Complex oxides have demonstrated various important physical properties such as various dielectric and unusual magnetic properties. These extraordinary phenomena are highly dependent upon the degrees of the freedom of the charge distribution, spin and orbital status, and the lattice structures. Among the perovskite cobalt oxide system, the complex cobalt oxides exhibit different cobalt and oxygen coordination varying from tetrahedral, pyramidal to octahedral combinations depending on the oxygen contents, leading to various crystal structures with a great flexibility of the oxygen frameworks. Thus, oxygen nonstoichiometry becomes a very crucial parameter for tuning their atomic structure and physical properties. LnBaCo2O5+d (LnBCO, Ln= rare transition metal elements) systems exhibit various unique physical properties not only due to the presence of A-site disordered and A-site ordered structures (the close ionic sizes of Ln and Ba), but also the degree of ordered oxygen vacancy structures. These defect engineered structures induce the formation of various double perovskite structures and the strong couplings of multifunctionalities from ferroelectricity, ferromagnetism, ferroelastics, and optic/magnetoelastic response in a single phase double perovskite thin films. More exact to say, defect engineered double perovskite LnBCO system is an only magic oxide system with a single phase oxide compound, two types of ionic charge carriers, three different atomic structures, four fields co-tuned multifunctionality system! These findings open a new avenue for material genetic design and synthesis by tailoring the atomic defect structures to facilitate the strong correlated multifunctionalities for energy harvest system and novel device development. Details will be discussed in the talk.