Exploration of BaBiO$_3$ in the two-dimensional limit: evolution of lattice and electronic structure

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The perovskite material BaBiO$_3$ is the parent compound of the oxide superconductors BaPb$_x$Bi$_2$O$_{2+x}$ and Ba$_{1-x}$K$_x$BiO$_3$, with critical temperatures 13 K and 30 K, respectively [1-4]. The stoichiometric compound BaBiO$_3$ could be naively expected to be metallic due to the nominal Bi$^{3+}$ valence state (6s$^1$ configuration). Instead, the material is a charge-ordered insulator, generally believed to exhibit charge disproportionation into the Bi$^{3+}$ and Bi$^{5+}$ valence states [2].

As a consequence, bulk BaBiO$_3$ exhibits two types of structural distortions from the ideal cubic perovskite: a tilting distortion of the perovskite octahedra due to the different ionic radii of Bi$^{3+}$ and Bi$^{5+}$, and a breathing-mode distortion associated with the charge disproportionation phenomenon lead to a lower-symmetry monoclinic lattice structure [5]. The octahedral tilting has been reported to be suppressed in epitaxial thin films of stoichiometric BaBiO$_3$ grown on suitable substrates, whereas the breathing distortion is claimed to be retained [6].

We study epitaxial BaBiO$_3$ thin films grown by pulsed laser deposition, as a function of film thickness. We use X-ray photoemission spectroscopy (XPS) to quantify the stoichiometry of our samples; spectra acquired on our as-grown BaBiO$_3$ films show that our samples are stoichiometric, with a Ba:Bi ratio of 1:1 within measurement uncertainty. Further, we determine the optical constants of these films using ellipsometric spectroscopy, and we probe the samples' Raman response that exhibits peaks characteristic for the breathing mode distortion. Both measurements show that thick films have properties identical to bulk BaBiO$_3$. With decreasing film thickness, however, the signatures of charge ordering and of the breathing distortion are suppressed concurrently. Lastly, we perform a detailed X-ray diffraction study to directly track distortions of the BaBiO$_3$ lattice as a function of film thickness. On the basis of these observations, we discuss the mechanism that controls the charge order and its suppression in very thin BaBiO$_3$ films.