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Crystal formation of Cu-Mn-containing oxides and oxyborates in bismuth-boron fluxes diluted by MoO_3 and Na_2CO_3

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ABSTRACT

The high-temperature crystallizing phases of fluxes (molten solutions) based on Bi_2O_3:MoO_3 = 1:3 and diluted by Na_2CO_3 and B_2O_3 (under varying of Na_2CO_3:B_2O_3), and by CuO and Mn_2O_3 ($0 \leq Mn_2O_3$:$CuO \leq 5$) are studied. The conditions of the stable crystallization of $Mn^{2+}_{1-x}Cu_xMoO_4$, $Mn_2{}^{3+}O_3$, $Mn^{2+}Mn_2{}^{3+}O_4$, $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ and $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ have been found. The influence of MoO_3 and Na_2CO_3 to the crystallization processes of Mn^{2+}- and Mn^{3+}-containing $Mn^{2+}_{1-x}Cu_xMoO_4$ and $Mn^{2+}Mn_2{}^{3+}O_4$ and $Mn_2{}^{3+}O_3$ are clarified. The occurrence of the chemical bonds of these types at the crystallization of Mn-heterovalent $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ and $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ oxyborates is studied. Single crystal growth techniques of these oxyborates are suggested. The results of the structural and magnetic characterization of some discussed compounds are presented.

1. Introduction

The flux technique for the growth of single crystals (or the molten solution technique) is a widely used technique for obtaining high-quality samples of sufficient size [1–8]. Depending on the crystal-chemical properties of the compound to be synthesized in frameworks of this technique it is necessary to choose the solvent. The solvent determines the properties of the flux system (molten solution system).

Bismuth-boron fluxes are widely used for growing single crystals of a high quality of different compound types. Some of the most bright and known examples are such structural types as garnets [6,9], spinels [3,10], and huntites [6,7,11,12]. Bismuth-boron fluxes are characterized by the low viscosity and low melting temperatures. That allows working with high-concentrated systems for growing and obtaining single crystals of high quality and of a large size.

The main idea of the present work is studying the crystal formation of Cu-Mn-containing oxides and oxyborates in bismuth-boron flux systems diluted by MoO_3 and Na_2CO_3. The study investigates the high-temperature crystallizing phase dependence on the varying of the solute and solvent components and determines the optimum conditions for growing Mn-heterovalent oxyborates with warwickite $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ and ludwigite $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ structures. It is supposed that the addition of the MoO_3 and Na_2CO_3 components to the solvent could have a special influence on the crystallization of the compounds containing the transition metal cations. And this influence is caused by the possibility of the formation in such fluxes of compounds which could include these cations in different valence states.

The main difficulty of the oxyborate growth (with warwickite $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ and ludwigite $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ structures) is the variable valence of the manganese cations. That is due to the thermal decomposition of the Mn_2O_3 oxide in the 900–1100 °C temperature range, which leads to the formation of an Mn_3O_4 oxide containing Mn^{2+} cations [13]. Divalent manganese from the flux can enter to the divalent copper subsystem that could significantly affect the magnetic and electrical properties of the synthesized compounds.

The work is composed in the following way: the high-temperature crystallizing phases of bismuth-boron fluxes, diluted by MoO_3 and Na_2CO_3, are discussed; the data on the structure of the grown crystals and the magnetic characterization of some of the obtained compounds are presented.

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2. Experimental details

The general form of the studied flux system could be presented as:

$$(100{-}n)\quad \%\ mass.\ (Bi_2Mo_3O_{12} + pB_2O_3 + q\ Na_2O) + \\ +n\quad \%\ mass.\ (r\quad CuO + s\quad Mn_2O_3) \qquad (1)$$

where n is the concentration of the solute, and p, q, r, s are variable parameters. The flux systems with different combinations of these parameters are being studied.

The synthesis of the single crystals of the phases described below has been performed in the framework of the flux (molten solution) technique at spontaneous nucleation. Next, the general conditions of the single crystal synthesis from the fluxes with the coefficients p, q, r, s are presented.

The fluxes in a mass of 70–90 g were prepared at the temperature $T = 1100\ ^\circ C$ in a platinum crucible with volume $V = 100\ cm^3$ by sequential melting of powder mixtures, first $Bi_2Mo_3O_{12}$, and B_2O_3, then Mn_2O_3 and CuO; finally, Na_2CO_3 (we use Na_2O in the system (1) taking into account the thermal decomposition of Na_2CO_3 ($Na_2CO_3 \rightarrow Na_2O + CO_2$) in the flux) was added in portions.

In the prepared fluxes, the sequence of the crystallizing phases was studied. For each set of p, q, r, s parameters, the high-temperature crystallizing phases and the saturation temperatures of the fluxes were determined. After determination of these parameters, the fluxes have been homogenized at the temperature $T = 1100\ ^\circ C$ for 3 h, then the temperature was first rapidly reduced to ($T_{sat} - 10$) °C and then slowly reduced with a rate of 2–4 °C/day. In 2–3 days, the growth was completed, the crucible was withdrawn from the furnace, and the flux was poured out. The grown single crystals were etched in a 20% water solution of nitric acid to remove the flux remainder.

2.1. $Mn^{2+}_{1-x}Cu_xMoO_4$ oxides

2.1.1. Crystal growth

The fluxes with the value of the variable parameters of the system (1) with $p = 0.3 \div 2$, $q = 0.15 \div 0.7$, $r = 0 \div 1$, $s = 1 \div 1.5$ have been studied. At the choice of the p, q, r, s, the relation $p > 2q$ should be satisfied. In such fluxes, the high-temperature crystallizing phase in a wide temperature range is an $Mn_{1-x}Cu_xMoO_4$ oxide. In these compounds, the cations of the transition metals — manganese and copper — have 2+ valence states. As the relation between the parameters satisfies the $p > 2q$ condition, the flux system (1) could be presented as:

$$(100{-}n)\quad \%\ mass.\ (Bi_2Mo_3O_{12} + (p{-}2q)B_2O_3 + q\ Na_2B_4O_7) + \\ +n\quad \%\ mass.\ (r\quad CuO + s\quad Mn_2O_3) \qquad (2)$$

Depending on the value of p, q, r, s parameters, the concentration was $n = 25 \div 38\%$, and the saturation temperature of the fluxes was $T_{sat} = 790 \div 910\ ^\circ C$.

Single crystals of manganese molybdenum oxide $MnMoO_4$ (Fig. 1a) and copper-manganese molybdenum oxide $Mn_{1-x}Cu_xMoO_4$ (Fig. 1b) with Mn:Cu = 3:1 ratio have been obtained. The single crystals are transparent reddish-brown plates with the maximum size of $1 \times 1.5 \times 0.4\ mm^3$ for manganese molybdenum oxide (Fig. 1a andc). It is clear from Fig. 1c that the addition of the copper influences the colour of the single crystals. The colour of Cu-containing samples gets darker than the colour of unsubstituted crystal. This observation is in agreement with the description of the $CuMoO_4$ single crystals presented in [14].

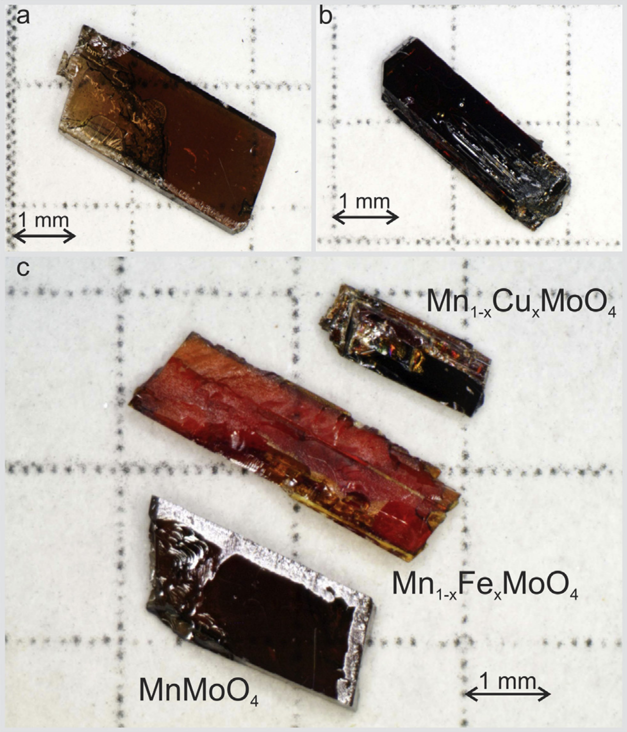

Fig. 1. Synthesized single crystals of $MnMoO_4$ (a and c), $Mn_{1-x}Cu_xMoO_4$ (b and c) and $Mn_{1-x}Fe_xMoO_4$ (c).

The authors have considered it necessary to show the picture of $Mn_{1-x}Fe_xMoO_4$ single crystals in Fig. 1c also. These crystals have been obtained from a similar flux, but instead of CuO oxide, it contains Fe_2O_3 oxide. A visual comparison of the presented samples shows the influence of the substitutions on the colour of the samples and the fact of the presence of divalent iron cations — the ability of the MoO_3 to affect the iron valence state (not only manganese) in the studied fluxes.

In agreement with (2), it is supposed that there is the formation of the bonds of the $Na_2B_4O_7$ compound in the flux; the condition $p > 2q$ provides the absence of "free" Na_2O oxide.

2.1.2. Crystal structure of $Mn^{2+}_{1-x}Cu_xMoO_4$ oxides

X-ray patterns of $Mn^{2+}_{1-x}Cu_xMoO_4$ ($x = 0$ and $x = 0.33$) and $Mn^{2+}_{1-x}Fe_xMoO_4$ ($x = 0.25$) compounds have been obtained using a D8 ADVANCE powder diffractometer (Cu-radiation, Vantec linear detector, with aperture of 0.6 mm, step size of 2θ of 0.016°, counting time of 0.5 s, and angle range of 5–70°) X-ray data from powders were obtained with the use of the analytical equipment of Krasnoyarsk Center of collective use of SB RAS.

For the identification of the studied compounds, the program Search-Match has been used. It was revealed that the studied compounds have a structure similar to that of $MnMoO_4$. No additional peaks corresponding to the impurities have been found. The lattice parameters have been calculated for two compounds $Mn^{2+}_{1-x}Cu_xMoO_4$ ($x = 0, 0.33$) and for one iron-substituted composition $Mn^{2+}_{1-x}Fe_xMoO_4$ ($x = 0.25$). The results are presented in Table 1.

Table 1
The crystal structure parameters of $Mn^{2+}_{1-x}Cu_xMoO_4$ ($x = 0,\ 0.33$) and $Mn^{2+}_{1-x}Fe_xMoO_4$ ($x = 0.25$) obtained by powder X-ray analysis.

Compound	$MnMoO_4$	$Mn_{0.67}Cu_{0.33}MoO_4$	$Mn_{0.75}Fe_{0.25}MoO_4$
Space group	*C2/m*	*C2/m*	*C2/m*
a, Å	10.5020 (4)	10.4973 (1)	10.4807 (6)
b, Å	9.5395 (4)	9.5309 (1)	9.5262 (8)
c, Å	7.1599(2)	7.1540 (9)	7.1452 (1)
β, deg.	106.165 (2)	106.193 (1)	106.330 (4)
V, $Å^3$	688.95(4)	687.36 (3)	684.61 (6)

2.2. Manganese oxides: $Mn_2^{3+}Mn^{2+}O_4$ and $Mn_2^{3+}O_3$

2.2.1. Crystal growth

The study continued at the values of the variable parameters of the system (1): $p = 0.6$, $q = 1 \div 1.23$, $r = 0$; the concentration was $n = 13 \div 14\%$. The mass concentration of the B_2O_3 oxide was more than two times bigger than the mass concentration of the Na_2O oxide. This condition is necessary for the presence of “free” Na_2O oxide in the flux along with $Na_2B_4O_7$ borax. The studied flux system, in this case, is identical to the system (1). Taking into account the formation of the borax chemical bonds ($Na_2B_4O_7$), the system studied in this paragraph could be presented as:

$$\begin{aligned}(100-n)\ \ \%\,mass.\ \ (Bi_2Mo_3O_{12} + 0.3\,Na_2B_4O_7)+ \\ +n\ \ \%\,mass.\ \ \ (Mn_2O_3 + tNa_2O)\end{aligned} \tag{3}$$

In (3), the “free” Na_2O sodium oxide has been moved to the soluble to show the relation between Mn_2O_3 and Na_2O oxides. In this system, we will vary only the coefficient t related to the quantity of “free” Na_2O (we are not taking into account Na_2O in borax). The investigation of the sequence of the high-temperature crystallizing phases in the flux system (3) reveals the change the phases even at the low quantity of “free” Na_2O. Along with $Mn^{2+}MoO_4$ molybdenum oxide (at $t = 0.5$), the simultaneous crystallization of black isometric crystals with evident triangle edges is observed. These crystals have been characterized as manganese oxide (2+, 3+) Mn_3O_4 (Fig. 2). So along with the compounds containing manganese only in the divalent state, there is a crystallization of the oxide containing trivalent manganese.

The study of the influence of the Na_2O oxide on the crystallization in the flux system (3) was continued by the increasing of the quantity of this oxide. At $t = 0.75$, the simultaneous crystallization of the (2+, 3+) Mn_3O_4 and (3+) Mn_2O_3 manganese oxides is observed. This means that the quantity of trivalent manganese increases with the increasing of the Na_2O concentration. Next, at $t = 1$ the crystallization only of the phase of Mn_2O_3 (Fig. 2) is observed — all manganese in the crystallizing matter has the 3+ valence state due to the increasing of Na_2O oxide.

This paragraph shows the role of the Na_2O oxide at the formation of the chemical bonds containing the ions of trivalent manganese in the flux experimentally. At the increasing of the sodium oxide content, the part of trivalent manganese in crystallizing phase also increases. The authors suppose that this role could be reflected as an occurrence of the intermediate chemical bonds (the compound corresponding to this chemical bonds is not a high-temperature crystallizing phase in the flux; the bonds of such type are formed at the temperature of flux preparation, and then this compound is initial for crystallization of the (2+, 3+) Mn_3O_4 and (3+) Mn_2O_3 manganese oxides) in the flux of the type:

$$Na_2O + Mn_2O_3 \rightarrow 2NaMnO_2 \tag{4}$$

The compound $NaMn^{3+}O_2$ is not a high-temperature crystallizing phase in the flux. The bonds of such type are formed at the temperature of flux preparation, and then this compound is initial for crystallization of the (2+, 3+) Mn_3O_4 and (3+) Mn_2O_3 manganese oxides.

In agreement with (4), all the manganese in the flux has the 3+ valence state if the t coefficient in (3) is equal to 1. This fact has been proved experimentally: at the ratio Mn_2O_3:Na_2O = 1 the crystallizing phase is Mn_2O_3 manganese oxide – all the manganese has 3+ valence state. It should be noted that the attempts to obtain the crystals of $NaMnO_2$ (delafossite structure type) were unsuccessful. So the occurrence of (4) chemical bonds is the only hypothesis.

Significant factors of the occurrence of the chemical bonds containing the manganese with 2+ and 3+ valence states are a competition between $Mn^{2+}MoO_4$ molybdenum oxide and $NaMn^{3+}O_2$ delafossite and the relative manganese concentration in the flux. Since if there is an excess of the manganese over the stoichiometry of $Mn^{2+}MoO_4$ and $NaMn^{3+}O_2$, the uncertainty of the manganese valence will appear. It is related to the thermal $Mn_2O_3 \rightarrow Mn_3O_4$ decomposition.

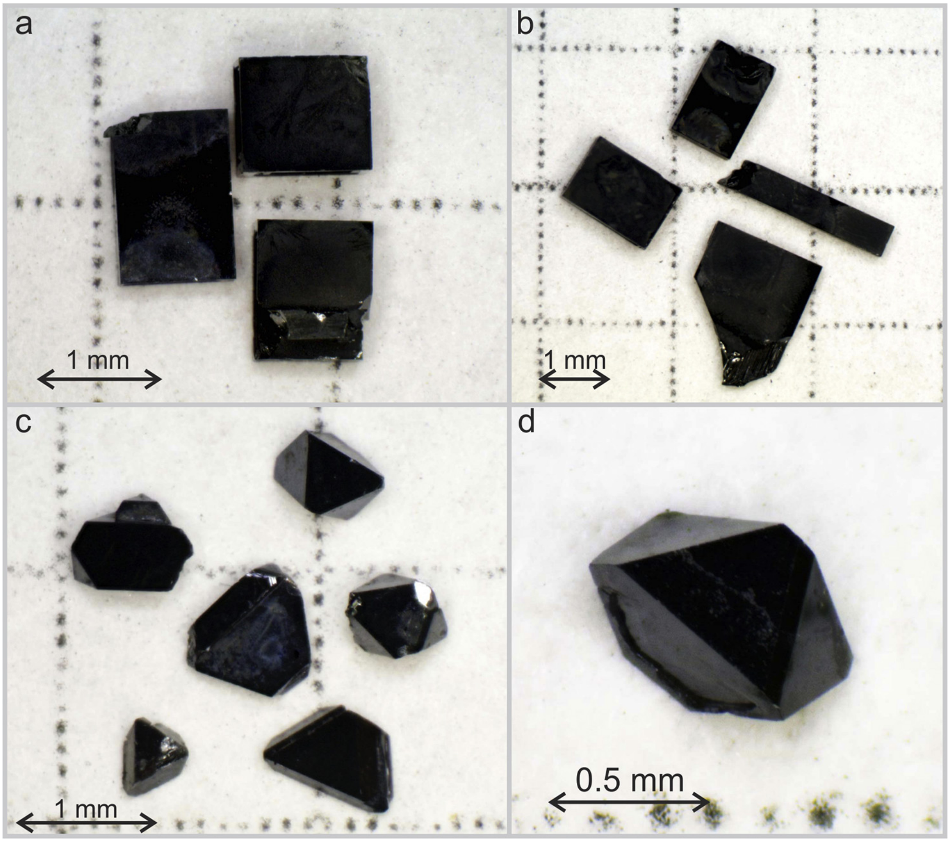

Fig. 2. Synthesized single crystals of $Mn_2^{3+}O_3$ (a and b) and $Mn_2^{3+}\ Mn^{2+}O_4$ (c and d).

Table 2
The crystal structure parameters of $Mn_2^{3+}Mn^{2+}O_4$ and $Mn_2^{3+}O_3$ oxides obtained by powder X-ray analysis.

Compound	$Mn_2^{3+}Mn^{2+}O_4$	$Mn_2^{3+}O_3$
Space group	$I4_1/amd$	$Ia\bar{3}$
a, Å	5.76356 (11)	9.41625 (15)
b, Å	5.76356 (11)	9.41625 (15)
c, Å	9.46782 (20)	9.41625 (15)
V, Å^3	314.508 (13)	834.90 (4)

2.2.2. Crystal structure of Mn_2^{3+} $Mn^{2+}O_4$ and $Mn_2^{3+}O_3$ manganese oxides

As in the previous paragraph, the X-ray patterns of $Mn_2^{3+}Mn^{2+}O_4$ and $Mn_2^{3+}O_3$ oxides have been obtained using a D8 ADVANCE powder diffractometer (Cu-radiation, Vantec linear detector, with aperture of 0.6 mm, step size of 2θ of 0.016°, counting time of 0.5 s, and angle range of 5–70°).

For the identification of the studied compounds, the program Search-Match has been used. It was revealed that the studied compounds have structures similar to that of Mn_3O_4 and Mn_2O_3, respectively. No additional peaks corresponding to the impurities have been found. The lattice parameters calculation results are presented in Table 2.

2.3. Oxyborates: $Mn_{1-x}^{2+}Cu_xMn^{3+}BO_4$ and $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$

Valence states of manganese play an important role in the crystallization of Mn-heterovalent compounds. Among them, the authors highlight the oxyborates with warwickite and ludwigite structures. The synthesis of the oxyborates with warwickite and ludwigite structures is a problem of high complexity. In these structures, there is a simultaneous presence of the metal cations with valence states (2+ and 3+) or (2+ and 4+), and they demonstrate high sensibility of the physical properties to small changes of composition [15–19]. In oxyborates $Mn_{1-x}^{2+}Cu_xMn^{3+}BO_4$ and $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$ with warwickite and ludwigite structures, respectively, the manganese cations are in different valence states. So for the synthesis of these compounds, it is very important to study the influence of the solvent on the high-temperature crystallizing phase and its valent composition that was described in the previous parts of the present work.

2.3.1. Crystal growth

The flux corresponding to the next system has been prepared for the synthesis of $Mn_{1-x}^{2+}Cu_xMn^{3+}BO_4$ oxyborates:

$$\begin{aligned}(100-n)\ \ \%\,mass.\ \ &(Bi_2Mo_3O_{12} + 1.53B_2O_3 + 0.7Na_2O)+\\ +n\ \ \%\,mass.\ \ &(rCuO + 1.25Mn_2O_3 + 0.5B_2O_3)\end{aligned} \tag{5}$$

In this system, only the *r* parameter and concentration *n* have been varied. The other parameters — *p*, *q* and *s* — have been fixed ($p = 1.53$, $q = 0.7$, $s = 1.25$). It was determined that the high-temperature crystallizing phase was $Mn_{1-x}^{2+}Cu_xMn^{3+}BO_4$ oxyborate with warwickite structure for $r = 0 \div 1.25$ ($n = 28.8 \div 33.2\%$, the saturation temperatures were $T_{sat} = 925 \div 885$ °C, T_{sat} decreased at the addition of copper oxide). It was shown that the value $r = 1.25$ corresponds to the stability limit of warwickite phase. At $r = 1.25$, the simultaneous crystallization of the phases of warwickite and ludwigite is observed.

Under further increasing of *r*, the only crystallizing phase was $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$ ludwigite. The fluxes with $r = 1.25 \div 1.67$ have been studied ($n = 33.2 \div 35.5\%$, the saturation temperatures were $T_{sat} = 870 \div 895$ °C).

Along with the system (5), for the synthesis of $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$ oxyborates the system with the other ratio of solvent components has been studied:

In comparison with the system (5), it was possible to stabilize the $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$ ludwigite phase by less quantity of the boron oxide by using the system (6). In (6), the parameter *r* has been varied in the range $1 \div 2.5$ ($n = 21.6 \div 30.9\%$, the saturation temperatures were $T_{sat} = 840 \div 910$ °C). The high-temperature crystallizing phase was $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$ oxyborate for all this range.

Single crystals of $Mn_{1-x}^{2+}Cu_xMn^{3+}BO_4$ and $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$ oxyborates are long black prisms (Fig. 3).

2.3.2. Crystal structure of $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$ and $Mn_{1-x}^{2+}Cu_xMn^{3+}BO_4$ oxyborates

Some solid solutions of $Mn_{1-x}^{2+}Cu_xMn^{3+}BO_4$ oxyborate with warwickite structure with $x = 0.18$, 0.33, and 0.5 has been obtained. These compounds have been characterized by powder X-ray diffraction. Along with the powder samples ($x = 0.18$, 0.33, and 0.5), the structure of the single crystal warwickite sample obtained from the flux with the ratio Mn:Cu = 2:1 (the case of simultaneous crystallization of the phases of warwickite and ludwigite) has been studied.

Four samples of $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$ oxyborate with ludwigite structure at $x = 1.5$, 1.8, 2, and 2.15 have been obtained. The structure of these samples as for the warwickite compounds was studied by powder X-ray diffraction. Also, along with the powder samples the structure of the single crystal ludwigite sample obtained from the flux with the ratio Mn:Cu = 2:1 (the case of simultaneous crystallization of the phases of warwickite and ludwigite) has been studied.

Powder X-ray patterns were collected at room temperature with a Bruker D8 ADVANCE powder diffractometer (Cu-Kα radiation) and

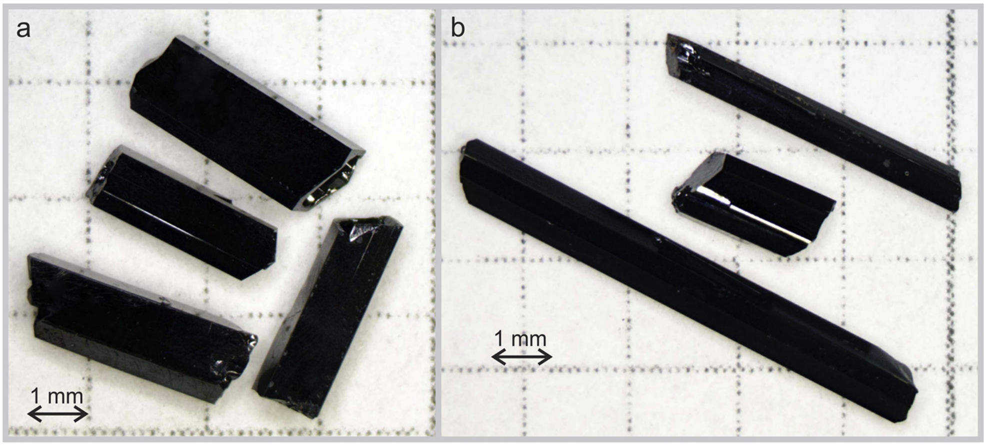

Fig. 3. Synthesized single crystal of $Mn_{2-x}^{2+}Cu_xMn^{3+}BO_5$ (a) and $Mn_{1-x}^{2+}Cu_xMn^{3+}BO_4$ (b).

Table 3
The main experimental parameters and the results of the structure parameters refinement of $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ (x = 1.5, 1.8, 2, and 2.15) oxyborates obtained by powder X-ray analysis.

x	0.5	0.33	0.18
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	9.2878 (2)	9.2924 (2)	9.2942 (3)
b, Å	9.5132 (3)	9.5246 (3)	9.5340 (3)
c, Å	3.24444 (8)	3.24592 (8)	3.2473 (1)
β, deg.	90.808 (2)	90.786 (2)	90.778 (2)
V, Å^3	286.64 (1)	287.26 (1)	287.72 (2)
2θ range, °	5–90	5–90	5–90
R_{wp}, %	2.11	1.97	2.39
R_p, %	1.61	1.55	1.90
R_B, %	1.23	0.78	0.58
χ^2	1.22	1.11	1.05

linear VANTEC detector. The angle range was 5–90°. The step size of 2θ was 0.016°, and the counting time was 0.3 s per step.

No additional peaks corresponding to the impurities have been found in X-ray patterns of $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ (x = 0.18, 0.33, and 0.5) compounds. All the peaks belong to the monoclinic phase ($P2_1/n$) with the parameters close to those of Mn_2BO_4 (warwickite) [20]. Therefore, this structure has been used as a starting model for Rietveld refinement. The refinement has been realized using the TOPAS 4.2 program [21]. The Mn/Cu ratio was not refined due to the proximity of the atomic scattering functions of these atoms. The refinement was stable and yielded low factors of unreliability (Table 3). The unit cell volume increases from sample to sample (Table 3), which is in agreement with the table values of the ionic radii. That could indicate the proportionality of the copper content in the samples to the calculated value in the flux.

A prismatic crystal of $(Cu,Mn)_2BO_4$ was selected for the single crystal experiment. Diffraction data were collected under room conditions on an Oxford Diffraction Xcalibur Gemini diffractometer (MoKα radiation, 0.5 mm collimator, graphite monochromator) equipped with a CCD detector. Data reduction, including a background correction and Lorentz and polarization corrections, was performed with the *CrysAlisPro* software. Semi-empirical absorption correction was applied using the multi-scan technique. The unit-cell metrics are monoclinic, space group $P2_1/n$. The structure was solved by the direct methods and refined in the anisotropic approach using the SHELX-97 program package [22]. The studied compound is proved to be an analogue of Mn_2BO_4 warwickite [20]. The main crystal data are shown in Table 4. Refinement shows that the final chemical formula is $Cu_{0.085}Mn_{1.915}BO_4$ — it does not coincide with the proposed concentration x = 0.66 (Mn/Cu ratio in flux). That disagreement could be related to the unstable growth at a simultaneous crystallization of two phases (warwickite and ludwigite) at Mn:Cu = 2:1.

X-ray diffraction study of powder samples of $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ has been carried out in the same experimental conditions as in the case of $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$. The obtained results are presented in Table 5. Each studied compound is characterized by phase homogeneity. The unit cell volume has a nonlinear dependence on the copper content: for the samples x = 1.5 and x = 1.8 the volume increases as for warwickite, but then it decreases despite the increasing copper content. The decreasing of the cell volume could be related to the appearance of the tetravalent manganese in the crystal and/or slight changes of the character of monoclinic distortions. The X-ray study of the structure of the $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ single crystal obtained from the flux with the ratio Mn:Cu = 2:1 (the case of simultaneous crystallization of the phases of warwickite and ludwigite) has been done previously [23] and is now presented in Table 4.

Table 4
The crystal structure parameters of $Cu_{0.085}Mn_{1.915}BO_4$ and $Cu_{1.53}Mn_{1.47}BO_5$ [23] obtained by single crystal X-ray analysis.

Phase	$Cu_{0.085}Mn_{1.915}BO_4$	$Cu_{1.53}Mn_{1.47}BO_5$
Space group	$P2_1/n$	$P2_1/c$
a, Å	9.27603(15)	3.13576(4)
b, Å	9.49529(13)	9.40981(12)
c, Å	3.24206(5)	12.05240(17)
β, deg.	90.8474(14)	92.1960(13)
V, Å^3	285.524(8)	355.368(8)

Table 5
The crystal structure parameters of $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ obtained by powder X-ray analysis.

x	1.5	1.8	2	2.15
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	3.14170(3)	3.14390(1)	3.14516(7)	3.14648(1)
b, Å	9.40516(4)	9.39681(4)	9.38932(2)	9.38245(2)
c, Å	12.02634(5)	12.02913(4)	12.02787(2)	12.02590(2)
β, deg.	92.2634(2)	92.2601(2)	92.2498(1)	92.2452(1)
V, Å^3	355.079(2)	355.096(2)	354.921(1)	354.752(1)

2.3.3. Magnetic properties of $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ and $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ oxyborates

The study of crystallization presented in this work focuses on the investigation of the mechanisms and the intermediate chemical bonds in the fluxes (1) aimed to synthesize the $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ and $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ oxyborates with ludwigite and warwickite structures, respectively. These compounds contain manganese in different valence states and have quasi-low-dimensional structures formed by ribbons, zig-zag walls and three-leg ladders [16–20]. The unit cells of these compounds are characterized by high Z (Z = 4 for both structures) and by several nonequivalent positions of heterovalent magnetic cations (4 for ludwigite structure and 2 for warwickite structure). These structural features are of significant influence on electrical and magnetic properties of ludwigites and warwickites [16–20].

For the additional description of the synthesized compounds, the authors consider it useful to present the data of the magnetic characterization of some $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ and $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ oxyborates. The magnetization study has been performed using a physical property measurement system PPMS-9 (Quantum Design), at temperatures T = 3–300 K and magnetic field value up to 90 kOe.

Magnetization measurements have been performed on a single crystal of one of the synthesized $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ (x = 0.18) oxyborates with warwickite structure. Thermal-field dependencies of magnetization obtained at the orientation of the external magnetic field along and across the c axis are presented in Fig. 4. As a result of the experiment, it was found that the synthesized warwickite, as the temperature decreases, passes from the paramagnetic state to the antiferromagnetic state with the ordering of magnetic moments in the plane $\perp c$. It should be noted that there is no thermal irreversibility between the FC and ZFC curves occurring below a critical temperature, which allows suggesting the antiferromagnetic spin arrangement in $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ (x = 0.18), that is the same as for Mn_2BO_4 [24]. The Neel temperature is T_N = 23 K. Small magnetizations and low paramagnetic Curie temperatures denote strong antiferromagnetic interaction ($\theta_{||} = -99$ K and $\theta\perp = -115$ K, the temperatures have been calculated using modified Curie-Weiss low approximation of the molar magnetic susceptibility [25] in the temperature range far from the phase transition point). Thermal dependencies of magnetization (Fig. 4a) also denote the existence of one more phase transition at T = 6 K. This feature could be associated with reorientation of magnetic moments in the plane $\perp c$.

The comparison of the data obtained for Cu-substituted warwickite with the properties of the "pure" Mn_2BO_4 [24] revealed the change of the magnetic properties of this compound even at low substitution

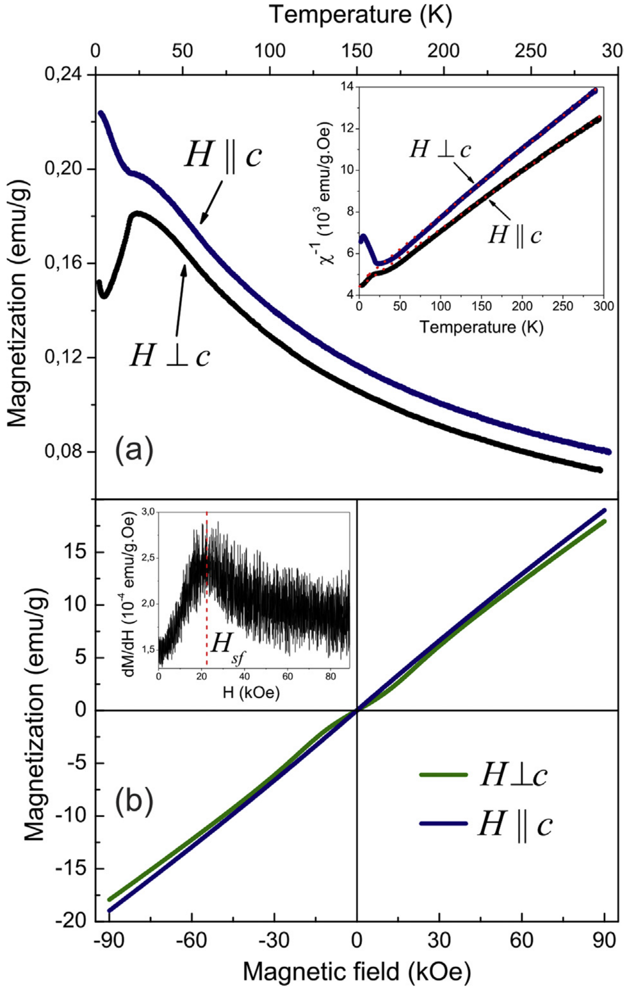

Fig. 4. (a) Thermal dependencies of magnetization of $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ ($x = 0.18$) oxyborate with warwickite structure obtained at $H = 1$ kOe, $H||c$, $H\perp c$ for FC (measurements of the magnetization at cooling at nonzero magnetic field) and ZFC (measurements of the magnetization at heating at nonzero magnetic field, after pre-cooling at zero magnetic field) regimes (inset (a): thermal dependencies of the reversal magnetic susceptibility at $H = 1$ kOe, $H||c$, $H\perp c$). (b) Magnetic field dependencies of magnetization of $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ ($x = 0.18$) oxyborate with warwickite structure obtained at $T = 3$ K, $H||c$, $H\perp c$ (inset (b): derivative of the magnetization ($H\perp c$) – presence of the maximum indicates the spin-flop transition, H_{sf} – spin-flop field).

degree. In particular, the decrease of the magnetic phase transition (paramagnet-antiferromagnet) temperature T from 26 to 23 K was observed. The change of the behavior of FC and ZFC dependencies at the orientation of the magnetic field along the c axis has been revealed (for Cu-substituted compound the magnetic moment in this direction is larger than the perpendicular moment and the increase of the magnetization in the ordered phase is observed). There are slight changes of the field dependencies behaviour: the lowering of the spin-flop field from $H_{sf} = 24$ kOe (for Mn_2BO_4) to $H_{sf} = 21$ kOe (for copper-contained sample). However, despite all these changes the primary behaviour of the magnetic properties remains the same: there is anisotropy of magnetization in paramagnetic phase, the antiferromagnetic ordering type is preserved (with a slight lowering of the Neel temperature), and the spin-flop transition is present as for unsubstituted Mn_2BO_4.

Magnetic properties of some $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ oxyborates with ludwigite structure have been already described in detail earlier [17,23]. The microscopic magnetic structure of one of the compounds (Cu_2MnBO_5) has been studied using powder neutron diffraction [17]. Cu_2MnBO_5 and $Cu_{1.5}Mn_{1.5}BO_5$ ludwigites are characterized by

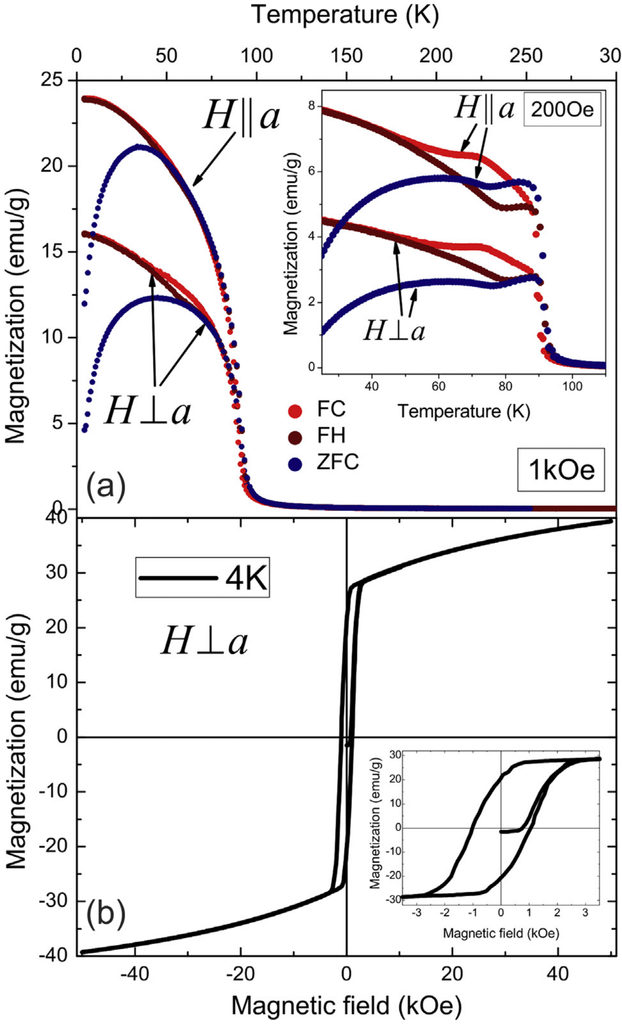

Fig. 5. (a) Thermal dependencies of magnetization of Cu_2MnBO_5 oxyborate with ludwigite structure obtained at $H = 1$ kOe, $H||c$, $H\perp c$ for FC (measurements of the magnetization at cooling at nonzero magnetic field), FH (measurements of the magnetization at heating at nonzero magnetic field, after precooling at nonzero magnetic field) and ZFC (measurements of the magnetization at heating at nonzero magnetic field, after pre-cooling at zero magnetic field) regimes (inset (a): thermal dependencies of magnetizationat $H = 0.2$ kOe, $H||c$, $H\perp c$). (b) Magnetic field dependence of magnetization of Cu_2MnBO_5 oxyborate with ludwigite structure obtained at $T = 4$ K, $H\perp c$.

ferrimagnetic ordering below the temperatures $T_c = 90$–92 K, large canting of magnetic moments and by the presence of the anisotropy as in the paramagnetic as in ferromagnetic phase. Due to that, these compounds significantly differ from the other ludwigites [17,23].

In order to show the difference of the magnetic property behaviour of the compounds with ludwigite and warwickite structures, we also present in this work the thermal-field magnetization dependencies of Cu_2MnBO_5 described in detail in [17] (see Fig. 5).

The analysis of the thermal-field magnetization dependencies of Cu_2MnBO_5 ludwigite has revealed the paramagnetic-ferrimagnetic phase transition at $T_c = 92$ K. And, below the temperature of this phase transition in a low magnetic field (up to $H = 1$ kOe) there is one more anomaly of the magnetization — there are some inflection points on the FC, FH and ZFC curves. This anomaly significantly depends on the value of the applied magnetic field and associates with the spin-reorientation transition [17]. Unlike $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ ($x = 0.18$) warwickite, in Cu-Mn ludwigites there is magnetic anisotropy not only for different orientations of the external magnetic field but also for FC and ZFC dependencies at the low-temperature range.

3. Discussion and conclusions

The present work is wholly devoted to the study of the manganese 3+ oxide (Mn_2O_3) behaviour in bismuth-boron flux systems diluted by MoO_3 oxide and Na_2CO_3 carbonate. This investigation is an essential step to obtaining single crystals of Mn-heterovalent oxyborates with the structures of warwickite and ludwigite natural minerals.

The particular study of the crystallization peculiarities of systems (1)–(6) was necessary due to the thermal decomposition of the manganese 3+ oxide (Mn_2O_3) to the manganese (2+, 3+) oxide Mn_3O_4 at high working temperatures (1100 °C) [13]. So, without an additional instrument it is very difficult or even impossible to control the composition of di- and trivalent manganese in the flux. It can cause the crystallization of the compounds with the Mn^{3+} and Mn^{2+} cation content uncertainty. And in the case of Cu-Mn-containing oxyborates, the content uncertainty can lead to a significant change of the properties.

This work is focused on the assumption of the arising of intermediate chemical bonds between the components of a multi-component flux system. That mechanism allows affecting the manganese cations (2+, 3+) valence state even at high temperature. The research experimentally showed the influence of the bismuth trimolibdate ($Bi_2Mo_3O_{12}$) to the high-temperature crystallizing phase. It was (without adding of sodium carbonate in (1) and (2)) $MnMoO_4$ oxide where the manganese has only the 2+ valence state. That is, there is no trivalent manganese in the crystallizing compound despite using Mn_2O_3 (Mn^{3+}) oxide. Crystallization of $MnMoO_4$ directly proves the formation of the chemical bond ($MnMoO_4$ oxide-type) that should be realized at warwickite and ludwigite crystallization.

After the addition of sodium carbonate (Na_2CO_3 — Na_2O is not bounded by B_2O_3 in $Na_2B_4O_7$) to the system (1), the situation changes. The high-temperature crystallizing phase is manganese warwickite (system (5)) where the manganese is presented by divalent and trivalent cations. So, the addition of sodium carbonate gives rise to the formation of trivalent manganese phase. For better studying of this phenomenon, the set of the experiments in the system (3) has been performed: the oxides Mn_2O_3 and Na_2O were dissolved in the melt of $Bi_2Mo_3O_{12}$-$Na_2B_4O_7$. It was shown experimentally that the composition of the crystallizing compounds corresponds to the occurrence of the chemical bonds of $NaMnO_2$ delafossite type (4) in which the manganese has only 3+ valence state. This conclusion was made on the basis of $Mn_2{}^{3+}O_3$ and $Mn_2{}^{3+}Mn^{2+}O_4$ oxide crystallization. When the weight coefficients of Mn_2O_3 and Na_2O (4) are equal, the only crystallizing phase is (3+) manganese oxide ($Mn_2{}^{3+}O_3$). If a lack of Na_2O takes place in the flux, there is the case of simultaneous crystallization of $Mn_2{}^{3+}O_3$ and $Mn_2{}^{3+}Mn^{2+}O_4$ oxides (2+, 3+) or the only phase is $Mn_2{}^{3+}Mn^{2+}O_4$ manganese oxide (2+, 3+). So, the influence of sodium carbonate adding to the trivalent manganese content in the system (1) has been demonstrated experimentally. After the research stage, the single crystals of Cu-Mn oxyborates with warwickite and ludwigite structures have been grown.

In the framework of the assumption of the Na_2O influence on the crystallization of the trivalent manganese containing compounds and of the MoO_3 influence on the crystallization of the divalent manganese containing compounds, the works [26] and [18] have been performed. The first of them is devoted to $Mn_{2-x}Fe_xBO_4$ warwickites, and the second one is devoted to $Cu_2Mn_{1-x}Fe_xBO_5$ ludwigites. In the case of $Mn_{2-x}Fe_xBO_4$ warwickites, three compounds with different x have been obtained. The composition of these samples corresponds to the composition of crystal-forming oxides in the fluxes in agreement with the X-ray analysis — the ratio of di- and trivalent manganese was controlled by the solvent components. In the case of $Cu_2Mn_{1-x}Fe_xBO_5$ ludwigites, three compounds with different x were also obtained. The structure study of these samples showed a qualitative correspondence of the real composition to the initial composition of crystal-forming oxides.

An important problem is a competition of the chemical bonds in the flux system (1). Based on the experimental data obtained in the present work, the following hierarchy could be supposed. In the absence of Na_2O oxide and presence of MoO_3 oxide, the crystallization of Mn^{2+}-containing compounds is observed ($MnMoO_4$-type bonds). However, after adding Na_2O the change of the high-temperature crystallizing phase takes place — the Mn^{3+}-containing compounds are crystallizing (delafossite-type bonds). So, the delafossite-type bonds are of higher priority.

It is necessary to note the difference between using the borax $Na_2B_4O_7$ compound and independent $Na_2O{\cdot}2B_2O_3$ oxides in the solvent. Using borax, the addition of “free” Na_2O oxide is needed for obtaining Mn^{3+}-containing compounds (in our case, the initial chemical is Na_2CO_3). Using $Na_2O{\cdot}2B_2O_3$ oxide mixture (or adding independently), the Mn^{3+}-compounds do not need “free” Na_2O oxide over the borax stoichiometry. That fact also reflects the competing of the chemical bonds in the flux system (1).

The crystallization processes in the flux system (1) have been studied under the varying of p, q, r, s weight coefficients. Depending on these coefficients (i.e. on the ratio between the flux components) the single crystals of $Mn^{2+}_{1-x}Cu_xMoO_4$, $Mn_2{}^{3+}O_3$, $Mn^{2+}Mn_2{}^{3+}O_4$, $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ and $Mn^{2+}_{2-x}Cu_xMn^{3+}BO_5$ phases have been obtained. The influence of MoO_3 and Na_2O components on the composition of the crystallizing phase has been studied, namely on the valence state of Mn^{2+} and Mn^{3+} manganese cations respectively. Based on the experimental results, the assumption about the occurrence of the intermediate chemical bonds of $MnMoO_4$ and $NaMnO_2$ types in the flux allowed to affect the valence states of the manganese cations (2+, 3+) at crystallization of Mn-heterovalent oxyborates was concluded. A hierarchy of the chemical bonds of these types has been established. All the synthesized compounds have been identified using X-ray analysis. The phase composition has been confirmed, and the lattice parameters have been determined. The results of the magnetic characterization of $Mn^{2+}_{1-x}Cu_xMn^{3+}BO_4$ ($x = 0.18$) warwickite and Cu_2MnBO_5 ludwigite are presented.

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