Ferroelectric Crossovers in $Pb_{0.7}La_{0.2}TiO_3$ Triggered by *A*-site Substitution

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Iso-valent cation *A*-site substitutions give rise to varying ferroelectric transitions in $Pb_{0.7}La_{0.2}TiO_3$, depending on both the type and amount of iso-valent cations on the *A*-site. A crossover from ferroelectric (FE) to relaxor ferroelectric (RFE) has been observed in $Pb_{0.7(1-x)}Ca_{0.7x}La_{0.2}TiO_3$, $Pb_{0.7(1-x)}Ba_{0.7x}La_{0.2}TiO_3$ and $Pb_{0.7(1-x)}Sr_{0.7x}La_{0.2}TiO_3$ with x=0.30, 0.40 and 0.60, respectively, as shown by both the compositional dependences of γ, ΔT, and ΔT_{relax} and the fitting to the Vogel-Fulcher relation. As compared to Ca^{2+} and Ba^{2+}, Sr^{2+} substitution is less effective in inducing ferroelectric transition due to the similar ionic size as that of Pb^{2+}, whereby only an enhancement in diffusive phase transition is observed in $Pb_{0.7(1-x)}Sr_{0.7x}La_{0.2}TiO_3$ with x<0.60. $Pb_{0.7(1-x)}Ba_{0.7x}La_{0.2}TiO_3$ exhibits ferroelectric to relaxor crossover at a lower level of Ba^{2+} substitution (x=0.40); however, Ba^{2+} substitution is less effective in reducing the transition temperature. This can be attributed to the local enhancement of Pb-O hybridization brought about by the stretching of O^{2-} to the direction of Pb^{2+} due to the existence of large Ba^{2+}. In contrast to $Pb_{0.7(1-x)}Ba_{0.7x}La_{0.2}TiO_3$ and $Pb_{0.7(1-x)}Sr_{0.7x}La_{0.2}TiO_3$, a subsequent crossover to quantum paraelectric-like behavior (QPB) is triggered in $Pb_{0.7(1-x)}Ca_{0.7x}La_{0.2}TiO_3$ with x=0.60 in addition to the ferroelectric to relaxor transition, in association with the suppression of ferroelectric order to the quantum regime, suggesting that a severe breakdown in long-range polar order, which together with the shrinkage of unit-cell volume, favor the paraelectric state. The manifestation of quantum mechanical fluctuations at T<171.6 K leads to the temperature independent ε' that deviates significantly from the classical Curie-Weiss relation.