

Temperature-induced transitions between metastable phases of perovskite solid solutions

Relevant for: Multiferroics, photovoltaic research, perovskites, polymorphism.

Variable temperature XRD studies are used to investigate the phase behavior of $\text{BiFe}_{1-y}\text{Sc}_y\text{O}_3$ solid solutions. The observed metastable phases and the annealing-stimulated transitions between them could be used to obtain new phase mixtures with desirable properties.



1 Introduction

Perovskite multiferroics based on modified bismuth ferrite (BiFeO_3) have recently attracted great interest due to their potential applications in the fields of magnetism, photovoltaics and spintronics amongst others. Such materials are also of interest on a fundamental level and so modified versions of bismuth ferrite are explored as a means to enhance their properties and the potential number of applications.

Modified bismuth ferrite with Bi-site substitutions can generally be produced in bulk polycrystalline form following conventional synthesis procedures. In contrast to this, to produce Fe-site substituted bismuth ferrites, high pressure synthesis must be employed which limits the quantity produced and also requires complex and expensive equipment.

Metastable perovskites with a 1:1 ratio of Fe^{3+} to a substituting B^{3+} cation are the most studied and several new phases have been found in their solid solutions. Competing phases form depending on the level of substitution and an antipolar *Pnma* phase, together with polar *R3c* and *Ima2* phases have also been observed.

There have also been several studies on the $(1-y)\text{BiFeO}_3 \cdot y\text{BiScO}_3$ solid solutions, where the metastable antipolar *Pnma* phase is present between

$y = 0.30$ and $y = 0.60$. The most studied solid solution within this series is that with $y = 0.50$, where there are two non-equivalent structures both in the *Pnma* space group which can be stabilized over the same temperature range.

The results presented here are on the temperature behavior of metastable perovskite phases in the $\text{BiFe}_{1-y}\text{Sc}_y\text{O}_3$ series studied by in-situ X-ray powder diffraction. (1) The phase behavior is compared with other metastable perovskite solid solutions derived from BiFeO_3 .

2 Experimental Details

Compositions of $\text{BiFe}_{1-y}\text{Sc}_y\text{O}_3$ with $y = 0.30, 0.40, 0.45, 0.50, 0.55,$ and 0.60 , were prepared by high pressure synthesis. The ceramics obtained were reduced to powders prior to further analysis.

X-ray powder diffraction studies were performed on a standard laboratory diffractometer equipped with the HTK 16N high-temperature chamber from Anton Paar GmbH to perform in-situ temperature measurements. Data were analyzed using the Rietveld method.

3 Results and Discussion

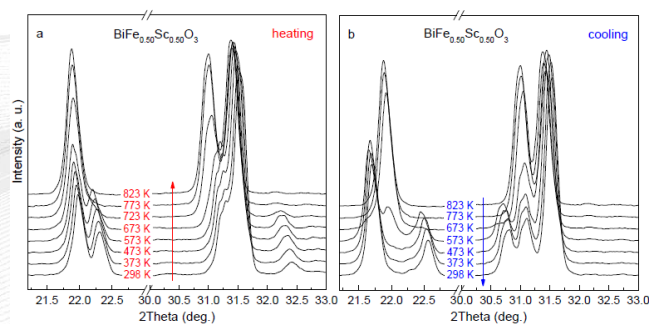


Figure 1: Diffraction patterns for the first thermal cycle of the as prepared $\text{BiFe}_{0.50}\text{Sc}_{0.50}\text{O}_3$: (a) heating up to 873 K and (b) cooling back down to room temperature.

Previous experiments have shown that a heating and cooling cycle of as-prepared $\text{BiFe}_{0.50}\text{Sc}_{0.50}\text{O}_3$ shows transitions from the antipolar orthorhombic *Pnma* phase to the polar orthorhombic *Ima2* phase with an intermediate high-temperature rhombohedral *R3c* phase. (2) Figure 1 shows the results collected in this work on the same compound, with the representative regions of the diffractograms displayed for the first heating cycle of the as-prepared perovskite. It can be seen that, on heating, the antipolar *Pnma* phase is the only one present up to ~ 720 K. This phase then coexists with the rhombohedral *R3c* phase up to ~ 770 K, while above these temperatures only the rhombohedral phase is present. On cooling, the polar orthorhombic *Ima2* phase appears at ~ 670 K, and below 570 K the *R3c* to *Ima2* transition is complete and only the orthorhombic phase remains.

During the second heating cycle up to 920 K, and in all subsequent cycles, the transition between the *Ima2* and *R3c* phases in $\text{BiFe}_{0.50}\text{Sc}_{0.50}\text{O}_3$ is found to be reversible. The *R3c* phase appears at ~ 570 K and disappears at ~ 500 K, while the *Ima2* phase disappears at ~ 720 K and reappears at ~ 670 K (Figure 2).

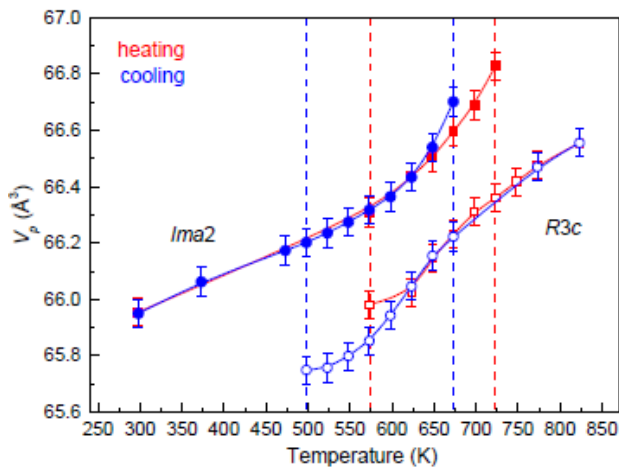


Figure 2: Changes in the normalized unit cell volume with temperature of the $\text{BiFe}_{0.50}\text{Sc}_{0.50}\text{O}_3$ perovskite during the second thermal cycle: the *Ima2* phase (solid symbols) and the *R3c* phase (open symbols) are shown.

For the perovskite with composition $\text{BiFe}_{0.70}\text{Sc}_{0.30}\text{O}_3$, the *R3c* phase is found to appear in the range 380 – 400 K and the transformation is complete at ~ 470 K when no trace of the *Pnma* phase remains (Figure 3). In this case, the transformation was irreversible and the rhombohedral phase remains when cooled back down to room temperature.

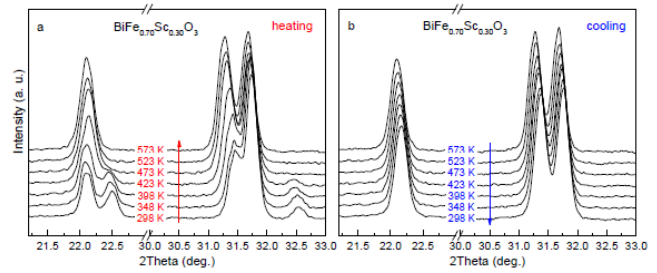


Figure 3: Diffraction patterns for the first thermal cycle of the as prepared $\text{BiFe}_{0.70}\text{Sc}_{0.30}\text{O}_3$: (a) heating up to 923 K and (b) cooling back down to room temperature.

In the sample with the intermediate composition of those presented so far, $\text{BiFe}_{0.60}\text{Sc}_{0.40}\text{O}_3$, the behavior is similar to those presented so far. On increasing the temperature the *R3c* phase forms and initially coexists with the *Pnma* phase, with only the rhombohedral phase observed above ~ 550 K. However, in this case the transformation to the *Ima2* phase on cooling is incomplete and the sample is a mixture of the rhombohedral *R3c* and orthorhombic *Ima2* phases at room temperature after annealing.

The data for the perovskite with the composition $\text{BiFe}_{0.55}\text{Sc}_{0.45}\text{O}_3$ also shows the transition from the initial *Pnma* phase to the *R3c* phase upon heating, and then from the *R3c* phase to the *Ima2* phase on cooling; though these transitions begin at higher temperatures than in $\text{BiFe}_{0.60}\text{Sc}_{0.40}\text{O}_3$. At room temperature, the transition to the orthorhombic phase was again incomplete resulting in a phase mixture in the annealed sample after cooling. The compositions with $y = 0.45$ and $y = 0.40$ also show a similar behavior.

The transition to the *R3c* phase in $\text{BiFe}_{0.45}\text{Sc}_{0.55}\text{O}_3$ begins at a higher temperature is not completed before decomposition occurs (Figure 4). The *R3c* phase that formed transforms to the *Ima2* phase on cooling, while the untransformed *Pnma* phase remains resulting in a mixture of the *Pnma* and *Ima2* phases.

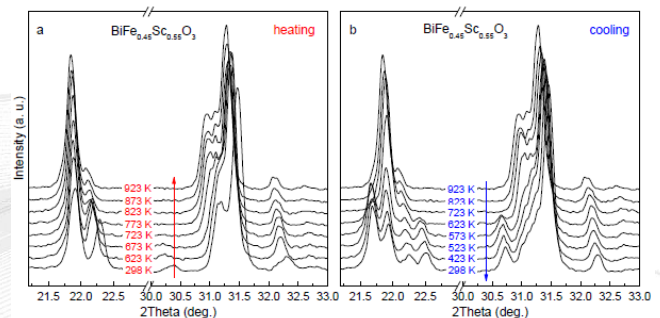


Figure 4: Diffraction patterns for the first thermal cycle of the as prepared $\text{BiFe}_{0.45}\text{Sc}_{0.55}\text{O}_3$: (a) heating up to 923 K and (b) cooling back down to room temperature.

Finally, in the case of $\text{BiFe}_{0.40}\text{Sc}_{0.60}\text{O}_3$, no phase transition is observed on heating or cooling and the initial *Pnma* phase remains unchanged.

irreversible transitions will likely decrease as the substitution rate increases.

4 Summary

In summary, perovskite compositions of the $\text{BiFe}_{1-y}\text{Sc}_y\text{O}_3$ series ($0.30 \leq y \leq 0.60$) were prepared by high pressure synthesis. The perovskites were studied using in-situ high temperature XRD and the as-prepared samples were found to display an antipolar *Pnma* structure. These phases are metastable and convert to other metastable phases on heating and cooling. Dependent on the composition, there may be irreversible transformation to an *R3c* phase, and in some cases further conversion to an *Ima2* phase; these transformation are not always complete. The transition temperatures also shift depending on the value of *y*. Phase mixtures are formed dependent on the maximum annealing temperature, so controlled phase mixtures can be produced on cooling the sample back to room temperature.

Based on the samples studied here, a tentative state diagram could be produced which shows the potential for annealing of the metastable phases to be used to produce materials with defined phase mixtures and therefore defined properties.

5 References

1. A. N. Salak *et al.* *Crystals* **2018**, *8*, 91.
2. D. D. Khalyavin *et al.* *Phys. Rev. B* **2014**, *89*, 174414.

6 Acknowledgements

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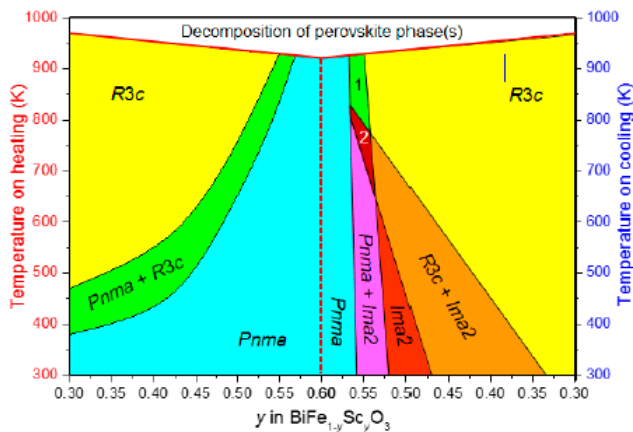


Figure 5: Tentative state diagram of the metastable perovskite phases for the $\text{BiFe}_{1-y}\text{Sc}_y\text{O}_3$ series upon heating to their temperature stability limit (left side of the graph) and on cooling to room temperature (right side of the graph). The areas marked 1 and 2 correspond to the *Pnma* + *R3c* phase mixture and the *Pnma* + *R3c* + *Ima2* phase mixture, respectively.

Based on the observed phase behaviors of the different perovskite compositions, a tentative state diagram can be produced (Figure 5). The as-prepared phase for all samples is the antipolar *Pnma* phase. The right side of the diagram shows the irreversible transitions from the *Pnma* phase to the *R3c* phase (both complete and incomplete), while the transitions shown on the left side are all reversible.

All of the perovskite phases studied in this work are metastable and decomposed when annealed above their temperature stability limits which are in the range 870 – 920 K when *y* is between 0.30 and 0.60. As these temperatures are well above the operating temperatures of any electronic devices, it is possible that these metastable perovskite phases in the $\text{BiFe}_{1-y}\text{Sc}_y\text{O}_3$ series could find application. A feature of this series is the fact that the state diagram is dependent on the maximum temperature of the first heating cycle and by means of controlled annealing it is possible to obtain materials containing different combinations of perovskite phases.

The antipolar orthorhombic *Pnma* phase and the polar rhombohedral *R3c* phase have been observed in all BiFeO_3 -derived solid solutions to date. However, the metastable polar orthorhombic *Ima2* phase has up to now only been observed in the $\text{BiFe}_{1-y}\text{Sc}_y\text{O}_3$ series. This is likely due to geometric factors associated with the cation size and it may be possible to find the *Ima2* phase in other perovskites series where the Fe^{3+} ion is substituted with a larger ion. The temperature stability of the metastable phases is expected to be correlated with the cation substitution rate; therefore, the chances of obtaining new phases by annealing-stimulated