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Crystal Structure and Magnetic Properties in Pyroxenes $Li_{0.7}Na_{0.3}FeGe_2O_6$

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The $Li_{0,7}Na_{0,3}FeGe_2O_6$ solid solution has been synthesized by the solid-phase reaction. The clinopyroxene compound has been investigated by X-ray diffraction and by bulk magnetic measurements. The structural properties of the cation substitution compound are presented. Using SQUID techniques the temperature dependence of the magnetic susceptibility was measured. It exhibits a sharp maximum, which is suggested the phase transition from the paramagnetic state to a magnetically ordered state below 15.5 K in the sample of pyroxene solid solution.

Keywords: solid solution, pyroxene, crystal structure, magnetic properties.
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Introduction

Pyroxene inorganic compounds with the general chemical formula ABX_2O_6 (A = Na, Li and Ca; B = Mg, Cr, Cu, Ni, Fe, etc.; X = Ge, Si) have significant interest in solid state physics due to their physical properties. Magnetic studies have been carried out for the family pyroxenes compound: there are various types of magnetic state (antiferromagnetic [1–4], ferromagnetic [3–5], modulated magnetic structure [6,7], spin gap state [8]) connected to the features of the pyroxene crystal structure which allows the existence of competing magnetic exchange interactions.

Characteristic feature of the iron pyroxene $AFe^{3+}X_2O_6$ crystal structure is the isolated chains FeO_6 octahedra running along the c axis (Fig. 1) [9]. Magnetic interaction between the chains (Fe–O–Ge(Si)–O–Fe) is weakened due to the presence of non-magnetic $Ge(Si)O_4$ tetrahedra. Type of magnetic structure depends critically on the geometric topologies of the atomic structure which is determined the ratio of the intrachain (Fe-O-Fe) and interchain (Fe-O-X-O-Fe) exchange interactions parameters.

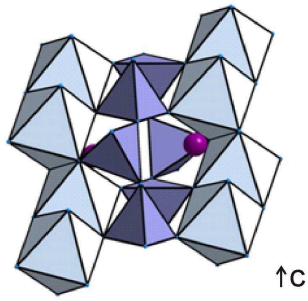


Fig. 1. Crystal structure of $AFeX_2O_6$ compounds: two chains of FeO_6 octahedra and its connections via $Ge(Si)O_4$ tetrahedra [9]. Balls represent Na(Li) ions

The $NaFeGe_2O_6$ and $LiFeGe_2O_6$ clinopyroxene-type germinates compounds exhibit different crystal and magnetic structures. The room temperature crystal structure of $LiFeGe_2O_6$ is monoclinic with space group $P2_1/c$ [10]. The room temperature crystal structure of $NaFeGe_2O_6$ is monoclinic with space group $C2/c$ [11].

Structures of magnetic subsystem are quasi-one-dimensional in $AFeGe_2O_6$ compounds [9]. The magnetic structure of $LiFeGe_2O_6$ pyroxene is described to have an antiferromagnetic arrangement of spins within and between the octahedral B chains (T_N= 20.5 K) [2]. $NaFeGe_2O_6$ characterized by Néel temperature T_N = 13 K, below T = 11.5 K the incommensurate magnetic structure with a helical spin modulation is realized [6,12].

In this way, the possibility to synthesize the $LiFeGe_2O_6$ and $NaFeGe_2O_6$ solid solution is discovered the interesting physical properties. We have recently studied the crystal and magnetic structures of the $Na_{0.5}Li_{0.5}FeGe_2O_6$ compound [13]. The room crystal structure of $Na_{0.5}Li_{0.5}FeGe_2O_6$ is monoclinic $C2/c$ (high temperature parameters of the cell: $a = 10.0333(1)$, $b = 8.8136(1)$, $c = 5.5295(9)$Å, $\beta = 108.921(1)^\circ$). Calorimetric investigations indicate a displacive first order phase transition at T = 276 K, and at temperature decreasing $Na_{0.5}Li_{0.5}FeGe_2O_6$ undergoes a space group change from $C2/c$ to $P2_1/c$ (low temperature parameters of the cell: a = 9.9692(3), b = 8.8545(3), c = 5.4752(2)Å, $\beta = 108.494(1)^\circ$). Magnetic order has been found below the Néel temperature $T_N \approx 18$ K and has been refined from neutron diffraction. The quasi-low-dimensional magnetic spin system $Na_{0.5}Li_{0.5}FeGe_2O_6$ exhibits a collinear antiferromagnetic

structure with the space group P_a2_1/c and the doubling of the unit cell along the crystallographic a-axis of the pyroxene crystal (propagation vector $\boldsymbol{k}$ = (1/2, 0, 0)).

No magnetic properties and a detailed crystal structure data are available for germinate clinopyroxene-type solid solution compound $Li_{0.7}Na_{0.3}FeGe_2O_6$. In the present contribution in pyroxenes research we report the experimental data on the room crystal structure and magnetic characteristics of the synthesized solid solution $Li_{0.7}Na_{0.3}FeGe_2O_6$.

1. Sample preparation and experimental procedure

Polycrystalline sample of solid solution $Li_{0.7}Na_{0.3}FeGe_2O_6$ was synthesized by a solid-phase reaction method from the stoichiometric mixture of oxides $GeO_2, Fe_2O_3, Na_2CO_3, Li_2CO_3$

$$2.00GeO_2 + 0.50Fe_2O_3 + 0.15Na_2CO_3 + 0.35Li_2CO_3 \rightarrow Li_{0.7}Na_{0.3}FeGe_2O_6 + CO_2.$$

The mixture of the oxides was ground under ethanol, pressed into pellets and fired under ambient pressure at temperatures of 800–1000° C in air at three stages each with duration of 24 h with intermediate regrinding. At each heating stage the samples were slowly cooled to room temperature, ground and pressed into pellets for next heat treatment. The prepared pellets were pale brown. The chemical and phase composition of the pellet milled into the powder was examined by X-ray diffraction and shows a single phase.

The X-ray powder diffraction data of $Li_{0.7}Na_{0.3}FeGe_2O_6$ for Rietveld analysis was collected at room temperature with a Bruker D8 ADVANCE powder diffractometer (Cu-Kα radiation) and linear VANTEC detector. Refinement of the powder pattern was performed with TOPAS 4.2 (Bruker) [14].

A SQUID magnetometer operating from 300 K to 4 K at magnetic field 500 Oe was used to perform the dc magnetic measurements.

2. Experimental results and discussion

The X-ray powder diffraction pattern at 300 K reveals that $Li_{0.7}Na_{0.3}FeGe_2O_6$ has the centrosymmetric $C2/c$ space group with 4 formula units per the unit cell and the lattice parameters are close to those of $NaFeGe_2O_6$ [7, 11]. Therefore the crystal structure of $NaFeGe_2O_6$ was used as the starting structural model for the Rietveld refinement of the room temperature crystal structure of $Li_{0.7}Na_{0.3}FeGe_2O_6$. The site of Na ion was occupied by Li and Na ions with fixed occupation $p_{Li} = 0.5$ and $p_{Na} = 0.5$ respectively. The refinement was stable and gave low R-factors (Tab. 1, Fig. 2). Main parameters of refinement are shown in Tab. 1.

To obtain information on the magnetic properties of polycrystalline sample material of $Li_{0.7}Na_{0.3}FeGe_2O_6$ compound the dc magnetic measurements were perform. Magnetic properties are determined by Fe^{3+} ions as a $3d^5$. The measured temperature dependence of the magnetic susceptibility in an external magnetic field of H = 500 Oe of monophased powder $Li_{0.7}Na_{0.3}FeGe_2O_6$ is shown in Fig. 3a. The magnetic susceptibility χ(T) of $Li_{0.7}Na_{0.3}FeGe_2O_6$ exhibits a sharp maximum at 24.8 K in its temperature dependence with the point of inflection being located at 15.5 K. This behavior is usually related to a phase transition from the paramagnetic to the magnetically ordered state. Note, the pyroxene reported here the diamagnetic contribution in the magnetic susceptibility is negligible (Fig. 3 b).

Table 1. Main parameters of crystal structure refinement in $Li_{0.7}Na_{0.3}FeGe_2O_6$ at 300 K

Space group	$C/2c$
a_i, Å	10.02346 (11)
b_i, Å	8.80980 (9)
c_i, Å	5.52550 (6)
β,^{o}	108.9286 (6)
V, Å^3	461.54 (1)
D_x, g/cm^3	4.445
Z	4
Angle range 2θ, deg.	5-140
Number of reflections	4391
Number of refined parameters	71
R_{wp}, %	2.155
R_p, %	1.643
χ^2	1.450
R_B, %	1.333

Designations: a, b, c, and β are the unit cell parameters; V is the unit cell volume; R_B, R_{wp}, R_p are the integrated (Bragg), weighted profile and profile factors, respectively; and χ^2 is the goodness-of-fit.

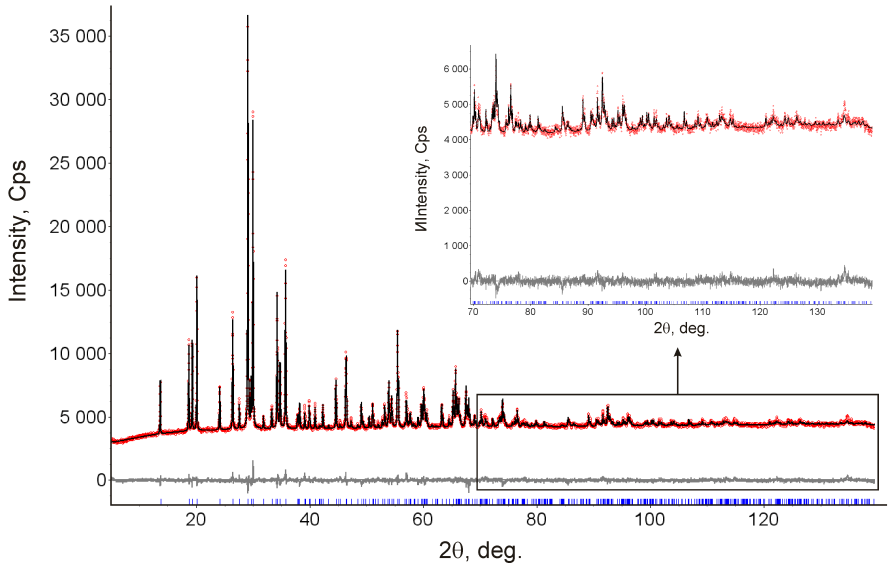
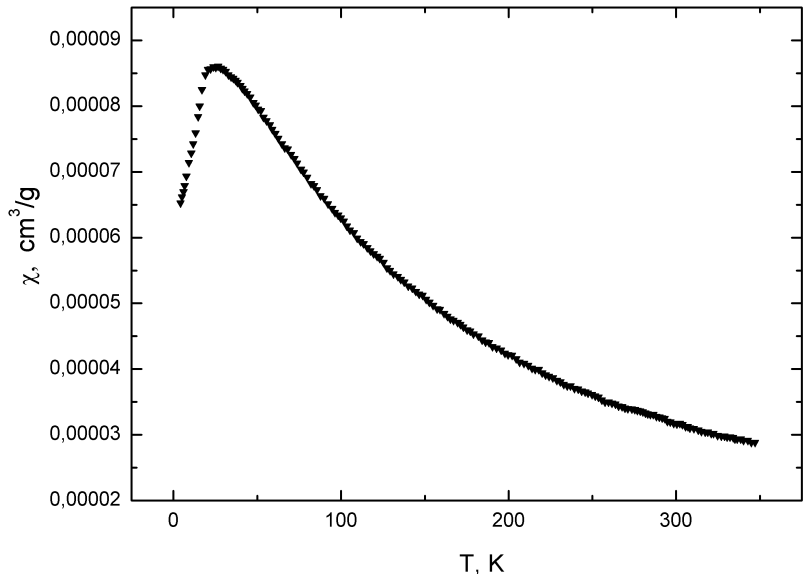
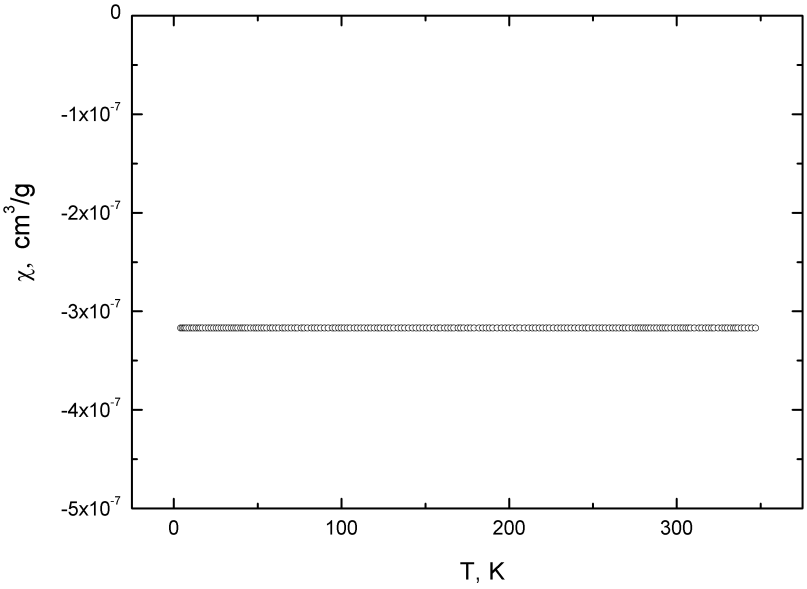


Fig. 2. Experimental (symbols), theoretical (line), and difference (lower line) X-ray powder diffraction pattern resulting from the Rietveld refinement of $Li_{0.7}Na_{0.3}FeGe_2O_6$ at 300 K



a)



b)

Fig. 3. Temperature dependence of the magnetic susceptibility, obtained in $Li_{0.7}Na_{0.3}FeGe_2O_6$ sample: the total magnetic susceptibility (a) and the diamagnetic contribution in the magnetic susceptibility (b)

In order to compare some details between $NaFeGe_2O_6$, $LiFeGe_2O_6$, $Na_{0.5}Li_{0.5}FeGe_2O_6$ and $Li_{0.7}Na_{0.3}FeGe_2O_6$ samples we summaries the room crystal structure and magnetic parameters in the Tabs. 2, 3.

Note, all materials of pyroxenes compound family $Na_xLi_{1-x}FeGe_2O_6$ (x = 1, 0.5, 0.3 and 0) are monoclinic. End members (x = 0, 1) exhibit different space group of crystal structure ($P2_1/c$, $C2/c$). Intermediate compositions (x = 0.5, 0.3) exhibit $C2/c$ space group at T = 300 K. It is interesting to examine the A cation substitution influences on magnetic properties too. In this solid solution the substitution Li^+ ions by Na^+ ions led to an increase in the lattice parameters and change the picture of the competing magnetic exchange interactions in the pyroxenes $Na_xLi_{1-x}FeGe_2O_6$ compound.

Table 2. Summary of the monoclinic crystal structure parameters for different pyroxene-type compounds at room temperature

Sample	a_i, Å	b_i, Å	c_i, Å	β,^{o}	Space group	Reference
$NaFeGe_2O_6$	10.0100	8.9400	5.5200	108.0000	$C/2c$	[11]
$Na_{0.5}Li_{0.5}FeGe_2O_6$	10.0333(1)	8.8136(1)	5.5295(9)	108.921(1)	$C/2c$	[13]
$Li_{0.7}Na_{0.3}FeGe_2O_6$	10.02346(11)	8.80980(9)	5.52550(6)	108.9286(6)	$C/2c$	this study
$LiFeGe_2O_6$	9.8792(7)	8.8095(5)	5.3754(3)	108.844(6)	$P/2_1c$	[10]

Table 3. Summary of the magnetic parameters for different pyroxene-type compounds

Sample	T_N, K	T_{max}, K	Reference
$NaFeGe_2O_6$	13	25	[12, 15]
$LiFeGe_2O_6$	20.2	24.4	[2]
$Na_{0.5}Li_{0.5}FeGe_2O_6$	18	27.5	[13]
$Li_{0.7}Na_{0.3}FeGe_2O_6$	15.5	24.8	this study

Conclusion

The solid solution clinopyroxene compound $Li_{0.7}Na_{0.3}FeGe_2O_6$ was synthesized by solid-phase reaction. The chemical and phase composition of clinopyroxenes compound was examined by X-ray diffraction and shows a single phase. The room crystal structure and magnetic properties of $Li_{0.7}Na_{0.3}FeGe_2O_6$ were investigated as function of temperature in range 4 K – 300 K.

The room temperature crystal structure of $Li_{0.7}Na_{0.3}FeGe_2O_6$ is characterized by monoclinic symmetry and space group $C2/c$ with parameters a = 10.02346(11), b = 8.80980(9), c = 5.52550(6)Å, β = 108.9286(6)°. $Li_{0.7}Na_{0.3}FeGe_2O_6$ is isostructural to $NaFeGe_2O_6$ at T = 300 K.

The transition from the paramagnetic state to the magnetic long-range ordered state occurring at T_N = 15.5 K.

Note, the clinopyroxene compounds show a variety of phase crystal structure transitions as a function of temperature. In the case of $LiFeGe_2O_6$ and $Na_{0.5}Li_{0.5}FeGe_2O_6$ compounds the changes in symmetry from a low temperature $P2_1/c$ to a high temperature $C2/c$ structure were observed at a transition temperature T_{tr} = 789 K and 276 K correspondingly [10,13]. $NaFeGe_2O_6$ compound exhibits $C2/c$ symmetry between 1.6 and 1000 K [10]. This result indicates that a change in composition of pyroxene-type compounds can have effect on the $P2_1/c \leftrightarrow C2/c$ dis-

placive phase transition. It is not clear the crystal structure of $Li_{0.7}Na_{0.3}FeGe_2O_6$ with temperature changes in symmetry or not. It is expected that this pyroxene compound transforms to $P2_1/c$ structure at some low temperatures. The possible magnetic structure depends on crystal structure at low temperatures. In order to further characterize the magnetic state of $Li_{0.7}Na_{0.3}FeGe_2O_6$ compound it is necessary the neutron diffraction investigation to determine the magnetic structure.

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Структурные и магнитные свойства пироксена $Li_{0.7}Na_{0.3}FeGe_2O_6$

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Поликристаллические образцы $Li_{0,7}Na_{0,3}FeGe_2O_6$ были получены твердофазным синтезом и исследованы методами рентгеновской дифракции и СКВИД-метрии. Представлены характеристики структурных свойств. Показано, что температурная зависимость магнитной восприимчивости при температуре 15,5 K имеет излом, характерный для переходов в магнитоупорядоченное состояние.

Ключевые слова: твердый раствор, пироксен, кристаллическая структура, магнитные свойства.