity analyzer (C-Therm TCi), and the compressive strength is determined using a hydraulic testing machine (INSTRON 5566).

2.2. Preparation method of the glass-ceramic foams

Glass-ceramic foams were made entirely from zeolite-poor rock by means of the alkali activation and reactive sintering procedures. Zeolite-poor rock powder was mixed with 15 wt % NaOH dissolved in distilled water and oven-dried at 200 °C for 2 days. Next, the alkali-activated material was milled for 20 min at 150 rpm in a planetary ball mill. The milled powders were then compressed using uniaxial compacting equipment under 18 MPa pressure to produce cylindrical discs having a diameter of around 20 mm and a height of around 10 mm. The manufactured pellets were

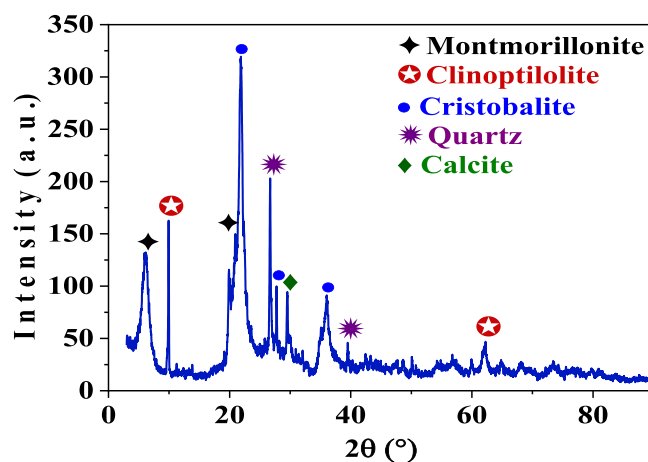


Fig. 1. XRD diffraction spectra of zeolite-poor rock

Table 1. Phases constituent of Tokaj's zeolite-poor rock as determined by XRD examination

Raw material	Phase composition					Total
	Clinoptilolite	Cristobalite	Montmorillonite	Quartz	Calcite	
Zeolite-poor rock	10.00	50.00	30.00	8.00	2.00	100

Table 2. Oxide composition of zeolite-poor rock acquired from XRF analysis

Raw material	Oxide content								Total
	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	CaO	CO ₂	H ₂ O	LOI	
Zeolite-poor rock	82.92	5.95	3.21	1.31	1.12	0.88	4.47	5.50	100

fired in a high-temperature controlled kiln for 10 min at temperatures ranging from 850 to 950 °C and 5 °C min⁻¹ heating rate. The kiln was then switched off, and the sample inside the kiln was left to cool to room temperature.

3. RESULTS AND DISCUSSION

3.1. Characterization findings of the raw materials

3.1.1. XRD and XRF investigations. The XRD pattern of zeolite-poor rock powder is shown in Fig. 1. Different minerals like cristobalite, quartz, montmorillonite, calcite, and clinoptilolite are found in zeolite-poor rock powder (Tokaj), as confirmed in Fig. 1. The quantitative phase composition of the samples was determined by the full profile fitting method.

Tables 1 and 2 indicate the phase constituent and oxide compositions of zeolite-poor rock resulted from XRD and XRF, respectively. Silica is found to be the basic oxide with alumina and other oxides in small amounts.

3.1.2. Thermal characteristics of alkali activated zeolite-poor rock. Figure 2 shows the ThermoGravimetric and Differential Thermal Analysis (TG/DTA) experimental investigation of alkali-activated materials. A total weight loss of 14.88% was detected that might be broken into three weight loss periods. The first weight loss in the temperature 40–192 °C was 6.9% is coincided with the DTA curve's endothermic peak at 121 °C. The elimination of free water from montmorillonite and adsorbed water from zeolite are connected to this weight loss. At a temperature range of 190–385.2 °C, a second weight loss of 5.12 is recorded, which can be attributed to the vaporization of the combined water in the alkali-activated material. Finally, at temperatures ranging from 380 to 803 °C, a weight reduction of 3.66% is achieved, which may be ascribed to the combustion of organic content and disintegration of the aluminosilicate framework.

Figure 3 show the foaming capability of alkali-activated zeolite-poor rock, which is carried out via heating microscope in a temperature range of 25–950 °C. The maximum expansion of the samples was inspected in the temperatures

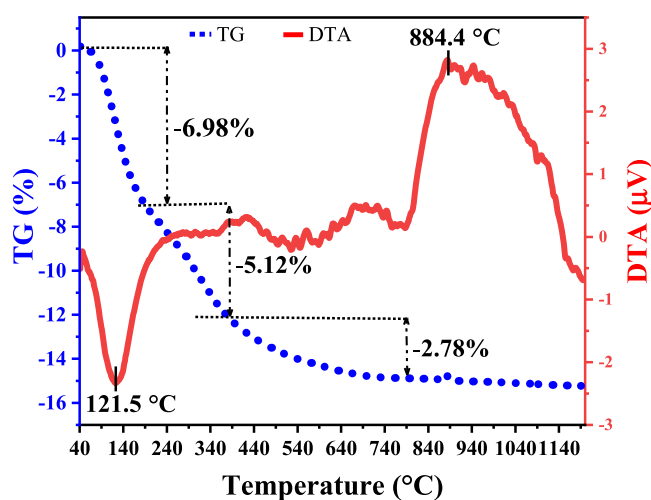


Fig. 2. DTA/TG profile of alkali-activated zeolite-poor rock

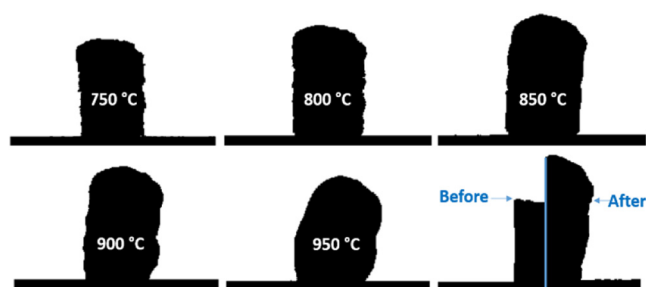


Fig. 3. Heating microscope photos of the alkali-activated zeolite-poor rock before sintering and after sintering at different temperatures

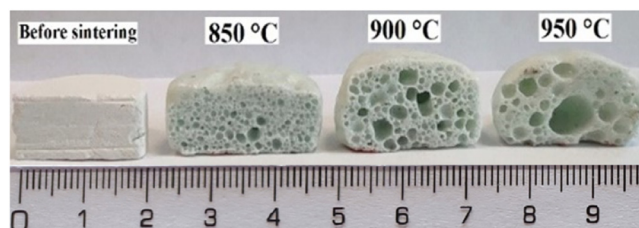


Fig. 4. Glass-ceramic foams showing the samples before sintering and after sintering at different temperatures

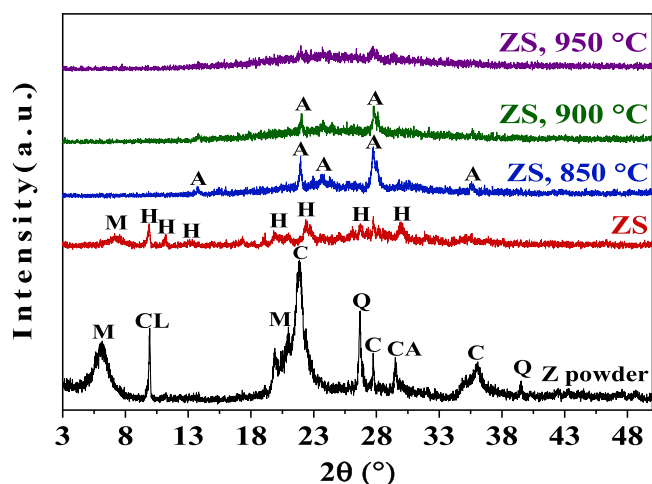


Fig. 5. XRD analysis of zeolite-poor rock powder, alkali-activated powder, and sintered samples (Z: zeolite-poor rock, ZS: zeolite-poor + sodium hydroxide, M: montmorillonite; CL: clinoptilolite; C: cristobalite; Q: quartz; CA: calcite; H: heulandite A: anorthite)

between 850 and 950 °C. At this temperature, the alkali-activated materials decompose, corresponding to a low-viscosity state, and are transferred into a semi-liquid phase associated with the decomposition of calcite that produces gas. The emitted gas pushed the viscous material and resulted in the formation of cellular porous ceramics with lightweight and good thermal insulation properties.

3.2. Characterization findings of the sintered glass-ceramic foams

3.2.1. Dimensional behavior after heat treatment. The dimensional variations of the several samples burnt at various temperatures are depicted in Fig. 4. As the sintering temperature rises from 850 to 950 °C, the pores expand and merge with the microscopic pores that surround them, lowering the surface energy of the system. The increase in the pore size could affect the technical characteristics of the samples.

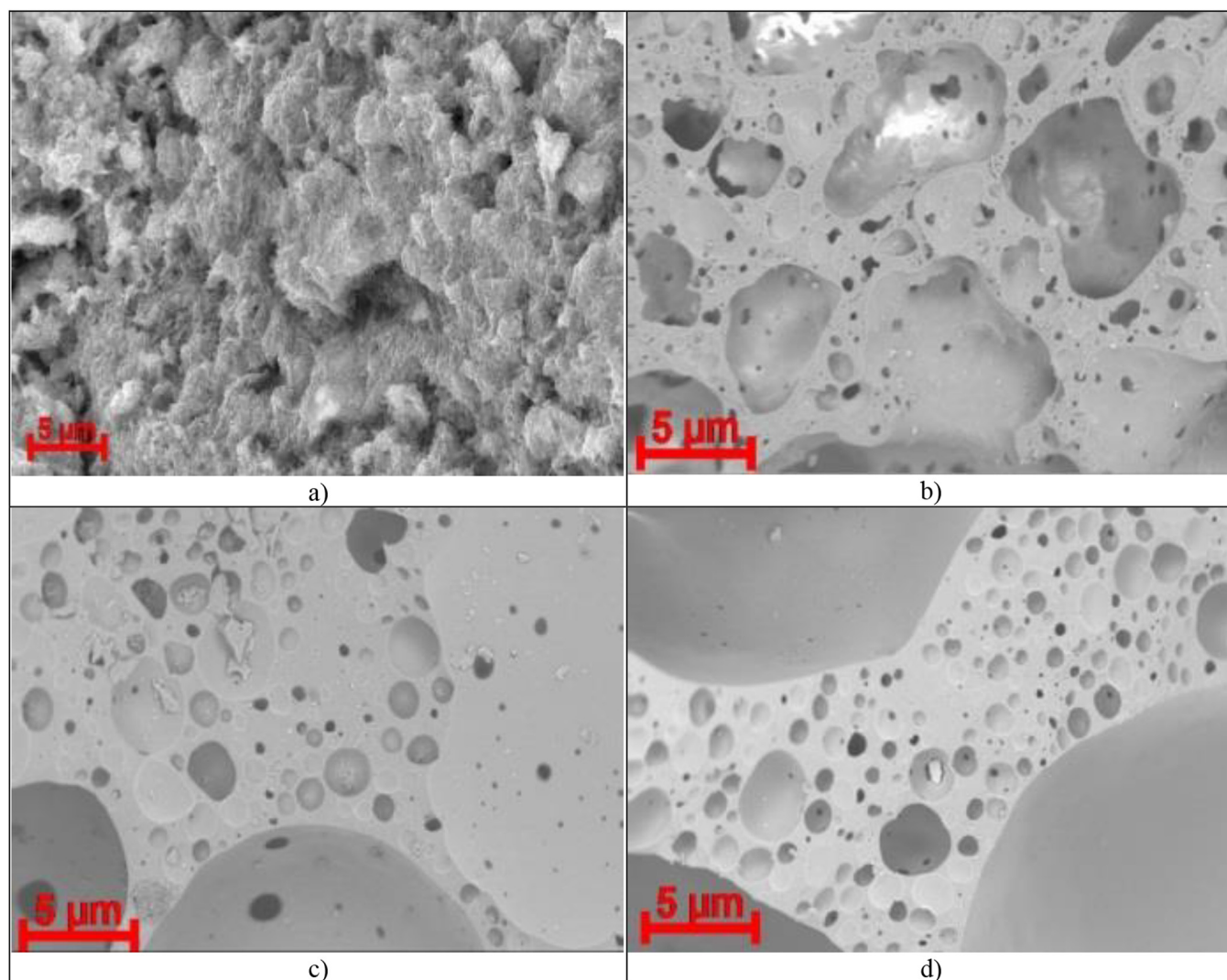


Fig. 6. SEM images of the fracture surface of a) alkali-activated, and sintered samples at b) 850 °C, c) 900 °C and d) 950 °C

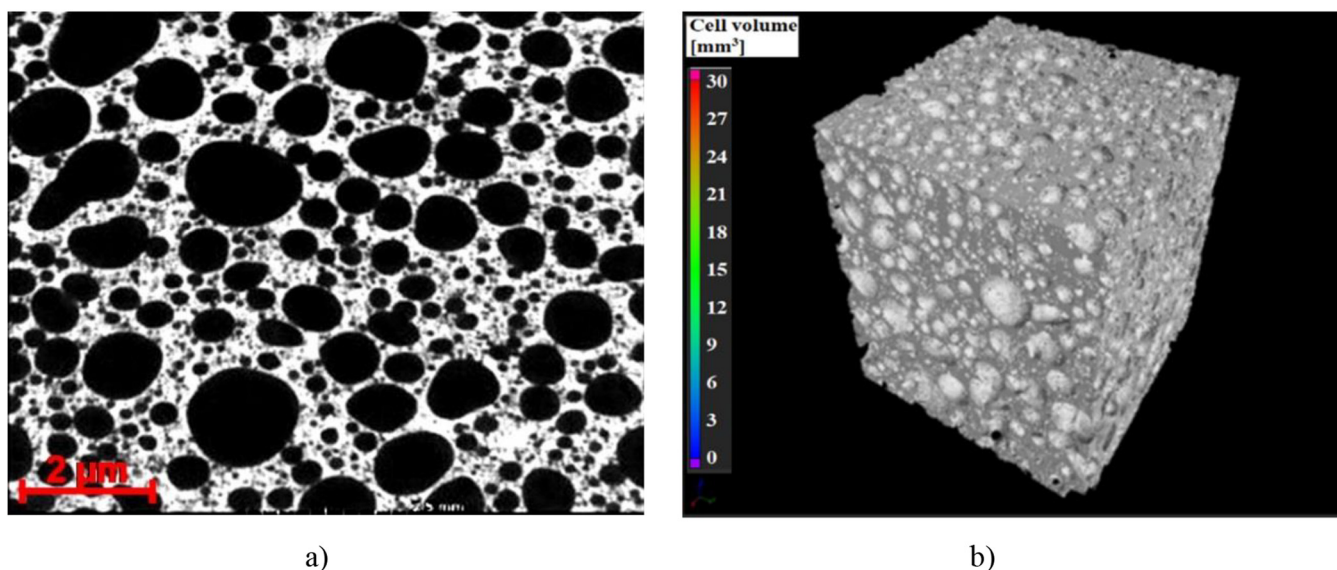


Fig. 7. CT scan images of the foam heat-treated at 850 °C a) top view image and b) 3D image

3.2.2. XRD investigations. Figure 5 shows the XRD spectra of samples heated at different temperatures. The reaction of zeolite-poor rock components with NaOH resulted in the creation of heulandite ($\text{Si}_{36}\text{Al}_{1.21}\text{Na}_{1.52}\text{O}_{97.84}$, PDF# 96-900-2185) after alkali activation. Firing at 850 °C produced an amorphous phase and anorthite ($\text{Na}_{1.92}\text{Ca}_{2.08}\text{Si}_{10}\text{Al}_6\text{O}_{32}$, PDF# 96-100-8758). At a temperature of 950 °C, anorthite decomposes into a completely amorphous phase.

3.2.3. SEM investigation. SEM images of the alkali-activated and sintered samples are shown in Fig. 6. The alkali-activated samples confirm the formation of a whiskers-like structure. All heat-treated samples demonstrate porosity, which is uneven in size and distribution. The pores seen are essentially round-like in form and depicted in the photos by various color differences. The detected different pore size and distribution is thought to be caused by interconnected cells. In general, porosity becomes larger with increasing temperature. This happens due to the reduction in viscosity and increase in the internal pressure of the produced gas that induces the pore coalescence.

3.2.4. CT scan analysis and pore structure characteristics. Figure 7 shows the CT scan images of the glass-ceramic foam sintered at 850 °C. The 3D picture was created by overlaying 1,000 binary photos along the z-axis. Because X-rays are absorbed differently by materials of various densities, the darker area in the 3D image represents the solid portion of the sample, whereas the bright spots indicate the pores. In contrary, the darker area in the top view image represents the pores, while the lighter areas indicate the solid material. It can be seen clearly the formation of semi-spherical pores of different sizes. Most of the large pores are surrounded by smaller pores, and the cell walls can be identified. Pore size and wall thickness have a substantial influence on mechanical properties; smaller pore sizes and broader cell walls are desirable for greater mechanical strength.

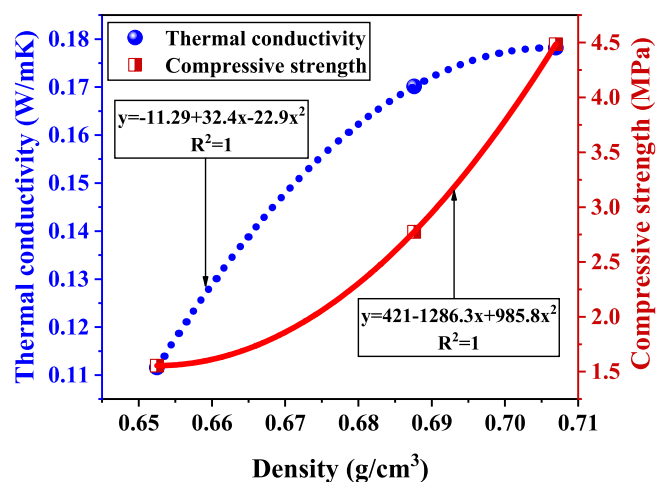


Fig. 8. The correlation between bulk density, thermal conductivity and compressive strength of the glass-ceramic foams sintered at variable temperatures

3.2.5. Technical properties. The connection among compressive strength, density, and thermal conductivity of the generated foams is depicted in Fig. 8. Because the compact material has fewer pores, increasing the density increases thermal conductivity and compressive strength. In contrast, increasing the porosity decreases thermal conductivity since the gaps are generally filled with gases that function as thermal insulators.

4. CONCLUSION

This research revealed that zeolite-poor rock (Tokaj) might be used as raw material to make glass-ceramic foams through alkali-activation and reactive sintering process. The calcite that exists in zeolite-poor rock composition acts as a

foaming agent, which decomposes at higher temperatures and produces gas leading to cellular structure formation. The alkali-activation leads to the formation of low-temperature melting compounds. The XRD and SEM analysis confirmed the formation of heulandite in a whiskers-like structure. The sintered samples showed good foamability in the temperature range of 850–950 °C. Increasing the sintering temperature resulted in large pores formation and transformation of crystalline phases to completely amorphous structure, which lowered the compressive strength. The obtained samples have a low density ($0.6\text{--}0.7\text{ g cm}^{-3}$), moderate thermal conductivity ($0.11\text{--}0.17\text{ W mK}^{-1}$), and good compressive strength ($1.5\text{--}4.4\text{ MPa}$). These satisfying technical characteristics confirm the potential use of the produced glass-ceramic foams for thermal and sound insulation.

ACKNOWLEDGMENTS

The described study was carried out as part of the EFOP-3.6.1-16-2016-00011 “Younger and Renewing University – Innovative Knowledge City – institutional development of the University of Miskolc aiming at intelligent specialisation” project implemented in the framework of the Szechenyi 2020 program. The realization of this project is supported by the European Union, co-financed by the European Social Fund.

REFERENCES

- [1] P. Ahmeti and I. Kistelegdi, “Energy consumption by the type of energy carrier used in residential sector in city of Pristina,” *Pollack Period.*, vol. 14, no. 1, pp. 201–212, 2019.
- [2] T. A. Nguyen, K. Nakagawa, H. P. Duong, Y. Maeda, and K. Otsuka, “Hot-spots and lessons learned from life cycle sustainability assessment of inedible vegetable-oil based biodiesel in Northern Viet Nam,” in *Biofuels for a More Sustainable Future*, J. Ren, A. Scipioni, A. Manzardo, and H. Liang, Eds, Elsevier Inc, chap. 6, 2019, pp. 165–212.
- [3] R. Ibrahim and B. Baranyai, “Developing migrants prototypes performance through bottom-up construction method,” *Pollack Period.*, vol. 16, no. 3, pp. 127–132, 2021.
- [4] M. Rais, S. Elhadad, A. Boumerzoug, and B. Baranyai, “Optimum window position in the building façade for high day-light performance: Empirical study in hot and dry climate,” *Pollack Period.*, vol. 15, no. 2, pp. 211–220, 2020.
- [5] A. M. Rashad, G. M. F. Essa, and W. M. Morsi, “Traditional cementitious materials for thermal insulation,” *Arab. J. Sci. Eng.*, vol. 79, pages 1–13, 2022.
- [6] Z. Chen, H. Wang, R. Ji, L. Liu, C. Cheeseman, and X. Wang, “Reuse of mineral wool waste and recycled glass in ceramic foams,” *Ceram. Int.*, vol. 45, no. 12, pp. 15057–15064, 2019.
- [7] A. Karamanov, E. M. A. Hamzawy, E. Karamanova, N. B. Jordanov, and H. Darwish, “Sintered glass-ceramics and foams by metallurgical slag with addition of CaF_2 ,” *Ceram. Int.*, vol. 46, no. 5, pp. 6507–6516, 2020.
- [8] D. I. Saparuddin, N. A. N. Hisham, S. A. Aziz, K. A. Matori, S. Honda, Y. Iwamoto, and M. H. M. Zaid, “Effect of sintering temperature on the crystal growth, microstructure and mechanical strength of foam glass-ceramic from waste materials,” *J. Mater. Res. Technol.*, vol. 9, no. 3, pp. 5640–5647, 2020.
- [9] C. Zhang, X. Wang, H. Zhu, Q. Wu, Z. Hu, Z. Feng, and Z. Jia, “Preparation and properties of foam ceramic from nickel slag and waste glass powder,” *Ceram. Int.*, vol. 46, no. 15, pp. 23623–23628, 2020.
- [10] M. Assefi, S. Maroufi, I. Mansuri, and V. Sahajwalla, “High strength glass foams recycled from LCD waste screens for insulation application,” *J. Clean. Prod.*, vol. 280, 2021, Paper no. 124311.
- [11] S. Abdollahi and B. E. Yekta, “Prediction of foaming temperature of glass in the presence of various oxidizers via thermodynamics route,” *Ceram. Int.*, vol. 46, no. 16, pp. 25626–25632, 2020.
- [12] J. König, V. Nemanič, M. Žumer, R. R. Petersen, M. B. Østergaard, Y. Yue, and D. Suvorov, “Evaluation of the contributions to the effective thermal conductivity of an open-porous-type foamed glass,” *Constr. Build. Mater.*, vol. 214, pp. 337–343, 2019.
- [13] P. Cimavilla-Román, J. Villafañe-Calvo, A. López-Gil, J. König, and M. Á. Rodríguez-Perez, “Modelling of the mechanisms of heat transfer in recycled glass foams,” *Constr. Build. Mater.*, vol. 274, 2021, Paper no. 122000.
- [14] L. K. Kazantseva and S. V. Rashchenko, “Optimization of porous heat-insulating ceramics manufacturing from zeolitic rocks,” *Ceram. Int.*, vol. 42, no. 16, pp. 19250–19256, 2016.
- [15] B. Liang, M. Zhang, H. Li, M. Zhao, P. Xu, and L. Deng, “Preparation of ceramic foams from ceramic tile polishing waste and fly ash without added foaming agent,” *Ceram. Int.*, vol. 47, no. 16, pp. 23338–23349, 2021.
- [16] Y. Guo, Y. Zhang, H. Huang, K. Meng, K. Hu, P. Hu, X. Wang, Z. Zhang, and X. Meng, “Novel glass ceramic foams materials based on red mud,” *Ceram. Int.*, vol. 40, no. 5, pp. 6677–6683, 2014.
- [17] K. S. Ivanov, “Extrusion method for producing microgranular foam-glass ceramic from zeolite rocks,” *Refract. Ind. Ceram.*, vol. 62, no. 2, pp. 157–161, 2021.
- [18] P. N. Lemougna, P. N. Lemougna, J. Yliniemi, A. Adediran, T. Luukkonen, P. Tanskanen, M. Finnilä, and M. Illikainen, “Synthesis and characterization of porous ceramics from spodumene tailings and waste glass wool,” *Ceram. Int.*, vol. 47, no. 23, pp. 33286–33297, 2021.
- [19] M. Sassi, J. F. M. Ibrahim, and A. Simon, “Characterization of foam glass produced from waste CRT glass and aluminium dross,” *J. Phys. Conf. Ser.*, vol. 1527, 2020, Paper no. 012037.
- [20] D. Kalló, J. Papp, and J. Valyon, “Adsorption and catalytic properties of sedimentary clinoptilolite and mordenite from the Tokaj Hills, Hungary,” *Zeolites*, vol. 2, no. 1, pp. 13–16, 1982.
- [21] J. E. F. M. Ibrahim, O. B. Kotova, S. Sun, E. Kurovics, M. Tihtih, and L. A. Gömze, “Preparation of innovative eco-efficient composite bricks based on zeolite-poor rock and hen’s eggshell,” *J. Build. Eng.*, vol. 45, 2022, Paper no. 103491.
- [22] J. E. F. M. Ibrahim, M. Tihtih, and L. A. Gömze, “Environmentally-friendly ceramic bricks made from zeolite-poor rock and sawdust,” *Constr. Build. Mater.*, vol. 297, 2021, Paper no. 123715.



- [23] J. E. F. M. Ibrahim, E. Kurovics, M. Tihtih, and L. A. Gömze, “Ceramic bricks with enhanced thermal insulation produced from natural zeolite,” *Pollack Period.*, vol. 16, no. 3, pp. 101–107, 2021.
- [24] L. K. Kazantseva and S. V. Rashchenko, “Chemical processes during energy-saving preparation of lightweight ceramics,” *J. Am. Ceram. Soc.*, vol. 97, no. 6, pp. 1743–1749, 2014.

