

Phase Composition and Crystal Structure of the *RE*-Substituted BiFeO₃ (*RE* = Er, Tm, Yb)

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Abstract. The work deals with the study of the phase and structural behaviour of the rare-earth substituted BiFeO₃. X-ray powder diffraction examinations revealed that the polar *R3c* phase in the Bi_{1-x}RE_xFeO₃ systems with *RE* = Er, Tm and Yb do not exceed 7, 4 and 3 mol.% of rare earth, respectively. Partial substitution of Er and Tm for the Bi sites in BiFeO₃ reduce the temperature of the ferroelectric phase transition *R3c*–*Pbnm* on 30–60 K.

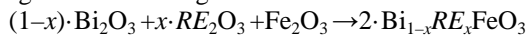
Key words: BiFeO₃-based solid solutions, multiferroics, crystal structure, thermal expansion, phase transition.

I. INTRODUCTION

Among multiferroic materials BiFeO₃ is one of the most promising compounds which have attracted extraordinary interest owing to its high-temperature ferroelectric and antiferromagnetic transitions. Substitution of the cations in the BiFeO₃ perovskite structure has been proven to be an effective method to enhance the ferroelectricity and to improve the magnetic properties and magnetoelectric coupling of the material [1]. Numerous studies are devoted to the structure and properties investigations of the Bi_{1-x}RE_xFeO₃ systems with *RE* = La–Er and Y [1-4]. However, to the best of our knowledge there are no mentions in the literature on the Tm and Yb substituted BiFeO₃. The aim of the present work is the study of the cation substitution in the BiFeO₃–*RE*FeO₃ systems with Er, Tm and Yb in order to evaluate the existence ranges of the polar *R3c* phases at room temperature (RT) and to establish the influence of substitution on the ferroelectric phase transitions in these systems.

II. EXPERIMENTAL

Series of Bi_{1-x}RE_xFeO₃ (*RE* = Er, Tm, Yb) specimens with *x* in the range of 0.05–0.25 for Er and Yb and 0.0–0.12 for Tm have been prepared from stoichiometric amounts of the RE oxides, Bi₂O₃ and Fe₂O₃ by solid-state reaction technique according to the following reaction scheme:



Appropriate amounts of the previously fired oxides were mixed and pressed to pellets which were subsequently loaded into alumina crucibles and reacted in air at 1093 K for 6 h. X-ray phase and structural characterisation of the samples at room temperature was performed by using imaging plate Guinier camera G670 (Cu *K*_{α1} radiation, λ = 1.54056 Å). Thermal behaviour of the structure has been studied *in situ* in the temperature range of 298–1173 K at synchrotron laboratory HASYLAB at DESY (powder

diffractometer at beamline B2, equipped with STOE capillary furnace and image plate detector OBI).

III. RESULTS AND DISCUSSION

X-ray powder diffraction examination revealed that all samples synthesised possess rhombohedral perovskite BiFeO₃ type of structure. Besides the main perovskite phase, minor amount of parasitic phases Bi₂₅FeO₄₀ and Bi₂Fe₄O₉ have been detected. The content of these phases was largest in the nominally pure BiFeO₃ sample and somewhat decreases with increasing of *RE*-component in the Bi_{1-x}RE_xFeO₃ specimens. According to the literature data, these phases are always present in BiFeO₃-based materials obtained by solid-state synthesis and its content strongly depends on the purity of the initial materials. Starting from the nominal compositions Bi_{0.95}RE_{0.05}FeO₃ the orthorhombic perovskite phases isotypic with GdFeO₃ appear in the systems with Tm and Yb. The amount of these phases increase with increasing *RE* content in Bi_{1-x}RE_xFeO₃, reaching 21.4 and 24.6 wt.% in the samples with nominal compositions Bi_{0.88}Tm_{0.12}FeO₃ and Bi_{0.75}Yb_{0.25}FeO₃, respectively. Fig. 1 represents the graphical results of multiphase Rietveld refinement of the sample with nominal composition Bi_{0.95}Yb_{0.05}FeO₃.

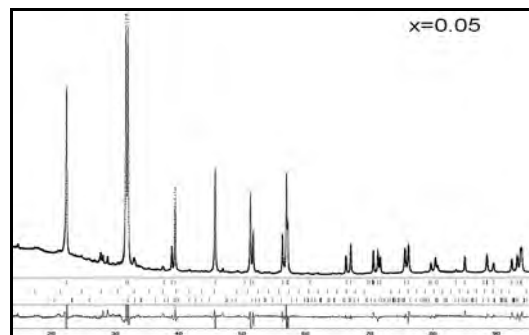


Fig. 1. Graphical results of three-phase refinement of crystal structures in the sample Bi_{0.95}Yb_{0.05}FeO₃. Vertical lines show the position of the peaks for the phases BiFeO₃ (top row), Bi₂₅FeO₄₀ (middle row) and YbFeO₃ (bottom row).

In contrast, the orthorhombic perovskite phase do not appears in the corresponding erbium system. Instead of the Er₃Fe₅O₁₂-based phase with the garnet structure has been found in the Bi_{0.90-0.75}Er_{0.10-0.25}FeO₃ samples in the amount of 10.3–38.3 wt.%, respectively.

From a comparison of the obtained values of the lattice parameters of rhombohedral and orthorhombic perovskite phases in the Bi_{1-x}Tm_xFeO₃ and Bi_{1-x}Yb_xFeO₃ specimens with the own and literature data for the “pure” BiFeO₃, as well as with the reference data for the thulium and ytterbium orthoferrites, the existence ranges of both perovskites phases can be evaluated (Fig. 2).

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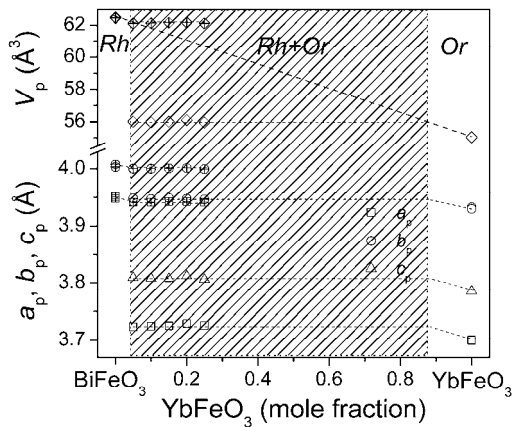


Fig. 2. Concentration dependencies of the lattice dimensions (normalised to the perovskite cell) in the BiFeO_3 - YbFeO_3 system.

In order to determine the existence range of the polar BiFeO_3 -type phases in the studied systems more precisely, the concentration dependencies of the cell volumes of $\text{Bi}_{1-x}\text{RE}_x\text{FeO}_3$ specimens were analyzed (Fig. 3). From this plot it is evident, that solubility of Er, Tm and Yb in $\text{Bi}_{1-x}\text{RE}_x\text{FeO}_3$ do not exceed 7, 4 and 3 mol.%, respectively. This finding is in a good agreement with the literature data [1], according of which the polar phases in the BiFeO_3 - REFeO_3 systems become less stable with a decrease of the rare earth ionic radii. According to structural phase diagram on $\text{Bi}_{1-x}\text{RE}_x\text{FeO}_3$ systems published in [1], the existence range of the polar $R3c$ phase decreases from 15 mol.% in the La system to 7.5 mol.% in the system of Dy.

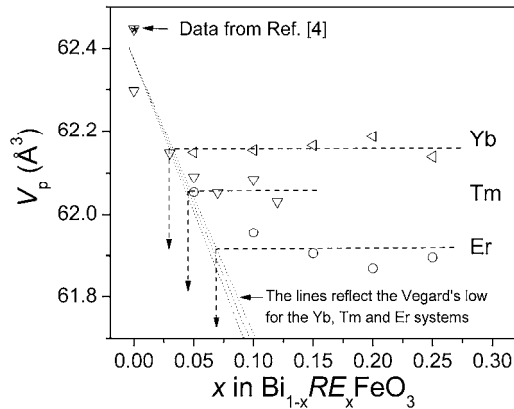


Fig. 3. Concentration dependencies of the normalized cell volumes in the BiFeO_3 - REFeO_3 ($\text{RE} = \text{Er}, \text{Tm}, \text{Yb}$) systems.

In situ high-temperature powder diffraction examinations of the $\text{Bi}_{0.95}\text{Er}_{0.05}\text{FeO}_3$ and $\text{Bi}_{0.95}\text{Tm}_{0.05}\text{FeO}_3$ specimens revealed onsets of the structural phase transitions from a rhombohedral $R3c$ to orthorhombic $Pbnm$ phase at 933 K and 993 K, respectively. According to the results of a multi-phase Rietveld refinement, the content of HT $Pbnm$ phase in $\text{Bi}_{0.95}\text{Er}_{0.05}\text{FeO}_3$ increases from 11.4 wt.% at 933 K to 50.5 wt.% at 1083 K and 95 wt.% at 1113 K, thus indicating on the completion of the phase transition. Further increase of the temperature lead to decomposition of the perovskite phase on $\text{Bi}_2\text{Fe}_4\text{O}_9$ and liquid Bi_2O_3 , which reacts with the walls of SiO_2 quartz capillary resulting in formation of $\text{Bi}_4(\text{SiO}_4)_3$ (eulytite) phase at 1173 K. Similar phase and

structural behaviour is also observed in the Tm-substituted BiFeO_3 , in which the $R3c$ - $Pbnm$ transition takes place at the temperatures 993–1083 K, and the phase decomposition and reaction with SiO_2 begins at 1023 K. The temperatures of the phase transitions in $\text{Bi}_{0.95}\text{Er}_{0.05}\text{FeO}_3$ (1070 K) and $\text{Bi}_{0.95}\text{Tm}_{0.05}\text{FeO}_3$ (1030 K) estimated as a middle point with the equal amount of polar $R3c$ and HT $Pbnm$ phases, are lower than in “pure” BiFeO_3 (1083–1103 K [1]). Temperature evolution of the cell dimensions of both modifications of $\text{Bi}_{0.95}\text{Tm}_{0.05}\text{FeO}_3$ illustrating a discontinuous phase transition $R3c$ - $Pbnm$ are shown in Fig. 4. The $R3c$ - $Pbnm$ transitions in $\text{Bi}_{0.95}\text{Er}_{0.05}\text{FeO}_3$ and $\text{Bi}_{0.95}\text{Tm}_{0.05}\text{FeO}_3$ are accompanied by an abrupt decrease of the cell volumes, which decrease more than at 2 % (Fig. 4).

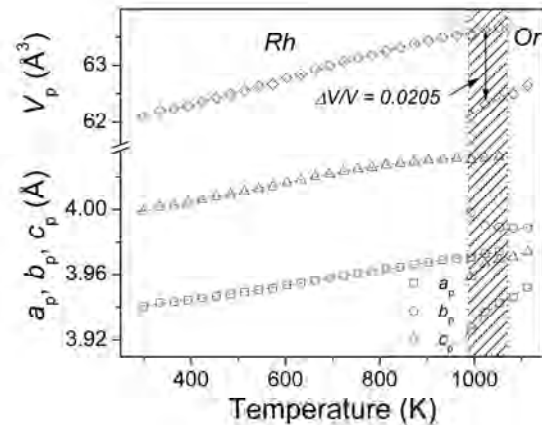


Fig. 4. Temperature dependencies of the normalized lattice parameters and cell volumes of $\text{Bi}_{0.95}\text{Tm}_{0.05}\text{FeO}_3$.

IV. CONCLUSIONS

Based on the results of X-ray phase and structural examinations it was established that the existence range of polar $R3c$ phase in the BiFeO_3 - REFeO_3 systems with Er, Tm and Yb do not exceed 7, 4 and 3 mol.% of RE, respectively. Partial substitution of Er and Tm for the Bi sites in BiFeO_3 reduce the temperature of the ferroelectric phase transition on 30–60 K.

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