Perovskite oxides have been at the forefront among catalysts for the oxygen evolution reaction (OER) in alkaline media offering a higher degree of freedom in cation arrangement. Several highly OER active Co-based perovskites have been known to show extraordinary activities and stabilities when the B-site is partially occupied by Fe. At the current stage, the role of Fe in enhancing the OER activity and stability is still unclear. In order to elucidate the roles of Co and Fe in the OER mechanism of cubic perovskites, two prospective perovskite oxides, La0.2Sr0.8Co1- xFe xO3-δ and Ba0.5Sr0.5Co1- xFe xO3-δ with x = 0 and 0.2, were prepared by flame spray synthesis as nanoparticles. This study highlights the importance of Fe in order to achieve high OER activity and stability by drawing relations between their physicochemical and electrochemical properties. Ex situ and operando X-ray absorption spectroscopy (XAS) was used to study the local electronic and geometric structure under oxygen evolving conditions. In parallel, density function theory computational studies were conducted to provide theoretical insights into our findings. Our findings show that the incorporation of Fe into Co-based perovskite oxides alters intrinsic properties rendering efficient OER activity and prolonged stability.