Characterization of porous glass-ceramic material as absorber of electromagnetic radiation

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Abstract. Investigations of a foam glass-ceramic material synthesized from raw siliceous earth material by the two-stage method at temperatures below 950°C have demonstrated the improvement of its physic mechanical properties in comparison with foam glass synthesized from glass cullet. This material actively interacts with microwaves and can be used for the development of protective screens reducing the adverse effect of microwaves on biological objects, anechoic chambers, and rooms with low level of electromagnetic background noise. Spectra of the transmission and absorption coefficients and of the complex dielectric permittivity for frequencies in the range 26–260 GHz are presented. The observed effects demonstrate the existence of regions with partial and total reflection arising on the glass–pore boundary and of the microwave interaction with ultradisperse carbon particles that remain after foaming with incomplete frother transition from the soot to the gas phase.

Introduction
The increased interest to environmentally safe heat insulation materials is observed at the present time. Such materials are fire proof, durable, do not evolve harmful substances at operation and do not rot. Foam glass is one of such materials. Problems of widening of raw material base are solved both in Russia and in abroad. European researches are directed mainly on use of various kinds of broken glass, for example glasses of electron-beam tubes, computer screens and so on [1–3]. Home researches use as feed composition both broken glass and various kinds of natural and technogeneous raw materials [4–6]. This work considers foam glass materials obtained using two stage low temperature technology. On the first stage a frit is synthesized at temperatures not more than 900 °C. On the second stage the frit powder with additions of gas-forming agent is used to prepare foam forming mixture that is foamed at 800 – 850 °C.

The foam glass material reduces the level of reflected and transmitted electromagnetic radiation [7] and has high heat engineering characteristics, in flammability, moisture resistance, and long lifetime [8, 9]. The materials of this group can be used as heat- and noise-insulating and structural ones. The foam glass radio absorbing granules, possessing rather low weight, are promising for application in aircraft engineering [10], since their placement inside the aircraft fuselage reduces the levels of heat losses and electromagnetic and radiation exposure inevitable at high altitudes and in building industry [11]. The urgency of such multifunctional materials is caused by their fire safety and...
Results of comprehensive investigation of the composition of the foam glass-ceramic material and of its mechanical and electromagnetic properties are discussed in the present study to reveal functional relationships that determine the possibility of obtaining the required physical and chemical characteristics.

**Experimental part**

The foam glass-ceramic material have rather high strength and low density in comparison with foam glasses. This is caused not only by high-quality macrostructure of the material, but also by the structural features of the interporous barrier. In the electron photomicrographs of the FGCM interporous barrier, nanosized structural elements are observed that can be represented as quartz or cristobalite particles on the surface of which one-dimensional Si-O chains are localized (Fig. 1). In our opinion, microglobules that are absent from the foam glass synthesized from the glass cullet are formed in this glass phase. Obviously, amorphous nature of the initial siliceous earth component promotes the formation of microglobular structures, which is finally manifested through an increase in the mechanical strength. The complex structure consisting of individual spheroids and their groups with sizes from 60 to 160 nm is clearly seen in the photomicrograph.

The IR spectral analysis demonstrated that the main differences were observed in the spectral ranges 1100–200 and 2800–3000 cm\(^{-1}\). For the foam glass crystal material, the band lying in the first spectral range was slightly broadened, and the new band arose at 1088 cm\(^{-1}\) that corresponded to non-bridge Si–O–Si bond vibrations and was absent from the foam glass synthesized from the glass cullet. In the second spectral range, the absorption was recorded that could be attributed to valence vibrations of the OH-groups. Hydration of the silicon-oxygen skeleton due to braking of siloxine bridge bonds leads to loosening of the structures. It is obvious that this data with allowance for the photomicrographs of the structure obtained by the method of electron microscopy demonstrated the globular structure of the amorphous component of the interporous barrier.

To investigate the electromagnetic response, flat samples with sizes of 30 × 30 mm were used. The thickness of the sample from commercially available glass cullet was 3.2 mm, and the thickness of the sample from foam glass crystal material was 6.2 mm. The absorption coefficient was calculated from the formula \(A = 1 - R - T\), where \(R\) is the reflection coefficient and \(T\) is the transmission coefficient. Our measurements demonstrated that the reflection coefficients of the samples from two materials were almost equal to zero. This was due to the absorbing properties of the materials and the scattering
properties of the diffuse foam glass surfaces whose allowance was troublesome; therefore, values of the coefficient A were calculated with a certain error.

From Figs. 2 and 3 it can be seen that both materials interact sufficiently actively with electromagnetic radiation. The electromagnetic energy absorption by the foam glass material was most likely caused by the presence of regions of partial and total reflection that arose on the glass-pore boundary. This problem was considered in ample detail in [12] where it was demonstrated that the radio absorbing properties depended on the glass dielectric permittivity, the content of pores, the degree of system porosity, and the pore diameter.

Korolenko [12] formulated requirements to the foam glass material effectively protecting from electromagnetic radiation: \( \varepsilon \) of the foam glass skeleton must be \( \varepsilon_g \geq 6 \) rel. units (in this case, \( \varepsilon_g \) of the pore content must tend to 1); the degree of system porosity must be less than 0.9 rel. units; and the maximum pore diameter must be \( d \leq 1.2 \text{ mm} \). The dielectric permittivity of the examined samples calculated from the measured electromagnetic responses (Figs. 4 and 5) demonstrated that the foam crystal material better satisfied to these requirements.

The other physical mechanism that explains the absorbing properties of the foam glass materials is the interaction of an electromagnetic field with carbon nanoparticles remained after foaming due to incomplete transition of the carbon frother to the gas phase. The localization of carbon nanoparticles and the configuration of conglomerates they formed are mainly determined by micropore sizes and structure of the interporous barrier. The formation of coordinated carbon groups leads to the formation of Rayleigh scattering structures, and the radio absorbing properties of the foam glass increase [11].

The carbon nanoparticles can form a volume conductive skeleton. In [11] it was demonstrated that values of the EMR reflection and absorption coefficients of a composite material can be regulated by changing the relative content of the ultradisperse carbon in the composition. In this case, quantum effects arose in the foam glass material, that provide the broadband radiation absorption on a set of the formed energy levels of the transition.

Conclusions

Our investigations have demonstrated that the foam crystal material synthesized from raw siliceous earth materials by the two-stage method at temperatures not exceeding 950°C possesses the improved physic mechanical properties in comparison with the foam glass synthesized from the glass cullet, including its lower density, smaller heat conductivity, and higher compression strength.
This material actively interacts with electromagnetic radiation and can be used for the development of protective screens reducing the adverse EMR effect on biological objects, anechoic chambers, and rooms with low level of electromagnetic background noise. The material interacts most actively with EMR whose frequency exceeds 60 GHz. The observed effects are explained by the existence of regions of partial and total reflection arising on the glass-pore boundary or by the EMR interaction with ultradisperse carbon particles remaining after foaming due to incomplete transition of the frother from soot to the gas phase. The electromagnetic characteristics can be controlled by changing of the composition of the foam glass crystal material and forming the shapes and sizes of micropores, the composition of interporous barriers, and the dielectric permittivity of the skeleton. The electromagnetic characteristics can change significantly after incorporation of carbon nanostructures, including single- and multiwall carbon nanotubes, bulbous structure, and fullerenes [13, 14].

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