Anomalous Enhancement in Photocatalytic Rate by Stabilizing a Metastable Phase in a BiFeO3-Based Photocatalyst

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$BiFeO_3$-based system exhibits a range of fascinating and exotic physical phenomena. While the multiferroic aspect of this material continues to receive extensive attention from peer research groups globally. In the recent past, its low band gap has attracted researchers for its interesting photovoltaic and photocatalytic applications. In this paper, we report the discovery of size effect on the structural stability and its anomalous consequence on the photocatalytic performance of a $BiFeO_3$-based perovskite. The multifunctional characteristics of $BiFeO_3$ has attracted great attention over the years. In addition to its well-known multiferroic behaviour, the small optical band-gap makes it interesting from the view point of photocatalytic and photovoltaic applications. Here, we report an unusual phenomenon of five times increase in the photocatalytic rate by trapping a metastable phase in $PbTiO_3$ modified $BiFeO_3$ (BF-PT) by crystallite size reduction. First, we show that the ground state structure changes from tetragonal (P4mm) to rhombohedral (R3c) by crystallite size reduction. We then show that a direct P4mm_R3c transformation can be prevented if the crystallite size is physically reduced at room temperature. The trapped tetragonal structure in small crystallites becomes a metastable phase. A systematic study of photocatalytic degradation of dyes belonging to the xanthene-fluorene class revealed that dye degradation rate anomalously increases nearly by five times if the BF-PT catalyst is in the metastable state. The work reported here is a summary of a series of novel results listed below:

1. Discovery that the ground state structure changes (while retaining ferroelectricity) on decreasing the crystallite size.
2. Discovery that it is possible to trap the metastable ferroelectric phase simply by reducing the size at room temperature.
3. Discovery that the metastable phase increases the photocatalysis rate nearly by five times.

Our results offer a new processing strategy for the design of efficient photocatalysts based on semiconductor ferroelectrics.