XAFS AND X-RAY DIFFRACTION STUDY OF THE CUBIC PHASE OF $Ni_3B_7O_{13}Br$

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Application of advanced experimental methods using synchrotron radiation makes it possible to resolve many long-standing challenging problems. One of such problems is the atomic structure of the cubic paraelectric phase of compounds belonging to the family of boracites (general formula $Me_3B_7O_{13}X$, where M is one of the divalent metals Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn or Cd, and X is a halogen Cl, Br, or I). Nearly all boracites undergo phase transitions to lower symmetry ferroelectric phases. The structures of most of known phases of boracites have been carefully studied using X-ray diffraction. As a result of the studies several alternative structural models of the paraelectric phase were proposed. Models assuming disorder of both halogen and metal atoms were intensively discussed along with generally accepted ideal cubic structure [1,2], however no clear evidences in favor of any of the proposed models were obtained. Application of X-ray absorption spectroscopy (XAS) allows to clearly reveal a disorder in this case, since the difference of metal-halogen distances in the alternative models is about 0.3 Å. By combining spectroscopic data with diffraction, a comprehansive model of atomic arrangements can be worked out. However only one boracite compound, namely $Fe_3B_7O_{13}Br$ has been studied so far by XAFS [3].

We studied the local environment around Br ion in the cubic phase of $Ni_3B_7O_{13}Br$ at the temperature of about 200° C using XAFS technique. The experiment was performed at the K1.3b station of synchrotron radiation source "Sibiria-2" at Kurchatov Institute (Moscow). Spectra were collected in transmission mode at Br K -edge.

The Fourier transform of Br K-XAFS of the cubic phase is shown in the Fig. 1 together with the one obtained for the orthorhombic ferroelectric phase of the compound. It can be clearly seen that the phase transition from ferroelectric to the paraelectric phase does not result in any significant change of the shortest Br-Fe distance, which was found to be 2.61 Å for the ferroelectric phase and 2.63 Å for the cubic paraelectric one.

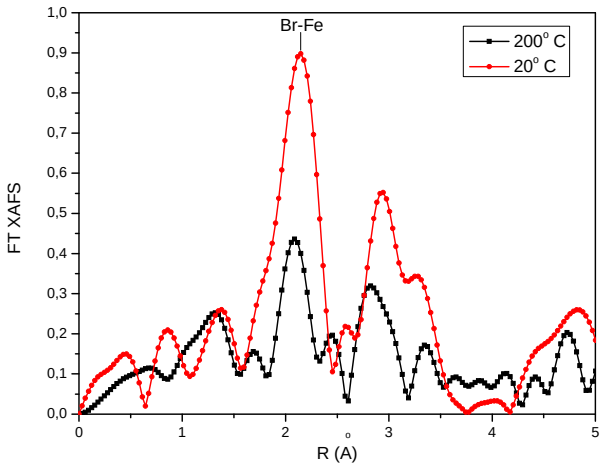

Figure 1. The Fourier transform of Br K-XAFS of $Ni_3B_7O_{13}Br$ measured at 20° and 200°C.

These results were incorporated into refinement of the structure of the cubic phase of the compound basing on the X-ray diffraction data, obtained from a single-crystalline sample. The study showed that only the model assuming disorder of both Fe and Br positions is in agreement with the data of both XAFS and X-ray diffraction. Besides the distribution of Br-Fe distances obtained from XAFS suggests a strong correlation of Fe and Br displacements in the cubic phase.

Thus a solid proof has been obtained that ferroelectric-to-paraelectric phase transition in $Ni_3B_7O_{13}Br$ boracite has an essential order-disorder component.

References

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