

Flux crystal growth of Cu_2GaBO_5 and Cu_2AlBO_5

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ABSTRACT

The results of growth of two oxyborate single crystals, Cu_2GaBO_5 and Cu_2AlBO_5 , with ludwigite structure from different flux systems using the spontaneous nucleation technique are reported. We obtained large Cu_2GaBO_5 and Cu_2AlBO_5 crystals of dimensions up to $3 \times 4 \times 15 \text{ mm}^3$ and $1 \times 1 \times 10 \text{ mm}^3$, respectively. Trimolybdate-bismuth fluxes diluted with the sodium carbonate for both Cu_2GaBO_5 and Cu_2AlBO_5 , as well as lithium-molybdate and lithium-borate fluxes for Cu_2AlBO_5 , were used. It was observed that the growth of Cu_2GaBO_5 and Cu_2AlBO_5 is accompanied by the growth of CuO , $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$, and $\text{Cu}_2\text{Al}_{1-x}\text{Ga}_x\text{BO}_5$ crystals as secondary phases. Structural and magnetic characterization of the crystals is also performed.

1. Introduction

Oxyborates with ludwigite structure are a large family of quasi-two-dimensional materials with general formula $\text{M}_1\text{M}_2\text{B}_2\text{O}_5$, where M1 and M2 are di- and trivalent metals, respectively. The other combinations of heterovalent cations such as di- and tetravalent [1–3] or di- and pentavalent [4] metals, accompanied by a change in the M1/M2 ratio for electroneutrality, are also possible.

The flux crystal growth technique is most often used to obtain large single crystal samples of oxyborates with ludwigite structure due to the presence of the growth anisotropy [5–9]. The undoubted merits of this method are the natural grow habit of single crystals and the possibility to use different solvent types for individual growth conditions, required for different compounds [10–12].

Currently, a few dozens of oxyborates with ludwigite structure having various combinations of M1 and M2 metals are known, synthesized, and studied [1–9,13–15]. In this work, we focus on the copper-containing ludwigites Cu_2MBO_5 ($\text{M} = \text{Ga}, \text{Al}$). These compounds, like other copper-containing ludwigites, have a monoclinically distorted ludwigite structure due to the Jahn-Teller effect of copper 2+ ions [5–9,13]. It is known that gallium-copper-borate is an antiferromagnet below the temperature $T_N = 4 \text{ K}$ [6,7]. The magnetic properties of aluminum-copper-borate haven't been studied. There are several studies aimed at the synthesis of Cu_2GaBO_5 and Cu_2AlBO_5 [5–7].

The growth of single crystals in these works was performed by the flux technique using fluxes, based on the borax $\text{Na}_2\text{B}_4\text{O}_7$ [5] system for

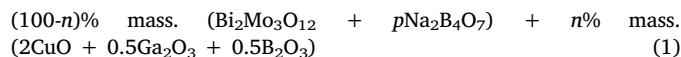
Cu_2AlBO_5 and B_2O_3 [6] or $\text{B}_2\text{O}_3\text{-Li}_2\text{O}$ [7] for Cu_2GaBO_5 . However, due to the high viscosity of most boron-based flux systems (in the cases of [5,6]), the sizes of single crystals were limited by $0.05 \times 0.05 \times 0.04 \text{ mm}^3$ [5]. In this work, we describe in detail our results of growth of Cu_2GaBO_5 and Cu_2AlBO_5 single crystals from the trimolybdate-bismuth fluxes diluted by the sodium carbonate (Cu_2GaBO_5 and Cu_2AlBO_5), lithium-molybdate fluxes (Cu_2AlBO_5), and lithium-borate fluxes (Cu_2AlBO_5).

2. Crystal growth

In this section, the growth of oxyborate single crystals, Cu_2GaBO_5 and Cu_2AlBO_5 , is described.

2.1. Growth of Cu_2GaBO_5 single crystals

To grow Cu_2GaBO_5 single crystals, the process of crystallization was studied for the following flux system:



Previously, bismuth-trimolybdate-based fluxes have been used for the synthesis of $\text{Cu}_{3-x}\text{Mn}_x\text{BO}_5$ single crystals [1,8], which belong to the family of Cu-containing oxyborates with ludwigite structure, just like Cu_2GaBO_5 and Cu_2AlBO_5 . The specified in Eq. (1) solvent allows to: (i) decrease the viscosity of the flux, (ii) increase the concentration of the

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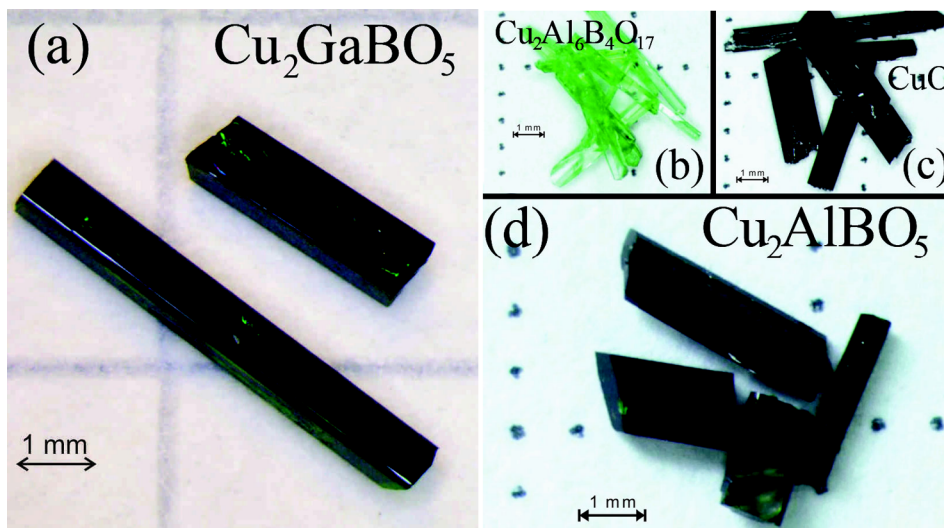


Fig. 1. Optical photographs of (a) Cu_2GaBO_5 , (b) $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$, (c) CuO , and (d) Cu_2AlBO_5 crystals.

crystal-forming oxides, (iii) use suitable operating temperatures ($T < 900\text{ }^\circ\text{C}$), that results in small losses of the components due to evaporation. As a result of varying flux parameters n and p in Eq. (1), we obtained the following optimal growth conditions: $n = 36\%$, $p = 1$. The corresponding flux saturation temperature and the cooling rate are $T_{\text{sat}} = 875\text{ }^\circ\text{C}$ and $dT/dt = 2\text{ }^\circ\text{C/day}$.

The above flux system (1) was prepared at temperature $T = 1100\text{ }^\circ\text{C}$ in a 100 cm^3 platinum crucible by sequential melting of the system components in the following order: (i) borax $\text{Na}_2\text{B}_4\text{O}_7$ was prepared from the powder of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ at $T = 1100\text{ }^\circ\text{C}$; (ii) powder mixture of B_2O_3 , Bi_2O_3 , MoO_3 oxides was added; (iii) Ga_2O_3 powder was added; (iv) CuO powder was added.

The prepared flux was homogenized at $T_{\text{hom}} = 1100\text{ }^\circ\text{C}$ for 4 h. The platinum rod-like crystal holder was inserted into the crucible at the stage of homogenization. The cooling of the sample was carried out in 2 stages. Firstly, the temperature was rapidly reduced to $(T_{\text{sat}} - 10)^\circ\text{C} = 865\text{ }^\circ\text{C}$ with the cooling rate of $100\text{ }^\circ\text{C/hour}$. Secondly, the temperature was slowly reduced with the cooling rate of $2\text{ }^\circ\text{C/day}$. The grown single crystals in the form of dark-green prisms up to $3 \times 4 \times 15\text{ mm}^3$ in size (Fig. 1a) were separated from the crystal holder. The remaining flux was removed by etching in a 20% aqueous solution of nitric acid HNO_3 .

2.2. Growth of Cu_2AlBO_5 single crystals

To grow Cu_2AlBO_5 , several flux systems were studied. At the first stage, we chose the flux system, similar to as in the case of Cu_2GaBO_5 and based on the bismuth-trimolibdate $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and borax $\text{Na}_2\text{B}_4\text{O}_7$:

$$(100-n)\% \text{ mass. } (\text{Bi}_2\text{Mo}_3\text{O}_{12} + \text{Na}_2\text{B}_4\text{O}_7 + q\text{B}_2\text{O}_3 + s\text{CuO}) + n\% \text{ mass. } (2\text{CuO} + 0.5\text{Al}_2\text{O}_3 + 0.5\text{B}_2\text{O}_3) \quad (2)$$

However, the high-temperature crystallizing phase of system (2) was $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$ (Fig. 1b) in a wide range of temperatures and for $q = s = 0$, $n = 10 \div 20\%$. Some difficulties of the flux (2) preparation process were related to the low solubility of Al_2O_3 due to the large difference between $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and Al_2O_3 solvent densities ($\rho = 6.07$ and 3.99 g/cm^3 , respectively). At the same time, the copper oxide CuO has a quite high density ($\rho = 6.31\text{ g/cm}^3$).

To decrease the density of the flux, B_2O_3 ($q = 0.5$) and CuO ($s = 1.13$) were added simultaneously into the flux system (2). Despite the change of flux density and the addition of CuO (the amount of CuO was 2.5 times higher than it is necessary for Cu_2AlBO_5 stoichiometry), the high-temperature crystallizing phase was $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$.

At the second stage, we studied the system, based on the lithium-molybdate Li_2MoO_4 ($\rho = 3.027\text{ g/cm}^3$):

$$(100-n)\% \text{ mass. } (\text{Li}_2\text{MoO}_4 + q\text{B}_2\text{O}_3 + s\text{CuO}) + n\% \text{ mass. } (2\text{CuO} + 0.5\text{Al}_2\text{O}_3 + 0.5\text{B}_2\text{O}_3) \quad (3)$$

Compared with flux (2), this one has a lower density and the same viscosity.

Flux (3) was prepared at $T = 1100\text{ }^\circ\text{C}$ in a 100 cm^3 platinum crucible by sequential melting of the components as follows: (i) the mixture of MoO_3 and B_2O_3 powders was melted; (ii) Li_2CO_3 powder was added in portions; (iii) Al_2O_3 and CuO powders were sequentially added. However, as a result of the crystallization process in a wide temperature range for $q = 0.6$, $s = 0$, and $n = 20\%$, the high-temperature crystallizing phase was the aluminum-enriched $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$ phase.

Sequential increase of coefficients q and s in Eq. (3) up to $q = 1.5$ and $s = 0.35$ (the amount of CuO was 2 times higher than needed for Cu_2AlBO_5 stoichiometry) led to the simultaneous crystallization of $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$ phase and the black crystals of copper oxide CuO in the form of defective flat prisms (Fig. 1c).

Simultaneous stabilization of the ludwigite structure and the crystallization of the $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$ and $\text{Cu}_2\text{Al}_{1-x}\text{Ga}_x\text{BO}_5$ phases was obtained by adding a small amount of the gallium oxide Ga_2O_3 to the system (3) so that the ratio $\text{Al}:\text{Ga}$ was 6:1. With the ratio $\text{Al}:\text{Ga} = 3:1$, $\text{Cu}_2\text{Al}_{1-x}\text{Ga}_x\text{BO}_5$ single phase with ludwigite structure was crystallized in a wide temperature range.

Next, we used the lithium-boron-based flux system:

$$(100-n)\% \text{ mass. } (\text{Li}_2\text{O} + q\text{B}_2\text{O}_3 + t\text{Al}_2\text{O}_3) + n\% \text{ mass. } (2\text{CuO} + 0.5\text{Al}_2\text{O}_3 + 0.5\text{B}_2\text{O}_3) \quad (4)$$

Probed with $n = 48.3\%$, $q = 1.72$, and $t = 0.44$, system (4) allowed to obtain simultaneous crystallization of $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$ and CuO phases, as in the case of system (3) without the gallium oxide Ga_2O_3 .

An increase in B_2O_3 weight content ($q = 1.9$), a decrease in Al_2O_3 weight content ($t = 0.3$), and an increase in the concentration n up to $n = 49.3\%$, led to the formation of the high-temperature crystallizing phase of Cu_2AlBO_5 in a form of long dark-green prisms (Fig. 1d). The flux was prepared at $T = 1100\text{ }^\circ\text{C}$ in a 100 cm^3 platinum crucible by sequential melting of the components: (i) B_2O_3 oxide, (ii) Li_2CO_3 carbonate, (iii) Al_2O_3 oxide, and (iv) CuO oxide were sequentially added. 1 h after the flux preparation, we inserted the rotated platinum rod-like crystal holder into the crucible. The velocity of rotation was $\omega = 20\text{ rpm}$ (rotations per minute). To complete the homogenization

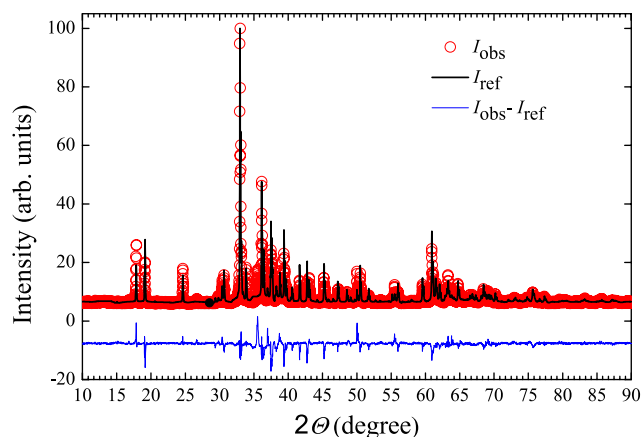


Fig. 2. Powder diffraction pattern of Cu_2AlBO_5 : measured intensities (circles), refined pattern (black solid line), and difference pattern $I_{\text{obs}} - I_{\text{ref}}$ (solid blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

process, the flux temperature has been kept fixed at $T_{\text{hom}} = 1050$ °C for 3 h. The temperature was reduced firstly rapidly to $(T_{\text{sat}} - 10)$ °C = 882 °C and then slowly with a cooling rate of 2 °C/day (without rotation of the crystal holder). In 6 days, the crystal holder with the grown crystals in the form of dark-green prisms of a size up to $1 \times 1 \times 10$ mm³ (Fig. 1d) was extracted from the flux. The remaining flux was removed by etching in a 20% aqueous solution of nitric acid HNO_3 .

3. Crystal structure and growth habit

The structural properties of the crystals were studied by the conventional X-ray diffraction on powdered single crystals at room temperature using a Bruker D8 ADVANCE diffractometer with $\text{CuK}\alpha$ radiation. The diffraction patterns are shown in Fig. 2 and Fig. 3 for Cu_2AlBO_5 and Cu_2GaBO_5 , respectively. The data were analyzed by the standard Rietveld refinement using the FULLPROF software [16]. No impurity phases were detected above the background. We notice that the refinement cannot completely describe the observed peak intensities. This may be due to the joint effect of texture, stacking faults, and strain of the sample when crushing into the powder. The structural analysis confirmed the $P2_1/c$ monoclinic structure of Cu_2AlBO_5 and

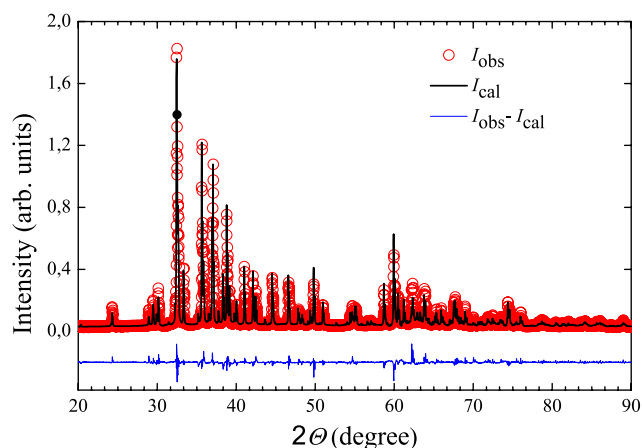


Fig. 3. Powder diffraction pattern of Cu_2GaBO_5 : measured intensities (circles), refined pattern (black solid line), and difference pattern $I_{\text{obs}} - I_{\text{cal}}$ (solid blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

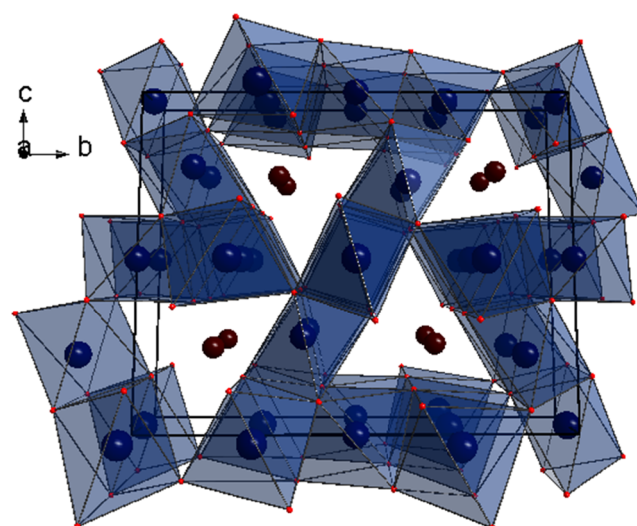


Fig. 4. Crystal structure of Cu_2MBO_5 ($M = \text{Ga}, \text{Al}$) ludwigites (Cu-O and M-O octahedra are blue-colored; B and O are shown in dark-red and red colors; axis a is directed towards the reader). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Cu_2GaBO_5 . The lattice parameters are $a = 3.066$ Å, $b = 11.767$ Å, $c = 9.366$ Å, $\beta = 97.734^\circ$ for Cu_2AlBO_5 and $a = 3.114$ Å, $b = 11.927$ Å, $c = 9.477$ Å, $\beta = 97.865^\circ$ for Cu_2GaBO_5 . These parameters are well consistent with the values reported in [6,7].

The crystal structure of Cu_2AlBO_5 and Cu_2GaBO_5 is shown in Fig. 4. The oxygen octahedra with di- or trivalent cation in the center are the main structure-forming elements of ludwigites. The octahedra form zig-zag chains connected to each other by the triangles of $[\text{BO}_3]^{3-}$ groups. It is clearly seen from Fig. 1 that the growth habit of the ludwigite single crystal is formed by the elongated prisms whose longitudinal size is at least an order of magnitude greater than the transverse one. The crystallographic indices were determined for all the transverse planes of each single crystal by means of X-ray diffraction. All the indices belong to the $[0\ K\ L]$ array. Therefore, the single crystal is grown along the crystallographic axis a . From the point of view of the single crystal growing, this direction is the easy-growth direction, and the perpendicular plane is not.

4. Magnetic susceptibility

The magnetization M of single-crystal samples was measured by the commercial Physical Properties Measurements System (PPMS-9 device) within a temperature range of $2\ \text{K} \leq T \leq 400\ \text{K}$ in field-cooled (FC) regime in a magnetic field of 1 kOe. Fig. 5 shows the FC magnetic susceptibility $\chi = M/H$ of Cu_2GaBO_5 and Cu_2AlBO_5 ludwigites as a function of the temperature with the magnetic field being parallel and perpendicular to the crystallographic axis a . The temperature dependencies of the derivative of the magnetic susceptibility $\partial\chi/\partial T$ measured in the FC regime at low temperatures are shown in the insets of Fig. 5. The magnetic phase transition temperature was obtained as the susceptibility anomaly which corresponds to the maximum of the derivative of the magnetic susceptibility: $T = 4.1 \div 5.5\ \text{K}$ for Cu_2GaBO_5 and $T = 2.1\ \text{K}$ for Cu_2AlBO_5 , respectively (Fig. 5). These values are in agreement with our published results [17]. The obtained temperature for Cu_2GaBO_5 is different from the previously observed Néel temperature $T_N = 3.4\ \text{K}$ [7]. The difference in Néel temperatures can result from the quality of the sample or from the destruction of the antiferromagnetic order by a sufficiently weak magnetic field.

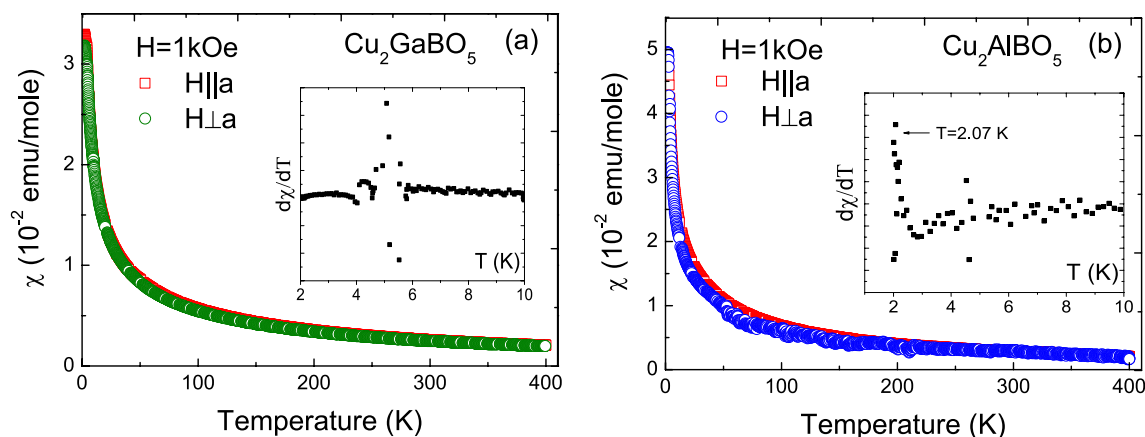


Fig. 5. Temperature dependencies of the magnetic susceptibility in (a) Cu_2GaBO_5 and (b) Cu_2AlBO_5 ludwigites measured in FC regime with the magnetic field ($H = 1$ kOe) being parallel and perpendicular to the crystallographic axis a . Insets show the temperature dependencies of the derivative of the magnetic susceptibility at low temperatures.

5. Summary

The keygoals of this work were to grow large single crystals of Cu_2GaBO_5 and Cu_2AlBO_5 ludwigites and to study their physical properties. We described in detail the research of flux systems used for growing these compounds. In the case of Cu_2GaBO_5 , the optimal growing system is based on bismuth trimolybdate. It has low viscosity and is characterized by high solubility of crystal-forming oxides. Flux crystal growth of Cu_2AlBO_5 was more complex due to the significant difference in densities of crystal-forming oxides. Three flux systems were studied to obtain the desired Cu_2AlBO_5 phase, and the optimal one is based on lithium-boron. As secondary phases, we have obtained single crystals of CuO , $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$, and $\text{Cu}_2\text{Al}_{1-x}\text{Ga}_x\text{BO}_5$. Thus, we have studied several areas of the phase stability diagram.

We obtained Cu_2GaBO_5 and Cu_2AlBO_5 crystals of dimensions up to $3 \times 4 \times 15 \text{ mm}^3$ and $1 \times 1 \times 10 \text{ mm}^3$, respectively. The monoclinically distorted ludwigite structure and the phase purity of Cu_2GaBO_5 and Cu_2AlBO_5 are confirmed by means of X-ray powder diffraction. The magnetic characterization revealed antiferromagnetic ordering in both compounds. The temperature of the antiferromagnetic phase transition is found to be $T_N = 4.1 \div 5.5 \text{ K}$ for Cu_2GaBO_5 and $T_N = 2.1 \text{ K}$ for Cu_2AlBO_5 .

CRedit authorship contribution statement

E.M. Moshkina: Conceptualization, Methodology, Investigation, Writing - original draft. **T.P. Gavrilova:** Investigation, Data curation, Writing - review & editing. **I.F. Gilmuddinov:** Investigation, Resources. **A.G. Kiiamov:** Investigation, Resources, Writing - review & editing. **R.M. Eremina:** Supervision, Writing - review & editing.

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.

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