

High-temperature interaction of water vapor with lithium ceramics Li_2TiO_3

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ABSTRACT

Selection of materials for fusion reactors and, in particular, for blanket systems is one of the most important tasks that determine the development of fusion energy. Lithium ceramics Li_2TiO_3 is considered as prospective candidate for solid breeders of future fusion reactors' blankets. The paper presents the results of high-temperature tests of $\text{Li}_2\text{TiO}_3 + 5 \text{ mol\% TiO}_2$ ceramics, performed under conditions of blowing with argon containing impurities of water vapor of different isotopic compositions (H_2O , HDO , D_2O) in the range of temperature from 100 °C to 1400 °C. The vapor–gas mixture for the experiment was prepared in a special mixing tank. The interaction of $\text{Li}_2\text{TiO}_3 + 5 \text{ mol\% TiO}_2$ ceramics with chemically active gases and water vapors was investigated by thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometry (MS) methods. As a result of experiment, the dependences of the sample mass change during heating under single purge gas composition was obtained. Mass spectra that characterize the changes in the qualitative composition of the gas mixture in the reaction chamber with the investigated sample were recorded and subsequently analyzed. An isotope effect is observed during the experiment: the release of D_2 gas begins significantly earlier than the release of HD gas. The observed effect appears only in the high-temperature region (above 1050 °C), which characterizes the investigated material as almost completely chemically neutral towards water vapor.

1. Introduction

Investigation of fusion reactor (FR) materials and, in particular, functional materials for blanket systems is one of the most important tasks that determine the development of fusion energy. Today, many studies have been performed to test blanket materials under conditions comparable to those of a FR [1–3].

Lithium metatitanate Li_2TiO_3 is considered as prospective candidate for producing tritium in solid breeder blanket concept of DEMO reactor. Several concepts of test blanket modules based on lithium ceramics are being developed for testing at the ITER reactor [4]. Lithium metatitanate Li_2TiO_3 has good tritium release parameters, as well as good thermal and thermomechanical characteristics [5,6].

Interaction of breeder materials with chemically active impurities, such as oxygen, hydrogen and water vapor, contained in the purge gas significantly affects the properties of these materials [7,8].

There are studies on the characteristics of changes in lithium ceramics' different properties during prolonged temperature exposure in

noble gas mediums [9] and in their interaction with a structural blanket material [10–13] are presented.

In [14,15] the release behavior of water vapor from Li_2TiO_3 pebbles was observed at high temperatures were studied. The materials and conditions of the experiments were similar. In [14] the H_2/N_2 gas purge was maintained at 900 °C for 5, 12, and 48 h in order to track the mass loss of the sample in the hydrogen atmosphere. In order to assess the impact of water vapor on mass loss, 5 and 24 h of 900 °C $\text{H}_2\text{O}/\text{Ar}$ purge gas were also conducted. In [15] the release of water vapor was observed at about 450 °C, caused by the decomposition of LiOH in addition to the release of adsorbed water at the beginning of heating. A large release peak of CO_2 was observed at 700 °C, caused by the decomposition of Li_2CO_3 . The change of pebble structure and the influences of LiOH and Li_2CO_3 is discussed. Continuation of works by the authors on investigation of water vapor concentration dependence and temperature dependence of Li mass loss from lithium metatitanate and lithium orthosilicate were given in [16].

Effect of surface water on tritium release behavior from lithium

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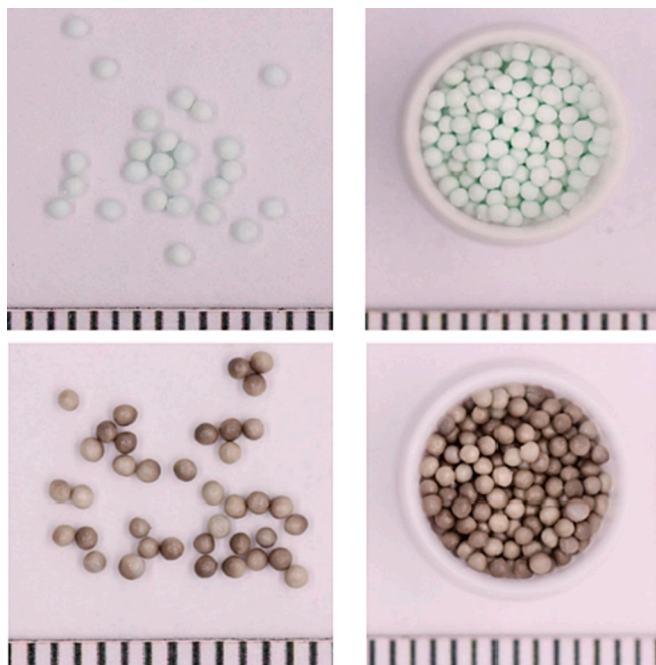


Fig. 1. Test samples of Li_2TiO_3 lithium ceramics before corrosion experiments (top) and after corrosion experiments (bottom).

orthosilicate is discussed by authors in [17]. Authors observed in this study that Li_4SiO_4 pebbles have the nature to react rapidly with water vapor and melts in water and conclude that water from the water generation reaction gives the profound effect on tritium release behavior from the Li_4SiO_4 blanket.

The study of the thermophysical parameters of two-phases lithium orthosilicate ceramics, as well as their changes depending on the phase composition is discussed in [18]. The decrease in strength and thermophysical characteristics after 500 h of annealing was less than 5 % was observed. The authors concluded that general trend of change in resistance to cracking as a result of prolonged thermal heating indicates that the presence of Li_2SiO_3 impurity phases leads to an increase in resistance to high-temperature degradation.

First results of the investigation of Li_2ZrO_3 and Li_2TiO_3 pebbles were given in [19]. Behavior on air exposure (moisture and CO_2 adsorption) was investigated for the Li_2TiO_3 powder, Li_2TiO_3 pebbles, and the sintered Li_2TiO_3 pebbles, using measurement of weight change as a function of exposure time.

Other experiments with oxide ceramics are also worth mentioning. For instance, various experiments with MgAl_2O_4 ceramics and its diverse exposures such as positron radiation and heavy ion irradiation are given and described in [20–22]. Authors presents a universal approach that can be used to study free volume in functional ceramic materials like magnesium aluminate, with pronounced porosity which should allow the application of the technique in the case of other functional nanoporous materials.

However, studying the interaction of blanket materials with reactive gases and water vapor under conditions simulating its actual operation is an important task that requires detailed clarification. The study of interaction between blanket materials with reactive gases and water vapor under conditions simulating its real operation allows drawing conclusions both about the applicability of these materials and, since the developed models and mechanisms of such interaction, to obtain information on the necessary technological features of their application, up to recommendations on change in manufacturing technology and preparation of these materials for work.

This paper presents the results of high-temperature tests of $\text{Li}_2\text{TiO}_3 + 5 \text{ mol\% TiO}_2$ ceramics, performed under conditions of blowing with

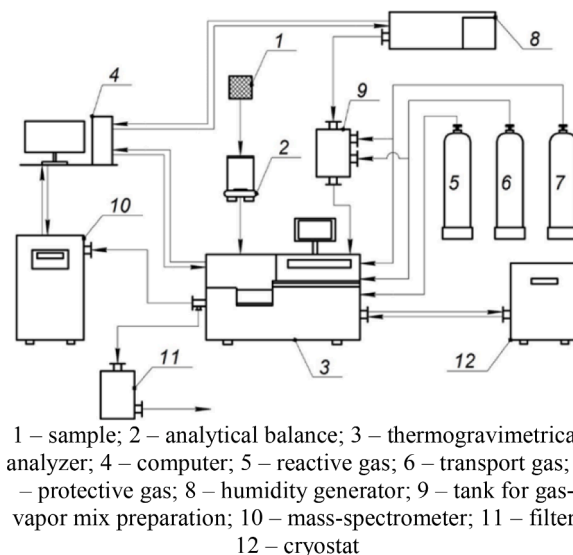


Fig. 2. Scheme of the experimental setup.

argon containing impurities of water vapor of different isotopic compositions (H_2O , HDO , D_2O).

The present experiments with lithium ceramics have been performed by a complex method that allows combining thermogravimetric, differential scanning calorimetry (DSC) and mass spectrometric methods in a single experiment.

2. Experimental part

Lithium metatitanate pebbles enriched up to 96 % in the ^6Li isotope with 5 % addition of TiO_2 were used as the test sample (Fig. 1). A pebble bed of 200 pebbles with a total mass of 305.66 mg was studied. Pebbles were obtained by the sol-gel technology.

The studies were carried out on the experimental complex (Fig. 2) [23], which allows TGA, DSC and mass-spectrometric measurements to be performed. The experiment parameters were as follows:

– sample heating temperatures	from 100 to 1400 °C;
– linear heating rate of samples	10 °C/min;
– cooling rate	~40 °C/min;
– medium	Ar + D_2O ;
– furnace purge time before heating	60 min;
– gas flow rate during experiments	50 ml/min.

In order to ensure correct operation of the experimental system, a calibration experiment using reference samples was performed. According to the results obtained during calibration, the measurement error was no more than 0.2 %.

Method of high-temperature tests consisted in the following. Before the experiments, the TGA-DSC 3 + module was heated and the weighing cell was stabilized. After this, the cell was purged with an Ar + D_2O mixture for 60 min at 100 °C. The sample was mounted on a platinum substrate of a TGA-SDTA ceramic sensor, installed in a TGA-DSC 3 + analytical device.

During the experiment, constant control measurements of the mass of the studied $\text{Li}_2\text{TiO}_3 + 5 \text{ mol\% TiO}_2$ samples were carried out. To achieve the goals of the study, a temperature program for heating and cooling the sample was set before the experiment (linear heating ranged from 100 °C to 1400 °C at a rate of 10 °C/min).

Argon with heavy water vapor was used as a purge gas to purge the reaction chamber at a given flow rate. The experimental data obtained as a result of the tests are saved and further processed using the STARE software built into the TGA-DSC 3 + analytical device.

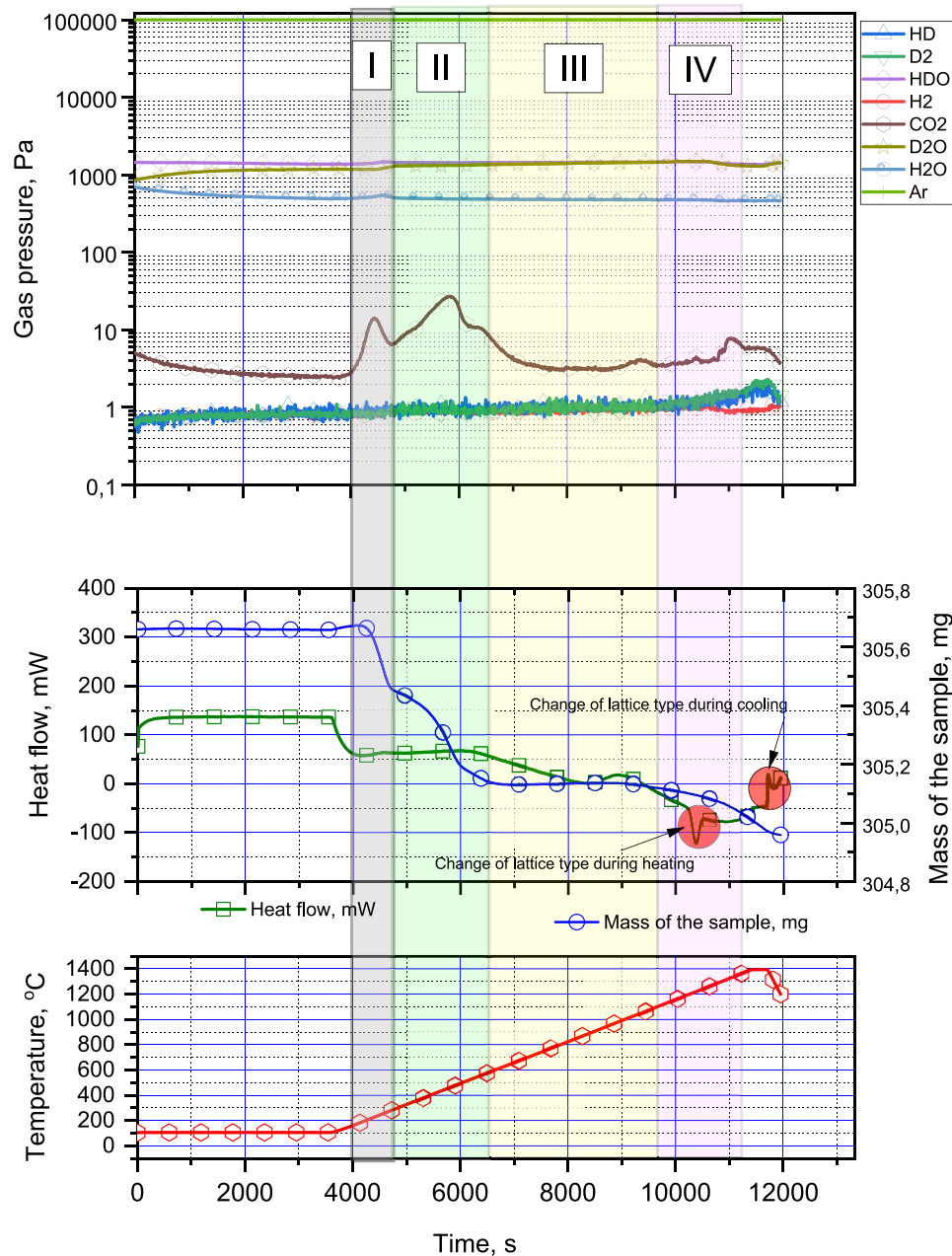


Fig. 3. Diagram of the experiment.

3. Results and discussion

The diagram of the experiment is shown in Fig. 3.

Analyzing the obtained dependencies, for convenience, we divide the diagram into 4 sections, which we characterize as follows:

Section I (155–285 °C) – initial experimental area, in which the interaction of oxygen with carbon on the surface of ceramics $C + O_2 \rightarrow CO_2$ occurs; the closure of oxygen vacancies on the surface of ceramics; (Mass loss begins, peak of CO_2 release is observed).

Section II (285–585 °C) – open porosity evolving (due to heating of the sample and appearance of vacant pathways to the area of closed pores); increase of the sample surface; continuation of oxygen interaction with carbon on the ceramic surface by $C + O_2 \rightarrow CO_2$ reaction. Mass loss continues with a local bend in the area of the interface between sections I and II, a second peak of CO_2 release is observed.

Here, the kinetics of CO_2 gas release indicates that the amount of carbon determines the release rate, and after decarburization of the

exposed surface of the ceramic, the reaction is ceased. Total amount of carbon on the ceramic surface $\sim 2.92 \cdot 10^{-2} \text{ mol/m}^2$;

The rate constant of a chemical reaction:

$$K = 2.1 \cdot 10^{-8} (\text{mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})) \cdot \exp(-13.5 \text{ kJ}/(\text{mol} \cdot (\text{R} \cdot \text{T})))$$

It is worth noting that the observed peaks can also be explained by the release of CO_2 gas from the ceramics. The presence of carbon-containing compounds on the ceramic surface (or CO_2 gas in the pores of the sample, which become open when heated) is apparently due to the peculiarities of sample manufacturing. One way or another, the mass loss of the pebbles is practically negligible (less than 0.2 % over the entire heating cycle) and stops after a temperature of 585 °C.

Section III (585–1050 °C) – the region where almost no interaction occurs; (no mass loss and gas phase change are observed).

Section IV (1050–1400 °C) – the moment of ceramics lattice change (from monoclinic to cubic), which is accompanied by the appearance of new vacant pathways into the pebble volume, water vapor interaction

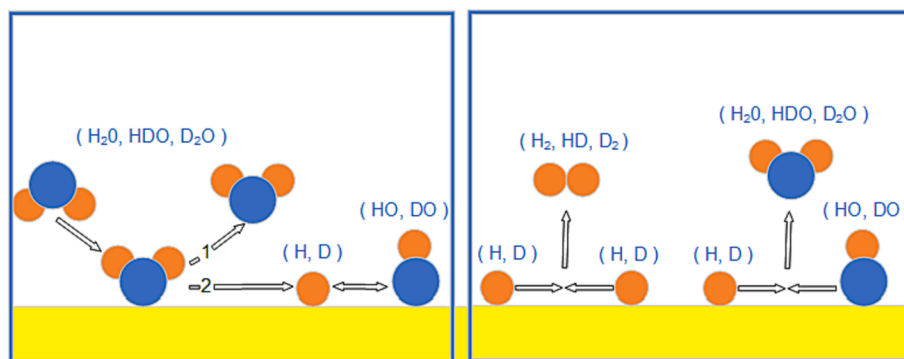


Fig. 4. The scheme of interaction of water vapor with the surface of ceramics.

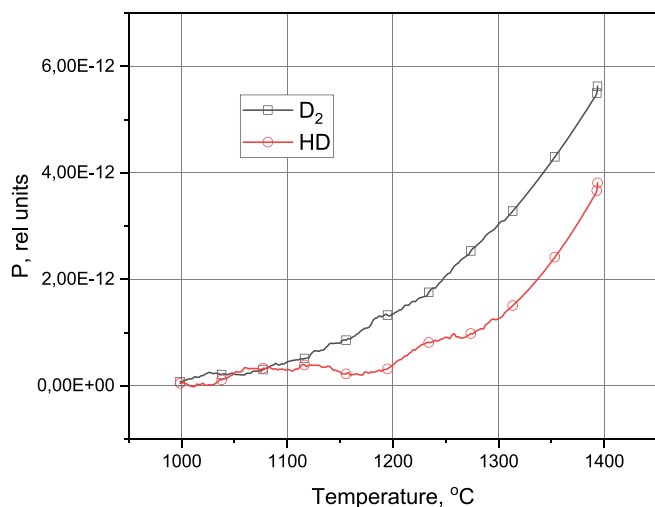


Fig. 5. Release of hydrogen-containing gases.

with ceramics occurs; the mass of the sample begins to drop and hydrogen gases are released. The process of formation of D_2 and HD molecules on the surface of ceramics is apparently associated with a chain of processes of adsorption and subsequent dissociation of water molecules into a hydrogen atom and an OH (or OD) complex (see Fig. 4) with subsequent association of hydrogen isotope atoms and their desorption.

There is a noticeable isotope effect, as shown in Fig. 5: the release of D_2 gas begins significantly earlier than the release of HD gas. The estimated activation energies of the effective reaction for the complex of processes (adsorption-dissociation-association-desorption) appeared to be equal for the chain, associated with the release of D_2 – 140 kJ/mol, and 244 kJ/mol for HD molecule.

The mechanism for the release of these molecules is associated with two stages of processes on the surface: initially, a water molecule (D_2O or HDO) from the gas phase is adsorbed on the surface of the ceramic, after which either its reverse desorption occurs or dissociation into a hydrogen isotope atom and an O–H(D) complex. Next, the association of atoms of hydrogen isotopes occurs on the surface of the ceramic. Since the release of D_2 molecules begins earlier than HD molecules (at approximately the same vapor pressure of water D_2O and HDO in the gas phase), it is logical to assume that when the HDO molecule dissociates on the ceramic surface, a free deuterium atom and an OH complex are

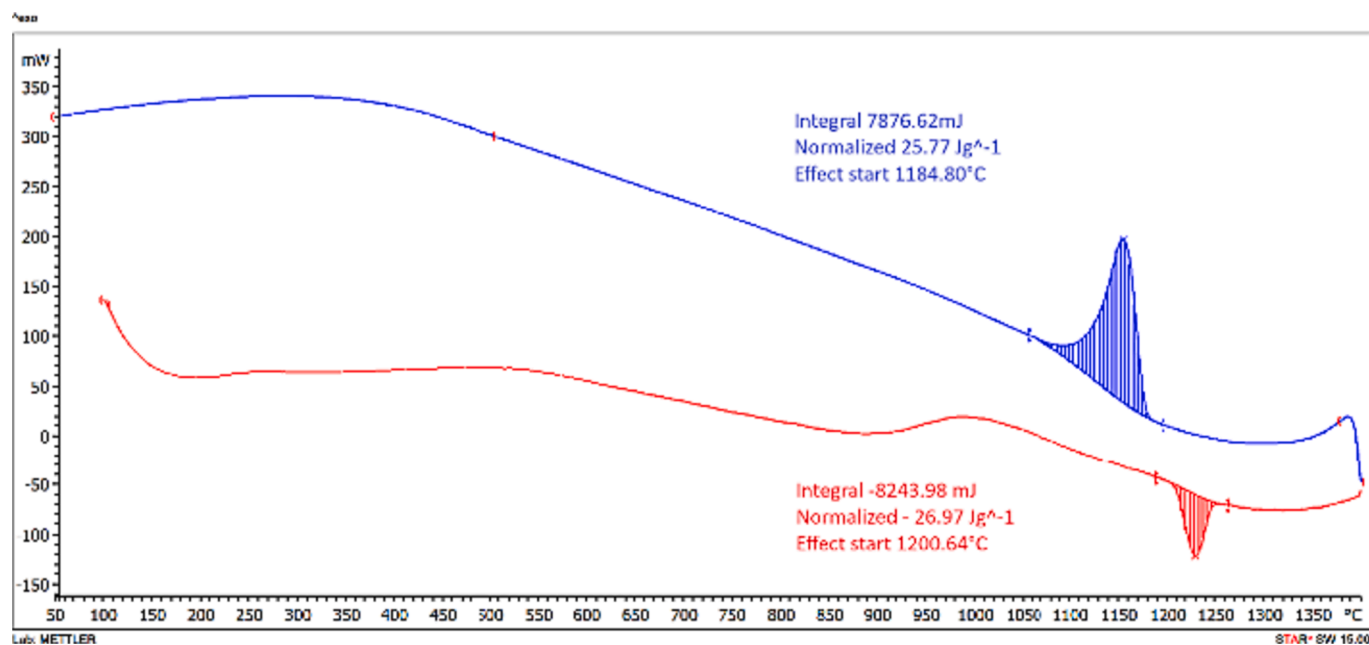


Fig. 6. Temperature dependence of heat flux variation from the sample during heating (red) and cooling (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

preferentially formed.

DSC curve, describing the temperature dependence of the sample heat flux is shown in Fig. 6. Processing of DSC analysis results was carried out using the built-in standard processor in STARe software. For visible thermal effects on the obtained DSC dependence the construction of the base line with calculation of the integral area under the curve is carried out. According to the obtained values after the integral area calculation. STARe software recalculates and determines the temperatures of the beginning and end of the effect as well as the heat of phase transition.

It is worth noting separately that the DSC curve shows peak deviations from monotonic trends in heat flux changes (Figs. 3 and 6), which are associated, as mentioned above, with lattice restructuring.

While processing the temperature dependence of the change in the heat flux of the ceramic sample during purging in argon medium with heavy water vapor, an endothermic thermal effect is observed during heating at temperatures of 1200.64 °C with reaction heat equal to −26.97 J/g. During cooling, a thermal effect of exothermic character is observed at 1184.80 °C with reaction heat of −25.77 J/g.

4. Conclusion

As a result of experiments to study the interaction of water vapor of different isotopic compositions with lithium ceramics $\text{Li}_2\text{TiO}_3 + 5 \text{ mol\% TiO}_2$, it was found that a noticeable interaction of water vapor with ceramics begins at temperatures above 1050 °C, and there is a noticeable difference in the beginning of the release of D_2 and HD molecules. A mechanism of processes on the ceramics surface was proposed that explains this difference.

The activation energies of the effective reaction for a complex of processes (adsorption-dissociation-association-desorption) were estimated, which turned out to be equal for the chain associated with the release of D_2 (140 kJ/mol) and HD (244 kJ/mol).

The release of CO_2 gas from the lithium ceramics was observed in the temperature range of 155–585 °C, which mainly determined the weight loss of the samples. This release was observed in the form of two peaks, and can be associated either with the interaction of oxygen with carbon-containing impurities on the surface of the ceramic, or with the release of CO_2 gas from the closed pores of the ceramic (which open when heated).

CRedit authorship contribution statement

Timur Kulsartov: Writing – review & editing, Supervision, Conceptualization. **Kuanysb Samarkhanov:** Writing – original draft, Investigation. **Inesh Kenzhina:** Validation, Formal analysis. **Zhanna Zaurbekova:** Writing – review & editing, Formal analysis. **Vadim Bochkov:** Investigation, Data curation. **Alexandr Yelishenkov:** Validation. **Yevgen Chikhray:** Methodology, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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