Bismuth oxide based materials exhibit the highest oxygen ion conductivities, making them of great interest for use in energy conversion devices such as solid oxide fuel cells. However, these materials exhibit chemical and thermal instabilities and understanding and their stabilization is an actively pursued research goal. In this study, we investigate the structural and electrical properties of erbium oxide stabilized bismuth oxide (Er0.4Bi1.6O3 − δ) as thin films. These are deposited by pulsed laser deposition onto several single crystal substrates (MgO, Al2O3 and SrTiO3). The films show new forms of instabilities, both upon aging treatments in air and even under conductivity measurements, with remarkable changes in the film composition and microstructure. © 2014 Published by Elsevier B.V.