Smart devices

Design and synthesis of metastable strongly correlated materials using first-principles calculations

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Abstract

In this study, we successfully synthesized a new perovskite-type oxide, (Ca,Ba)$FeO_{3-\delta}$, incorporating the anomalously high-valence Fe^{4+} ion. This was achieved by visualizing the stability of hypothetical compositions and structures at various pressures using first-principles calculations, and designing a stepwise synthetic route based on these results. Furthermore, precise structural analysis using synchrotron X-ray diffraction revealed the formation of ordering at the A-site and in the oxygen-vacancy arrangement. Magnetic measurements, together with first-principles calculations assuming magnetic order, suggest the possible emergence of helical magnetism. This work demonstrates the effectiveness of a strategy that reaches metastable phases by iterating between computation and synthetic experimentation.

Background & Results

We are advancing the development of functional quantum materials–such as spintronic materials and thermoelectric converters–by integrating high-pressure synthesis with computational and information science. Perovskite-type oxides containing the unusually high-valence Fe^{4+} ion, on which we have focused, exhibit unconventional magnetic properties arising from their peculiar electronic states. However, these metastable oxides are thermodynamically unstable at ambient pressure, and optimizing the synthesis conditions is challenging, making systematic materials exploration difficult.

In this study, we investigated synthetic pathways for candidate compounds in the Ca–Ba–Fe–O system using DFT calculations, aiming for the strategic discovery of perovskite-type oxides incorporating Fe^{4+}. Enthalpy calculations were performed at various pressures for six systems, including oxygen-deficient and fully oxygenated phases (Fig. 1, lower left). The results indicated that two types of A-site–ordered oxygen-deficient phases, $CaBaFe_2O_5$ and $CaBa_2Fe_3O_8$, become accessible under high pressure, and we successfully synthesized both compounds. Moreover, gentle ozonation of these phases yielded rare perovskites, $CaBaFe_2O_{6-\delta}$ and $CaBa_2Fe_3O_{9-\delta}$, in which the isovalent Ca^{2+} and Ba^{2+} ions exhibit site ordering. For the latter compound, magnetization measurements together with DFT calculations assuming magnetic order suggested the emergence of helical magnetism originating from Fe^{4+}. The exploration strategy combining DFT calculations with high-pressure synthesis developed in this study is expected to accelerate the discovery of metastable, strongly correlated oxides with novel properties.

Significance of the research and Future perspective

This study demonstrates that multidimensional synthetic pathways can be visualized through first-principles calculations under various pressures, enabling the strategic design and development of metastable perovskites exhibiting unusual helical magnetism. This approach is expected to facilitate the efficient discovery of metastable, strongly correlated materials with novel spintronic functionalities.

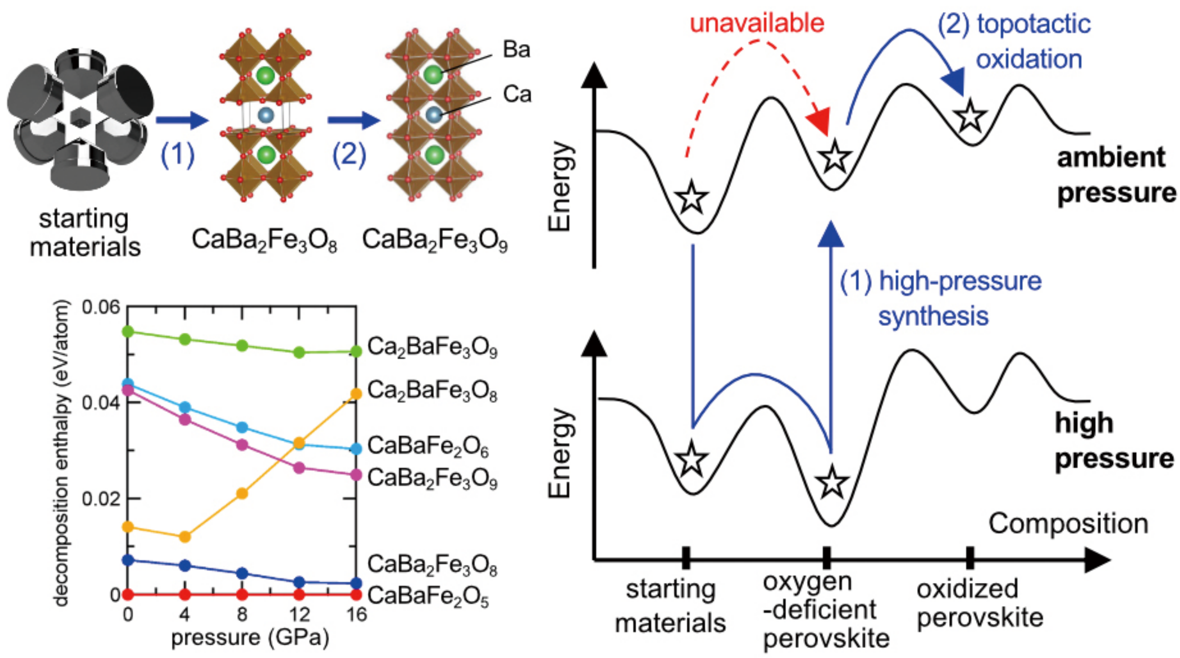

Fig. 1 Synthesis of novel A-site ordered perovskite (Ca,Ba)FeO_3 using first-principles calculations

Patent

Treatise: Onose, Masaho et al. Exploration of metastable A-site-ordered perovskites (Ca,Ba)$FeO_{3-\delta}$ by computationally guided multistep synthesis. J. Am. Chem. Soc. 2025, 147(10), 8260–8266. doi: 10.1021/jacs.4c15392

URL

Keyword: strongly correlated oxides, high pressure synthesis, first-principles calculations