

Temperature and concentration driven phase transitions in BiMnO₃-based ceramics

M.V. Silibin^{*,1}, D.V. Karpinsky^{1,2}, D.V. Zhaludkevich^{1,2}, S.I. Latushka^{1,2}, V.A. Khomchenko³, Yu.P. Shaman^{1,5}, A.V. Sysa^{1,5}, V.V. Sikolenko^{1,4}

¹ National Research University of Electronic Technology "MIET", 124498 Moscow, Russia

² Scientific-Practical Materials Research Centre of NAS of Belarus, 220072 Minsk, Belarus

³ CFisUC, Department of Physics, University of Coimbra, 3004-516 Coimbra, Portugal

⁴ Joint Institute for Nuclear Research, 141980 Dubna, Moscow region, Russian Federation

⁵ Scientific-Manufacturing Complex "Technological Centre", Zelenograd, Moscow, 124498, Russian Federation

Abstract

Crystal structure and magnetic state of the (1-x)BiFeO₃-(x)BiMnO₃ solid solution has been analyzed by laboratory and synchrotron X-ray diffraction, magnetization measurements and differential thermal analysis and scanning calorimetry. Dopant concentration increase leads to the room temperature structural transitions from the polar active rhombohedral phase to the antipolar orthorhombic phase and then to the monoclinic phase accompanied by a formation of two-phase regions consisting of the adjacent structural phases in the concentration ranges $0.25 < x_1 < 0.30$ and $0.50 \leq x_2 < 0.65$ respectively.

The accompanied changes in the magnetic structure refer to the magnetic transitions from the modulated antiferromagnetic structure to the non-collinear antiferromagnetic and then to the orbitally ordered ferromagnetic structure. A relationship between the crystal structure and magnetic state of the compounds having metastable structure is studied and discussed depending on the chemical composition and heating prehistory.

Examination of the X-ray diffraction patterns the compounds BiFe_{1-x}Mn_xO₃ crystal structure of the compounds over the entire range of the solid solution obtained by laboratory and synchrotron techniques confirms the changes of the crystal structure from the rhombohedral (sp. gr. R3c) to the orthorhombic (Pnma) and then to the monoclinic structure (C2/c) occurred upon increase in the dopant concentration which is in agreement of the available results.

Increase in the dopant content up to 25 mol. % leads to a stabilization of the orthorhombic phase (sp. gr. Pnma) described by the metric $\sqrt{2}a_p \cdot 4a_p \cdot 2\sqrt{2}a_p$ (a_p - primitive perovskite cell) which is four times larger than that of conventional orthorhombic cell specific for orthoferrites with perovskite structure. The compound with $x = 0.3$ is characterized by the two-phase structural state with the dominant orthorhombic phase and minor amount (~ 10 mol. %) of the rhombohedral phase.

A stabilization of the monoclinic phase is observed in the concentration range of $0.6 < x < 0.65$ which is accompanied by slight decrease in the volume of unit cell.

Temperature increase leads to drastic modification of the solution. The rhombohedral compounds, i.e. those having Mn content less than 25 mol. %, show temperature induced phase transition similar to that observed for the initial compound BiFeO₃, viz. from the polar active rhombohedral phase to the non-polar orthorhombic phase.

The magnetic structure of the compounds also notably changes upon the chemical doping and one can assume three different concentration regions ascribed to the different magnetic states. Chemical doping with Mn ions leads to a disruption of the modulated magnetic structure formed by Fe³⁺ ions thus leading to a stabilization of the non-collinear antiferromagnetic structure accompanied with a release of the remanent magnetization in the compounds with $0.3 < x < 0.5$.

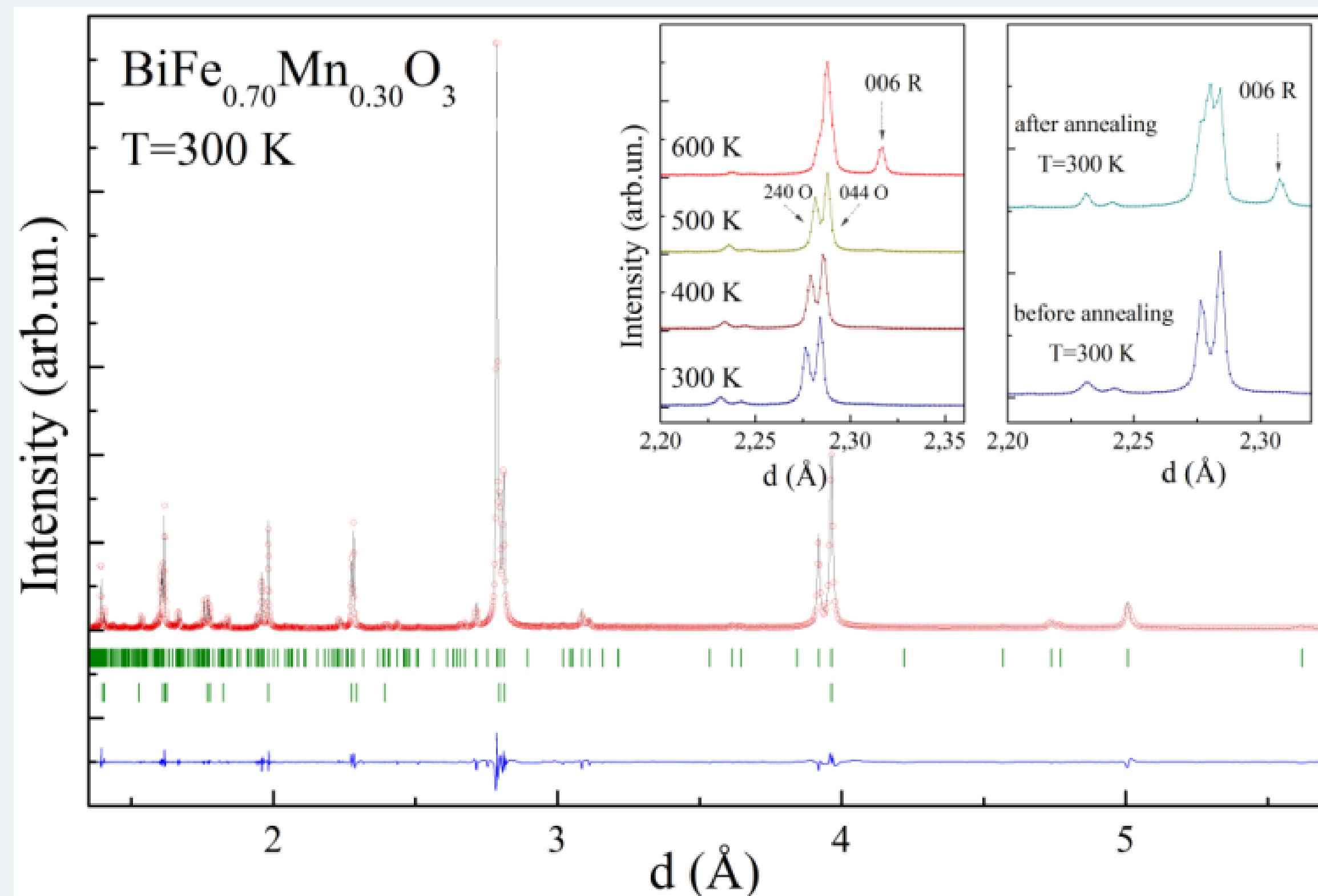
Further increase in the Mn content leads to a frustration of the long range antiferromagnetic structure and the compounds within the concentration range $0.4 < x < 0.6$ are characterized by a formation of a short range magnetic order as confirmed by magnetometry data.

The compounds with Mn rich chemical compositions ($x > 0.6$) are characterized by a notable increase in the low temperature magnetization thus denoting a formation of a new type of magnetic structure ascribed to ferromagnetic state.

The results of isothermal magnetization measurements of the compound with $x = 0.7$ show a distinct hysteresis like loop at temperature of 5 K while long range ferromagnetic order is not formed.

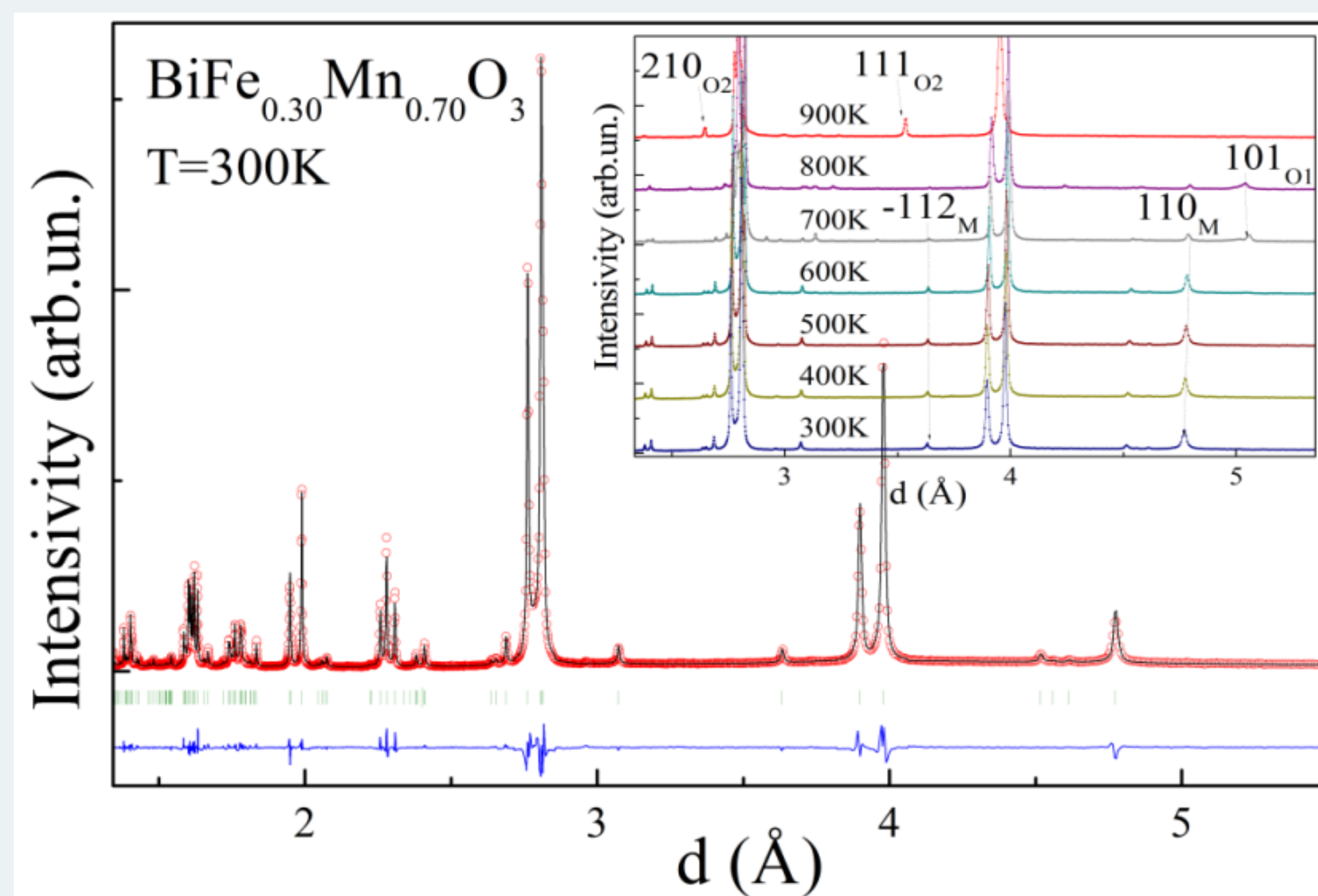
Acknowledgements

The authors would like to acknowledge the financial support from RSF (grant # 21-19-00386).



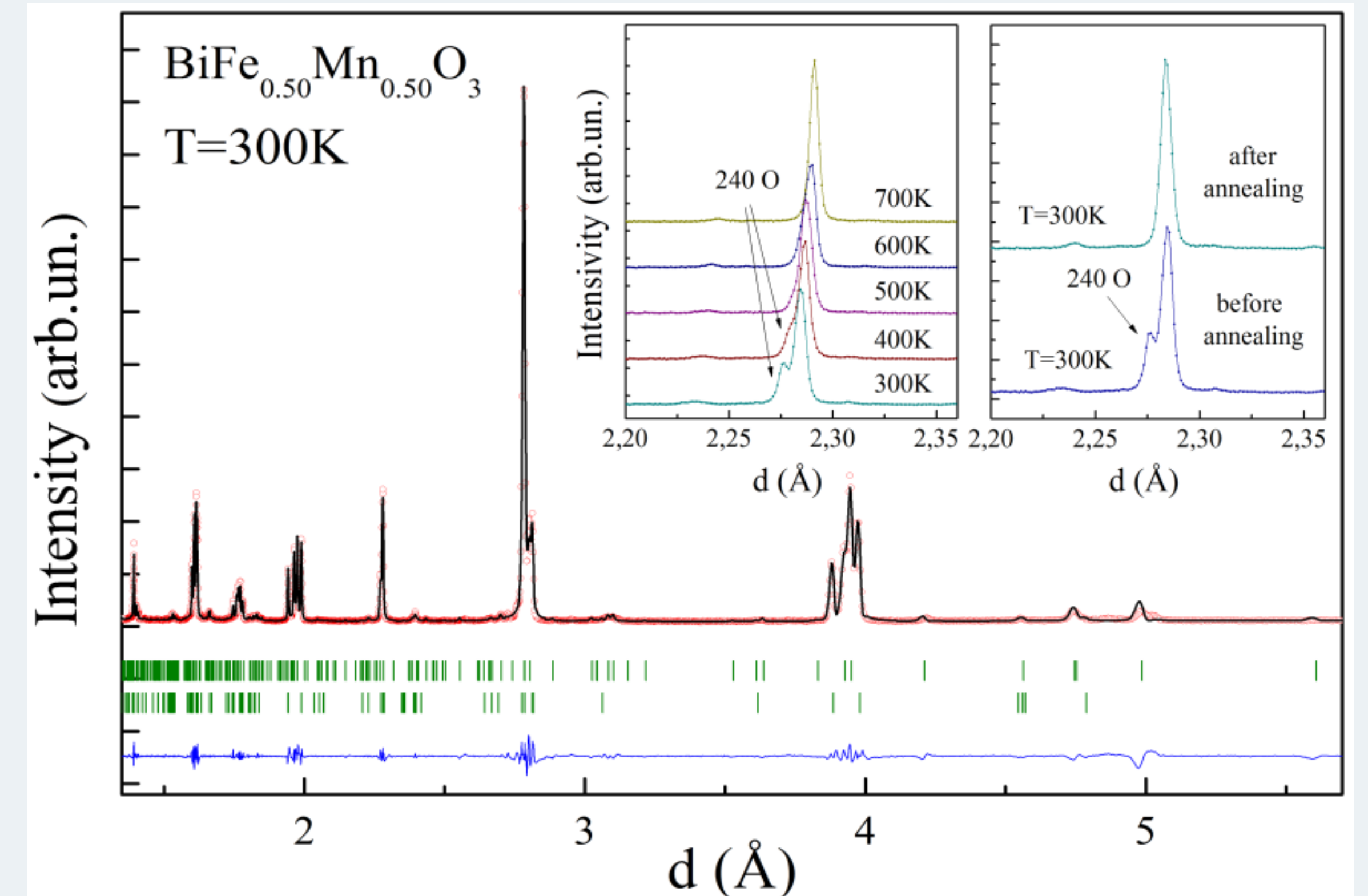
Room temperature synchrotron diffraction pattern of BiFe_{0.70}Mn_{0.30}O₃, left inset shows temperature driven changes of the reflections attributed to the different structural phases (O – Pnma phase; R – R3c phase) and specific reflections at room temperature for the compound before and after annealing at ~ 650 K.

The temperature dependent diffraction patterns of the compound with $x = 0.3$ having dominant orthorhombic phase at room temperature above a temperature of $T \sim 500$ K show a rapid increase in the intensity of the reflections specific for the rhombohedral phase. The amount of the rhombohedral phase increase at the expense of the orthorhombic phase but the transition is not completed up to a temperature of ~ 750 K, above this temperature a chemical decomposition starts.



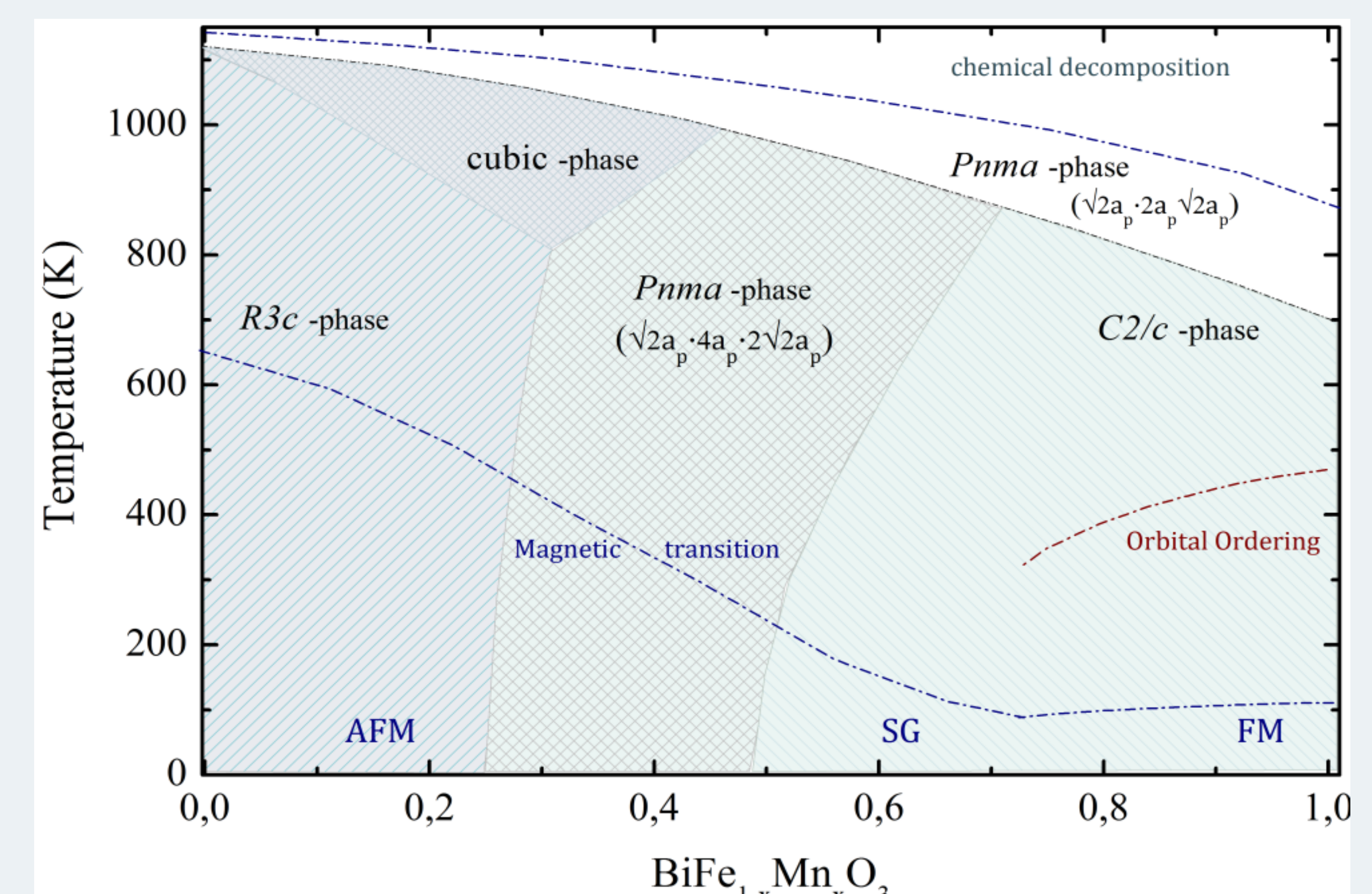
Room temperature synchrotron diffraction pattern of BiFe_{0.30}Mn_{0.70}O₃, the inset shows temperature evolution of the reflections specific for the monoclinic and orthorhombic phases (M – C2/c phase; O2 – Pnma phase with metric $\sqrt{2}a_p \cdot 4a_p \cdot 2\sqrt{2}a_p$, a_p – primitive perovskite unit cell parameter).

The two-phase structural state remains stable up to 850 K and in the narrow temperature range of 820 – 870 K the compound becomes to be single phasic with orthorhombic structure, at temperatures above 870 K a new non-polar orthorhombic phase stabilizes.

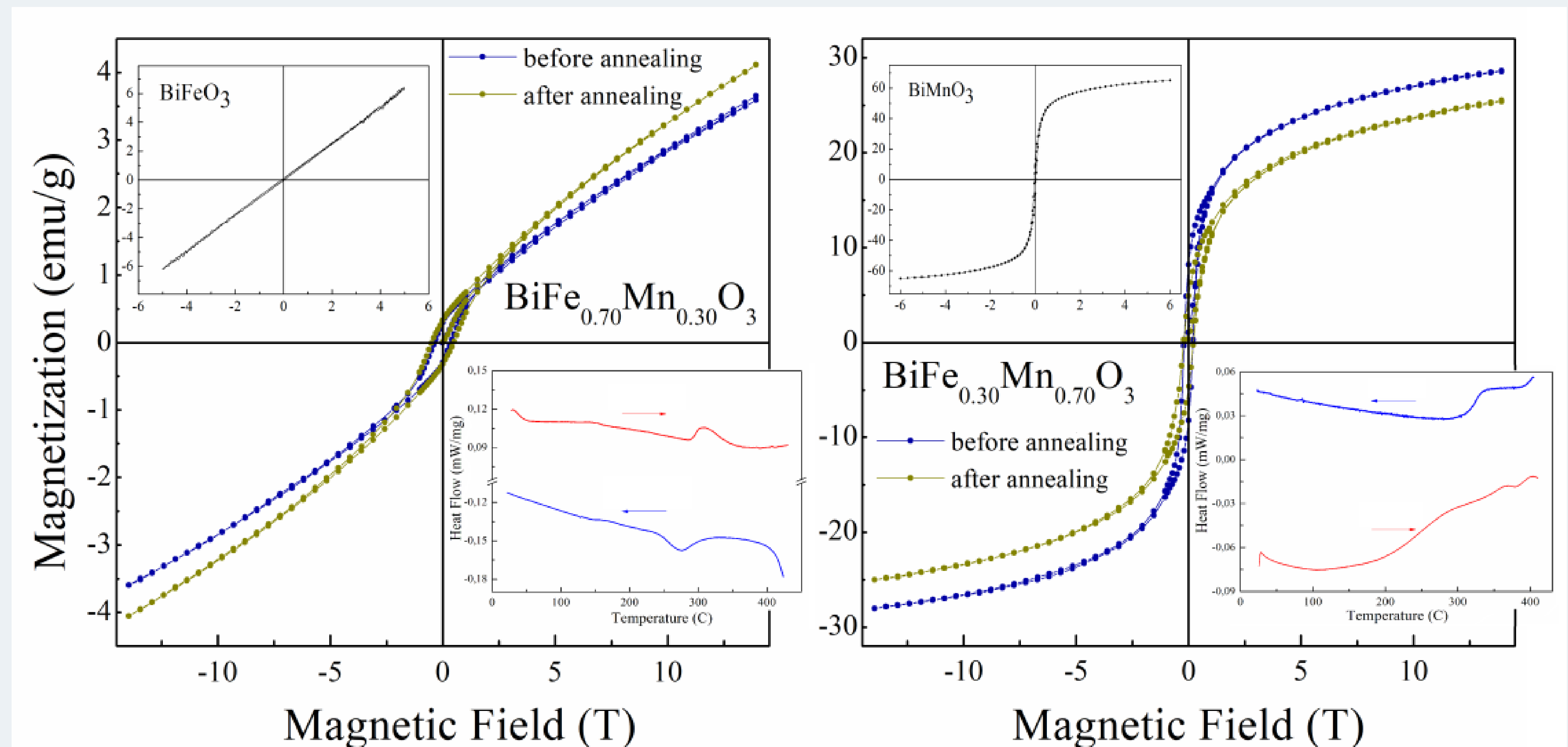


Room temperature synchrotron diffraction pattern of BiMn_{0.5}Fe_{0.5}O₃ refined in the two-phase model (upper row of vertical ticks denote Bragg positions of the orthorhombic phase, bottom – monoclinic phase), left inset shows temperature dependent modification of the reflections specific for the dominant orthorhombic phase; right inset shows specific reflections before and after annealing of the compound at ~ 700 K (O – Pnma phase).

Temperature dependent diffraction measurements of the compound with $x = 0.5$ having dominant orthorhombic structural state and a minor amount of the monoclinic phase at room temperature show even more pronounced irreversible structural transformations.



Preliminary structural and magnetic phase diagram of the solid solution BiMnO₃ - BiFeO₃ depending on temperature and chemical composition.



Isothermal dependent magnetization curves recorded for compounds BiMn_{1-x}Fe_xO₃ ($x = 0.3, 0.7$) at 5 K before and after annealing at $T \sim 700$ K. The insets show DSC curves of the compounds and M(H) dependencies obtained at $T \sim 5$ K for the extreme compounds BiFeO₃ and BiMnO₃.

Conclusions

- The dopant concentration increase causes the phase transition from rhombohedral to the orthorhombic structure leading to a disruption of the modulated antiferromagnetic structure and a stabilization of the non-collinear antiferromagnetic structure associated with weak ferromagnetism.
- Annealing of the compounds at high temperature (~ 700 K) causes irreversible transitions in the structural state of the compounds thus favoring a stabilization of the crystal structure specific for high temperature range.
- The magnetic states of the compounds significantly change after thermal annealing; transformation of the magnetic state is caused by an increase in the amount of the appropriate structural phase. Thus, in the Fe-rich compounds the changes in the magnetic state are associated with an increase of the rhombohedral phase characterized by weak ferromagnetism, the magnetic state of the Mn-rich compounds is determined by an increased amount of the orthorhombic phase having frustrated magnetic order.
- Based on the results obtained by the diffraction techniques as well as magnetometry measurements one can conclude about a strong correlation between the type of magnetic structure and the structural state of the compounds.
- The compounds with two-phase structural state at room temperature are characterized by irreversible temperature driven structural transitions which favor a stabilization of high temperature structural phases, the magnetic structure of the compounds also exhibits an irreversible temperature induced transition resulted in an increase of the contribution from the magnetic phase associated with the high temperature structural phase.