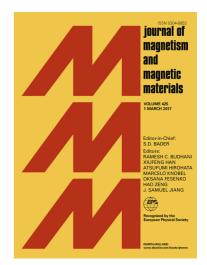
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Chemical Disorder Reinforces Magnetic Order in Ludwigite (Ni,Mn)₃BO₅ with Mn⁴⁺ Inclusion

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Abstract

Crystals of ludwigite $Ni_{2.14}Mn_{0.86}BO_5$ were synthesized by flux growth technique. We show in the paper that it contains Mn^{3+} and Mn^{4+} . A possible mechanism of the manganese valence states stabilization has been proposed. The structural and magnetic characterization of the synthesized samples has been carried out in detail. The cations composition and Mn valence states of the crystal were determined using X-ray diffraction and EXAFS technique. The comparative analysis was carried out between the studied crystal and Ni_2MnBO_5 synthesized previously. Magnetic susceptibility measurements were carried out. The magnetic transition in the studied composition occurs at the 100 K that is higher than in Ni_2MnBO_5 although the studied composition is more disordered. The calculations of the exchange integrals in the frameworks of indirect coupling model revealed strong antiferromagnetic interactions. The several magnetic subsystems existence hypothesis was supposed. The possible magnetic structure was suggested from the energies estimation for different ordering variants.

Keywords

oxide, oxyborate, magnetism, crystal growth, EXAFS

Introduction

Oxiborates Ni_{3-x} Mn_xBO_5 belong to the family of ludwigites [1]. The peculiarity of these compounds is the presence of quasi-low-dimensional elements in the structure - three-legged ladders, as well as triangular groups, which in some cases leads to very interesting physical properties. In addition to this, there are different valence metal ions in the structure; they can be di- and tri- [2, 3], as well as di- and tetravalent ions [4, 5, 6].

There are monometallic ludwigites: Fe_3BO_5 and Co_3BO_5 , in which Fe (Co) ions are represented in the diand trivalent state. Both compounds exhibit interesting physical properties.

In Fe₃BO₅ at high temperatures, the Fe³⁺ ions with spin 5/2, are localized in one of the two 3LL (3-legged ladder) formed by Fe³⁺-Fe²⁺-Fe³⁺ ions, and one additional electron is smeared out between three ions. With increasing temperature, this additional electron is localized in one of the pairs, as a result, a dimer is formed, and a structural phase transition occurs with an increase in the crystalline cell by the factor of two. In addition, a singularity is also observed on the magnetization curves. Magnetic ordering occurs at lower temperatures in two stages: at 112 K and 74 K, while the two subsystems are ordered mutually orthogonally. [3]

In $Co_3BO_{5,}$ charge ordering arises immediately at high temperatures, and unlike iron ludwigite, magnetic ordering occurs in one stage at 42 K. However, the Co^{3+} ion is in the low-spin state, and its spin is zero.

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