Crystal Formation of Cu-Mn-containing oxides and oxyborates in bismuth-boron fluxes diluted by MoO$_3$ and Na$_2$CO$_3$

Evgeniya Moshkina$^{1,2,*}$, Yurii Seryotkin$^{3,4}$, Asya Bovina$^1$, Maxim Molokeev$^{1,5,6}$, Evgeniy Eremin$^{1,5}$, Nadejda Belskaya$^2$, Leonard Bezmaternykh$^1$

*eKoles@iph.krasn.ru

$^1$Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, 660036 Russia
$^2$Siberian State Aerospace University, Krasnoyarsk, 660014 Russia
$^3$V.S. Sobolev Institute of Geology and Mineralogy, SB RAS, 630090 Novosibirsk, Russia
$^4$Novosibirsk State University, 630090 Novosibirsk, Russia
$^5$Siberian Federal University, Krasnoyarsk, 660041, Russia
$^6$Far Eastern State Transport University, Khabarovsk 680021, Russia

Abstract – The high-temperature crystallizing phases of fluxes (molten solutions) based on Bi$_2$O$_3$:MoO$_3$:1:3 and diluted by Na$_2$CO$_3$, B$_2$O$_3$ (under varying of Na$_2$CO$_3$:B$_2$O$_3$) and CuO and Mn$_2$O$_3$ (0≤Mn$_2$O$_3$:CuO≤5) are studied. The conditions of the stable crystallization of Mn$^{2+}_{1-x}$Cu$_x$MoO$_4$, Mn$^{2+}$O$_3$, Mn$^{2+}$Mn$^{2+}$O$_4$, Mn$^{2+}_{1-x}$Cu$_x$Mn$^{3+}$BO$_4$ and Mn$^{2+}_{2-x}$Cu$_x$Mn$^{3+}$BO$_5$ have been found. The influence of MoO$_3$ and Na$_2$CO$_3$ to the crystallization processes of Mn$^{2+}$- and Mn$^{3+}$-containing Mn$^{2+}_{1-x}$Cu$_x$MoO$_4$ and Mn$^{2+}$Mn$^{2+}$O$_4$ and Mn$^{2+}$O$_3$ are clarified. The occurrence of the chemical bonds of these types at the crystallization of Mn-heterovalent Mn$^{2+}_{1-x}$Cu$_x$Mn$^{3+}$BO$_4$ and Mn$^{2+}_{2-x}$Cu$_x$Mn$^{3+}$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.

Keywords: flux growth; single crystals; manganese cations; crystallization processes; ludwigites and warwickites.

I. Introduction

Flux technique for growth of single crystals (or the molten solution technique) is a widely used technique for obtaining the 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 of the single crystals of a high quality of different compounds types. Some of the most bright and known examples are such structural types as garnets [6, 9], spinels [3, 10], 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 at growing, and obtaining the single crystals of high quality and of a large size.

The main idea of the present work is studying of the crystal formation in the bismuth-boron flux systems diluted by MoO$_3$ and Na$_2$CO$_3$, of Cu-Mn-containing oxides and oxyborates. The investigation of the high-temperature crystallizing phase dependence on the varying of the solute and solvent components and the determination of the optimum conditions for growing of Mn-heterovalent oxyborates with warwickite Mn$^{2+}_{1-x}$Cu$_x$Mn$^{3+}$BO$_4$ and ludwigite Mn$^{2+}_{2-x}$Cu$_x$Mn$^{3+}$BO$_5$ structures. It is supposed that the addition of the MoO$_3$ and Na$_2$CO$_3$ components to the solvent could have a special influence on the crystallization
of the compounds contained 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 oxyborates growth (with warwickite Mn\(^{2+}\)\(_{1-x}\)Cu\(_x\)Mn\(^{3+}\)BO\(_4\) and ludwigite Mn\(^{2+}\)\(_{2-x}\)Cu\(_x\)Mn\(^{3+}\)BO\(_3\) structures) is the variable valence of the manganese cations. That is due to the thermal decomposition of the Mn\(_2\)O\(_3\) oxide in the 900–1100°C temperature range, which leads to the formation of Mn\(_3\)O\(_4\) 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 a next way: the high-temperature crystallizing phases of bismuth-boron fluxes, diluted by MoO\(_3\) and Na\(_2\)CO\(_3\), are discussed; the data on the structure of the grown crystals and the magnetic characterization of some of the obtained compounds are being presented.

II. Experimental details

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

\[
(100-n)\% \text{mass } \left(\text{Bi}_2\text{Mo}_3\text{O}_{12} + p\text{B}_2\text{O}_3 + q\text{Na}_2\text{O} \right) \\
+ n\% \text{mass } (\text{CuO}+s\text{Mn}_2\text{O}_3)
\]

where \(n\) – is the concentration of the solute; \(p, q, r, s\) – 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 a 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 \(T=1100°C\) in a platinum crucible with the volume \(V=100 \text{ cm}^3\) by sequential melting of powder mixtures, first Bi\(_2\)Mo\(_3\)O\(_{12}\), and B\(_2\)O\(_3\), then Mn\(_2\)O\(_3\) and CuO; finally, Na\(_2\)CO\(_3\) (we use Na\(_2\)O in the system (1) taking into account the thermal decomposition of Na\(_2\)CO\(_3\) (Na\(_2\)CO\(_3\)→Na\(_2\)O+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 temperature \(T=1100°C\) for 3 hours, then the temperature was first rapidly reduced to \((T_{\text{sat}}-10)°C\) 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\(_x\)MoO\(_4\) oxides

a. Crystal Growth

The fluxes with the value of the variable parameters of the system (1) \(- p=(0.3\div2), q=(0.15\div0.7), r=(0\div1), s=(1\div1.5)\) – have been studied. At the choice of the \(p, q, r, s\) the relation \(p>2q\) should take place. In such fluxes, the high-temperature crystallizing phase in a wide temperature range is Mn\(_{1-x}\)Cu\(_x\)MoO\(_4\) oxide. In this compound, 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:

\[
100 - n \text{ mass } Bi_2Mo_3O_{12} + (p - 2q)B_2O_3 + qNa_2B_4O_7 + n \text{ mass } CuO + s Mn_iO_3
\]  

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

Single crystals of manganese molybdenum oxide MnMoO\(_4\) (Figure 1a) and copper-manganese molybdenum oxide Mn\(_{1-x}\)Cu\(_x\)MoO\(_4\) (Figure 1b) with Mn:Cu=3:1 ratio have been obtained. The single crystals are transparent reddish-brown plates with the maximum size of \( 1 \times 1.5 \times 0.4 \text{ mm}^3 \) – for manganese molybdenum oxide (Figure 1a, c). It is clear from Figure 1c that the adding of the copper has an influence on the color of the single crystals – the color of Cu-containing samples gets darker. This observation is in agreement with the description of the CuMoO\(_4\) single crystals presented in [14].

The authors have considered necessary to show the picture of Mn\(_{1-x}\)Fe\(_x\)MoO\(_4\) single crystals in Figure 1c also. These crystals have been obtained from the similar flux, but instead of CuO oxide, it contains Fe\(_2\)O\(_3\)oxide. The look comparison of the presented samples shows the influence of the substitutions on the color 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.

\[ \text{Figure 1. Synthesized single crystal of Mn}_{1-x}\text{Cu}_x\text{MoO}_4. } \]

In agreement with (2), it is supposed that there is the formation of the bonds of Na\(_2\)B\(_4\)O\(_7\) compound in the flux; the condition \( p > 2q \) provides the absence of “free” Na\(_2\)O oxide.
b. Crystal Structure of Mn$^{2+}$$_1$$_x$ Cu$_x$MoO$_4$ oxides

X-ray patterns of Mn$^{2+}$$_1$$_x$Cu$_x$MoO$_4$ ($x = 0$, 0.33) and Mn$^{2+}$$_1$$_x$Fe$_x$MoO$_4$ ($x = 0.25$) compounds have been obtained using D8 ADVANCE powder diffractometer (Cu-radiation, Vantec linear detector, the apertures –0.6 mm, the step size of 20 – 0.016º, the counting time – 0.5 sec, the angle range – 5-70º, X-ray data from powders were obtained with use 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 the similar structure to 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$Cu$_x$MoO$_4$ ($x=0$, 0.33) and for one iron-substituted composition Mn$^{2+}$$_1$$_x$Fe$_x$MoO$_4$ ($x=0.25$). The results are presented in Table 1.

Table 1. The crystal structure parameters of Mn$^{2+}$$_1$$_x$Cu$_x$MoO$_4$ ($x=0$, 0.33) and Mn$^{2+}$$_1$$_x$Fe$_x$MoO$_4$ ($x=0.25$) obtained by powder X-ray analysis

<table>
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<tr>
<th>Compound</th>
<th>Space group</th>
<th>MnMoO$_4$</th>
<th>Mn$<em>{0.67}$Cu$</em>{0.33}$MoO$_4$</th>
<th>Mn$<em>{0.75}$Fe$</em>{0.23}$MoO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C2/m</td>
<td>C2/m</td>
<td>C2/m</td>
<td></td>
</tr>
<tr>
<td>a, Å</td>
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<td>10.4973 (1)</td>
<td>10.4807 (6)</td>
<td></td>
</tr>
<tr>
<td>b, Å</td>
<td>9.5395 (4)</td>
<td>9.5309 (1)</td>
<td>9.5262 (8)</td>
<td></td>
</tr>
<tr>
<td>c, Å</td>
<td>7.1599 (2)</td>
<td>7.1540 (9)</td>
<td>7.1452 (1)</td>
<td></td>
</tr>
<tr>
<td>β, deg.</td>
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<td>106.193 (1)</td>
<td>106.330 (4)</td>
<td></td>
</tr>
<tr>
<td>V, Å$^3$</td>
<td>688.95(4)</td>
<td>687.36 (3)</td>
<td>684.61 (6)</td>
<td></td>
</tr>
</tbody>
</table>

2.2. Manganese oxides: Mn$_2^{3+}$Mn$^{2+}$O$_4$ and Mn$_2^{3+}$O$_3$

a. Crystal Growth

The study continued at the values of the variable parameters of the system (1): $p=0.6$, $q=(1÷1.23)$, $r=0$; the concentration was $n=(13÷14)$ %. And the mass concentration of the B$_2$O$_3$ oxide was two and more times bigger than the mass concentration of Na$_2$O oxide. This condition is necessary for the presence of “free” Na$_2$O oxide in the flux along with Na$_2$B$_4$O$_7$ 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$_2$B$_4$O$_7$) the studied in this Paragraph system could be presented as:

$$\frac{(100-n)\%\text{mass} \cdot \text{B}_2\text{Mo}_5\text{O}_{12} + 0.3\text{Na}_2\text{B}_4\text{O}_7}{n\%\text{mass} \cdot (\text{Mn}_2\text{O}_3 + t\text{Na}_2\text{O})}$$

(3)

In (3) the “free” Na$_2$O sodium oxide has been moved to the soluble to show the relation between Mn$_2$O$_3$ and Na$_2$O oxides. In this system, we will vary only $t$ coefficient related to the quantity of “free” Na$_2$O (we are not taking into account Na$_2$O 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$_2$O. Along with Mn$^{2+}$ MoO$_4$ molybdenum oxide (at $t=0.5$) it is observed the simultaneous crystallization of black isometric crystals with evident triangle edges. These crystals have been characterized as manganese oxide (2+, 3+) Mn$_3$O$_4$ (Figure 2). So along with the compounds containing manganese only in divalent state, there is a crystallization of the oxide containing trivalent manganese.
The study of the influence of the Na$_2$O 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$_3$O$_4$ and (3+) Mn$_2$O$_3$ manganese oxides is observed. It means that the quantity of trivalent manganese increase with the increase of the Na$_2$O concentration. Next, at $t=1$ the crystallization only of the phase of Mn$_2$O$_3$ (Figure 2) is observed – all manganese in the crystallizing matter has the 3+ valence state due to the increasing of Na$_2$O oxide.

This Paragraph shows the role of the Na$_2$O 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 in the flux of the type:

\[
Na_2O + Mn_2O_3 \rightarrow 2NaMnO_2
\]  

(4)

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$_3$O$_4$:Na$_2$O=1 the crystallizing phase is Mn$_3$O$_4$ manganese oxide – all the manganese has 3+ valence state. It should be noted that the attempts to obtain the crystals of NaMnO$_2$
Important 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\(_2\)O\(_3\)→Mn\(_3\)O\(_4\) decomposition.

b. Crystal Structure of Mn\(^{2+}\)Mn\(^{3+}\)O\(_4\) and Mn\(^{2+}\)O\(_3\) manganese oxides

As in the previous Paragraph, the X-ray patterns of Mn\(^{2+}\)Mn\(^{3+}\)O\(_4\) and Mn\(^{2+}\)O\(_3\) oxides have been obtained using D8 ADVANCE powder diffractometer (Cu-radiation, Vantec linear detector, the apertures – 0.6 mm, the step size of 2\(\theta\) – 0.016\(^\circ\), the counting time – 0.5 sec, the angle range – 5\(^\circ\)-70\(^\circ\)).

For the identification of the studied compounds the program Search-Match has been used. It was revealed that the studied compounds, have the similar structure to Mn\(_3\)O\(_4\) and Mn\(_2\)O\(_3\), respectively. No additional peaks corresponding to the impurities have been found. The lattice parameters calculation results are presented in Table 2.

Table 2. The crystal structure parameters of Mn\(^{2+}\)Mn\(^{3+}\)O\(_4\) and Mn\(^{2+}\)O\(_3\) oxides obtained by powder X-ray analysis

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mn(^{2+})Mn(^{3+})O(_4)</th>
<th>Mn(^{2+})O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>I(4)/amd</td>
<td>I(\bar{4}3)</td>
</tr>
<tr>
<td>(a, \text{Å})</td>
<td>5.76356 (11)</td>
<td>9.41625 (15)</td>
</tr>
<tr>
<td>(b, \text{Å})</td>
<td>5.76356 (11)</td>
<td>9.41625 (15)</td>
</tr>
<tr>
<td>(c, \text{Å})</td>
<td>9.46782 (20)</td>
<td>9.41625 (15)</td>
</tr>
<tr>
<td>(V, \text{Å}^3)</td>
<td>314.508 (13)</td>
<td>834.90 (4)</td>
</tr>
</tbody>
</table>

2.3. Oxyborates: Mn\(^{2+}\)\(_{1-x}\)Cu\(_x\)Mn\(^{3+}\)BO\(_4\) and Mn\(^{2+}\)\(_{2-x}\)Cu\(_x\)Mn\(^{3+}\)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 the 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\(^{2+}\)\(_{1-x}\)Cu\(_x\)Mn\(^{3+}\)BO\(_4\) and Mn\(^{2+}\)\(_{2-x}\)Cu\(_x\)Mn\(^{3+}\)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.

a. Crystal Growth

The flux corresponding to the next system has been prepared for synthesis of Mn\(^{2+}\)\(_{1-x}\)Cu\(_x\)Mn\(^{3+}\)BO\(_4\) oxyborates:
In this system, only the \( r \) parameter and concentration \( n \) have been varied. The others 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 \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{4} \) oxyborate with warwickite structure for \( r=0 \div 1.25 \) (\( n=28.8 \div 33.2\% \), the saturation temperatures were \( T_{\text{sat}}=925 \div 885^\circ \text{C} \), \( T_{\text{sat}} \) decreased at an addition of copper oxide). It was shown that the value \( r=1.25 \) corresponds to 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 one crystallizing phase was \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{5} \) ludwigite. The fluxes with \( r=1.25 \div 1.67 \) have been studied (\( n=33.2 \div 35.5\% \), the saturation temperatures were \( T_{\text{sat}}=870 \div 895^\circ \text{C} \)).

Along with the system (5), for the synthesis of \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{5} \) oxyborates the system with the different ratio of solvent components has been studied:

\[
(100-n)\% \text{mass } \text{Bi}_{2}\text{Mo}_{3}\text{O}_{12}+1.53\text{B}_{2}\text{O}_{3}+0.7\text{Na}_{2}\text{O} \rightarrow \\
+n\% \text{mass } (r\text{CuO}+1.25\text{Mn}_{2}\text{O}_{3}+0.5\text{B}_{2}\text{O}_{3})
\]  

(6)

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

Single crystals of \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{4} \) and \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{5} \) oxyborates are black long prisms (Figure 3).

Figure 3. Synthesized single crystal of \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{5} \) (a) and \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{4} \) (b).

b. Crystal Structure of \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{5} \) and \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{4} \) oxyborates

A number of the solid solutions of \( \text{Mn}^{2+} \text{Cu}_{x} \text{Mn}^{3+} \text{BO}_{4} \) oxyborate with warwickite structure with \( x=0.18 \), 0.33, 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, 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\(^{2+}_{2-x}Cu_xMn^{3+}BO_5\) oxyborate with ludwigite structure at \(x = 1.5, 1.8, 2, 2.15\) 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-K\(\alpha\) radiation) and linear VANTEC detector. The angle range was 5-90°. The step size of 2\(\theta\) was 0.016°, and the counting time was 0.3 s per step.

Table 3. The main experimental parameters and the results of the structure parameters refinement of Mn\(^{2+}_{1-x}Cu_xMn^{3+}BO_4\) (\(x = 0.18, 0.33, 0.5\)) oxyborates obtained by powder X-ray analysis

<table>
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<th>(x)</th>
<th>0.5</th>
<th>0.33</th>
<th>0.18</th>
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<td>Space group</td>
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<td>(P2_1/n)</td>
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<tr>
<td>(a), Å</td>
<td>9.2878 (2)</td>
<td>9.2924 (2)</td>
<td>9.2942 (3)</td>
</tr>
<tr>
<td>(b), Å</td>
<td>9.5132 (3)</td>
<td>9.5246 (3)</td>
<td>9.5340 (3)</td>
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<td>(c), Å</td>
<td>3.2444 (8)</td>
<td>3.2492 (8)</td>
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<td>(\beta), deg.</td>
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<td>90.786 (2)</td>
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<td>(V), Å(^3)</td>
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<td>(R_B), %</td>
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<td>0.58</td>
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<td>(\chi^2)</td>
<td>1.22</td>
<td>1.11</td>
<td>1.05</td>
</tr>
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</table>

No additional peaks corresponding to the impurities have been found in X-ray patterns of Mn\(^{2+}_{1-x}Cu_xMn^{3+}BO_4\) (\(x = 0.18, 0.33, 0.5\)) compounds. All the peaks belong to the monoclinic phase (\(P2_1/n\)) with the close parameters to Mn\(_2\)BO\(_4\) (warwickite) [20]. Therefore, this structure has been used as a start model for Rietveld refinement. The refinement has been realized using 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 the low factors of unreliability (Table 3). The unit cell volume increases from sample to sample (Table 3) that 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.

Prismatic crystal of (Cu,Mn)\(_2\)BO\(_4\) was selected to the single-crystal experiment. Diffraction data were collected under room conditions on an Oxford Diffraction Xcalibur Gemini diffractometer (MoK\(\alpha\) 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. A semi-empirical absorption correction was applied using the multi-scan technique. The unit-cell metrics is monoclinic, space group $P2_1/n$. The structure was solved by the direct methods and refined in the anisotropic approach using SHELX-97 program package [22]. The studied compound is proved to be an analog of Mn$_2$BO$_4$warwickite [20]. The main crystal data are shown in Table 4. Refinement shows that final chemical formula is $\text{Cu}_{0.085}\text{Mn}_{1.915}\text{BO}_4$–it doesn’t coincide to 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.

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

<table>
<thead>
<tr>
<th>Phase</th>
<th>Cu$<em>{0.085}$Mn$</em>{1.915}$BO$_4$</th>
<th>Cu$<em>{1.53}$Mn$</em>{1.47}$BO$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$P2_1/n$</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>9.2760(2)</td>
<td>3.13576(4)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>9.4953(1)</td>
<td>9.40981(12)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>3.2421(0)?</td>
<td>12.05240(17)</td>
</tr>
<tr>
<td>$\beta$, deg.</td>
<td>90.85(0)?</td>
<td>92.1960(13)</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>285.52(1)</td>
<td>355.368(8)</td>
</tr>
</tbody>
</table>

Table 5. The crystal structure parameters of Mn$^{2+}$$_{2-x}$Cu$_x$Mn$^{3+}$BO$_5$ obtained by powder X-ray analysis

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

X-ray diffraction study of powder samples of Mn$^{2+}$$_{2-x}$Cu$_x$Mn$^{3+}$BO$_5$ have been carried out in the same experimental conditions as in the case of Mn$^{2+}$$_{1-x}$Cu$_x$Mn$^{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 the 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 studying of the structure of the Mn$^{2+}$$_{2-x}$Cu$_x$Mn$^{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 now presented in Table 4.

c. Magnetic properties of Mn$_{2-}^{2+}$Cu$_x$Mn$_{3}^{3+}$BO$_5$ and Mn$_{1-}^{2+}$Cu$_x$Mn$_{3}^{3+}$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$_{2-}^{2+}$Cu$_x$Mn$_{3}^{3+}$BO$_5$ and Mn$_{1-}^{2+}$Cu$_x$Mn$_{3}^{3+}$BO$_4$ oxyborates with ludwigite and warwickite structures respectively. These compound contain the 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 great influence to electrical and magnetic properties of ludwigites and warwickites [16-20].

For the additional describing of the synthesized compounds, the authors consider being useful to present the data of the magnetic characterization of some Mn$_{2-}^{2+}$Cu$_x$Mn$_{3}^{3+}$BO$_5$ and Mn$_{1-}^{2+}$Cu$_x$Mn$_{3}^{3+}$BO$_4$ oxyborates. Magnetization study has been performed using Physical properties measurements system PPMS-9 (QuantumDesign), at temperatures $T=3$÷300 K and magnetic field value up to 90 kOe.

Magnetization measurements have been performed on the single crystal of one of the synthesized Mn$_{1-}^{2+}$Cu$_x$Mn$_{3}^{3+}$BO$_4$ ($x=0.18$) oxyborate with warwickite structure. Thermal-field dependencies of magnetization obtained at the orientation of the external magnetic field along and across $c$ axis are presented in Figure 4. As a result of the experiment it was found that the synthesized warwickite, as the temperature decreases, passes from the paramagnetic state to antiferromagnetic state with the ordering of magnetic moments in plane $\perp c$. It should be noted that there is no thermal irreversibility between the FC and ZFC curves occurs below a critical temperature, which allows suggesting the antiferromagnetic spin arrangement in Mn$_{1-}^{2+}$Cu$_x$Mn$_{3}^{3+}$BO$_4$ ($x=0.18$), that the same as for Mn$_2$BO$_4$ [24]. The Neel temperature is $T_N=23$ K. Small magnetizations and low paramagnetic Curie temperatures denote strong antiferromagnetic interaction ($\theta||=-99$ K, $\theta\perp=-115$ 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 (Figure 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 plane $\perp c$. 
Figure 4. (a) Thermal dependencies of magnetization of Mn$^{2+}_{1-x}$Cu$_x$Mn$^{3+}$BO$_4$ ($x=0.18$) oxyborate with warwickite structure obtained at $H=1$ kOe, $H\parallel c$, $H\perp c$ 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, $H\parallel c$, $H\perp c$). (b) Magnetic field dependencies of magnetization of Mn$^{2+}_{1-x}$Cu$_x$Mn$^{3+}$BO$_4$ ($x=0.18$) oxyborate with warwickite structure obtained at $T=3$ K, $H\parallel c$, $H\perp c$ (inset (b): derivative of the magnetization ($H\perp c$) – presence of the maximum indicates the spin-flop transition, $H_{sf}$ – spin-flop field).

The comparison of the data obtained for Cu-substituted warwickite with the properties of the “pure” Mn$_2$BO$_4$ [24] revealed the change of the magnetic properties of this compound even at low substitution degree. In particular, it was observed the decreasing of the magnetic phase transition (paramagnet-antiferromagnet) temperature from $T=26$ K to $T=23$ K. The change of the behavior of FC and ZFC dependencies at the orientation of the magnetic field along $c$ axis has been revealed (for Cu-substituted compound the magnetic moment in this direction is larger than perpendicular moment and the increasing of the magnetization in the ordered phase is observed). There are slight changes of the field dependencies behavior – the lowering of the spin-flop field from $H_{sf}=24$ kOe (for Mn$_2$BO$_4$) to $H_{sf}=21$ kOe (for copper-contained sample). However despite all these changes the main behavior 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$_2$BO$_4$.

Magnetic properties of some Mn$^{2+}_{2-x}$Cu$_x$Mn$^{3+}$BO$_5$ oxyborates with ludwigite structure have been already described in detail earlier [17, 23]. Microscopic magnetic structure of one of the compounds (Cu$_2$MnBO$_5$) has been studied using powder neutron diffraction [17]. Cu$_2$MnBO$_5$ and Cu$_{1.3}$Mn$_{1.5}$BO$_5$ ludwigites are characterized by ferrimagnetic ordering below the temperatures $T_c=90\div92$ K, large canting of magnetic moments and by the presence of the anisotropy as in paramagnetic as in ferromagnetic phase. Due to that, these compounds significantly differ from the others ludwigites [17, 23].

In order to show the difference of the magnetic properties behavior of the compounds with ludwigite and warwickite structures we also present in this work the thermal-field magnetization dependencies of Cu$_2$MnBO$_5$ described in detail in [17].

![Thermal dependencies of magnetization](image)

**Figure 5.** (a) Thermal dependencies of magnetization of Cu$_2$MnBO$_5$ 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 pre-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 magnetization at $H=0.2$ kOe, $H||c$, $H\perp c$). (b) Magnetic field dependence of magnetization of Cu$_2$MnBO$_5$ oxyborate with ludwigite structure obtained at $T=4$ K, $H\perp c$. 
The analysis of the thermal-field magnetization dependencies of Cu$_2$MnBO$_5$ ludwigite has revealed the paramagnet-ferrimagnet 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 applied magnetic field and associates with spin-reorientational transition [17]. Unlike Mn$^{2+}$$_2$$_3$Cu$_x$Mn$^{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 low-temperature range.

III. Discussion and Conclusions

The present work is completely devoted to the study of the manganese oxide 3+ (Mn$_2$O$_3$) behavior in the bismuth-boron flux systems diluted by MoO$_3$ oxide and Na$_2$CO$_3$ carbonate. This investigation is an important step to the obtaining of the single crystals of Mn-heterovalent oxyborates with the structures of warwickite and ludwigite natural minerals.

The special studying of the crystallization peculiarities of (1-6) systems was necessary due to the thermal decomposition of manganese oxide 3+ (Mn$_2$O$_3$) to the manganese oxide (2+, 3+) Mn$_3$O$_4$ 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$^{2+}$ cations content uncertainty. And in the case of Cu-Mn-containing oxyborates the content uncertainty can lead to the significant change of the properties.

This work is focused on the assumption of the arising of the intermediate chemical bonds between the components of 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$_2$Mo$_3$O$_{12}$) 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 2+ valence state. That is there is no trivalent manganese in crystallizing compound despite the using Mn$_2$O$_3$ (Mn$^{3+}$) oxide. Crystallization of MnMoO$_4$ directly proves the formation of the chemical bond (MnMoO$_4$ oxide – type) that should realize and at the warwickite and ludwigite crystallization.

After the addition of sodium carbonate (Na$_2$CO$_3$ – Na$_2$O is not bounded by B$_2$O$_3$ in Na$_2$B$_2$O$_7$) to the system (1), the situation totally 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 experiment in the system (3) has been performed: the oxides Mn$_2$O$_3$ and Na$_2$O were dissolved in the melt of Bi$_3$Mo$_3$O$_{12}$-Na$_2$B$_2$O$_7$. It was showed 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$_3$$^{3+}$O$_3$ and Mn$_3$$^{3+}$Mn$^{2+}$O$_4$ oxides crystallization. When the weight coefficients of Mn$_2$O$_3$ and Na$_2$O (4) are equal the only crystallizing phase is (3+) manganese oxide (Mn$_2$$^{3+}$O$_3$). If a lack of Na$_2$O takes place in the flux there is the case of simultaneous crystallization of Mn$_2$$^{3+}$O$_3$ and Mn$_2$$^{3+}$Mn$^{2+}$O$_4$ oxides (2+, 3+) or the only phase is
Mn\textsuperscript{3+}Mn\textsuperscript{2+}O\textsubscript{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\textsubscript{2}O influence to the crystallization of the trivalent manganese containing compounds and of the MoO\textsubscript{3} influence to the crystallization of the divalent manganese containing compounds the works [26] and [18] have been performed. First of them is devoted to Mn\textsubscript{2-x}Fe\textsubscript{x}BO\textsubscript{4} warwickites, the second one – to Cu\textsubscript{2}Mn\textsubscript{1-x}Fe\textsubscript{x}BO\textsubscript{5} ludwigites. In the case of Mn\textsubscript{2-x}Fe\textsubscript{x}BO\textsubscript{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 divalent and trivalent manganese was controlled by the solvent components. In the case of Cu\textsubscript{2}Mn\textsubscript{1-x}Fe\textsubscript{x}BO\textsubscript{5} ludwigites, it was also obtained three compounds with different \(x\). Structure studying 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). Basing on the experimental data obtained in the present work it could be supposed the next hierarchy. In the absence of Na\textsubscript{2}O oxide and presence of MoO\textsubscript{3} oxide the crystallization of Mn\textsuperscript{2+}-containing compounds is observed (MnMoO\textsubscript{4}-type bonds). However, after adding of Na\textsubscript{2}O the change of the high-temperature crystallizing phase takes place – the Mn\textsuperscript{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\textsubscript{2}B\textsubscript{2}O\textsubscript{7} compound and independent Na\textsubscript{2}O·2B\textsubscript{2}O\textsubscript{3} oxides in the solvent. Using borax the addition of “free” Na\textsubscript{2}O oxide is needed for obtaining Mn\textsuperscript{3+}-containing compounds (in our case – the initial chemical is Na\textsubscript{2}CO\textsubscript{3}). Using Na\textsubscript{2}O·2B\textsubscript{2}O\textsubscript{3} oxides mixture (or adding independently) the Mn\textsuperscript{3+}-compounds do not need “free” Na\textsubscript{2}O 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\textsuperscript{2+1-x}Cu\textsubscript{x}Mn\textsubscript{3+x}MoO\textsubscript{4}, Mn\textsubscript{2}Fe\textsubscript{2+}O\textsubscript{3}, Mn\textsubscript{2}Mn\textsubscript{2}O\textsubscript{4}, Mn\textsubscript{2}Cu\textsubscript{1-x}Mn\textsubscript{3+x}BO\textsubscript{4} and Mn\textsubscript{2+2-x}Cu\textsubscript{x}Mn\textsubscript{3+x}BO\textsubscript{5} phases have been obtained. The influence of MoO\textsubscript{3} and Na\textsubscript{2}O components to the composition of the crystallizing phase has been studied – namely to the valence state of Mn\textsuperscript{2+} and Mn\textsuperscript{3+} manganese cations respectively. Based on the experimental results the assumption about the occurrence of the intermediate chemical bonds of MnMoO\textsubscript{4} and NaMnO\textsubscript{2} types in the flux allowed to affect to 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\textsuperscript{2+1-x}Cu\textsubscript{x}Mn\textsuperscript{3+x}BO\textsubscript{4} (\(x=0.18\)) warwickite and Cu\textsubscript{2}MnBO\textsubscript{3} ludwigite are presented.
Acknowledgement
This study was supported by Russian Foundation for Basic Research (RFBR) according to the research project No. 17-02-00953 A.

References