Perovskites constitute one of the most widely studied and technologically important families of inorganic oxides. The flexibility of the structure in accommodating multiple substitutions of cations has enabled a myriad of functional responses both in film and bulk form. Their complex chemistries can lead to many frustrations in their local bonding and to ordering phenomena and defect formation that are often critical in mediating the property response. This talk will focus on families of alkali-based perovskite oxides where the multiple occupancy of the “A-site” position in the ABO3 structure induces the formation of unusual nanoscale “checkerboard” modulations. Studies of their local atomic structures using aberration corrected TEM indicate these modulations produce unusual periodic ferrielectric nanodomain structures. The factors responsible for the formation of these unique structures and their remarkable sensitivity to small changes in bulk stoichiometry will be discussed.