The term hardsetting is used to describe tropical soil horizons, which are highly weathered and present high hardness degree when dry, becoming friable when humid. Some studies revealed that in these soils, the Kaolinite tends to present isomorphic substitutions, in which Fe atoms substitute Al in their octahedral sites, deforming its crystalline structures. Thus, the objective of this study was to analyze the Kaolinite isomorphic substitution degree in hardsetting through X-ray Diffraction and the Rietveld Method (XRD-RM) and compare it with its microdeformation average values and the crystallite average size. Five soils samples were collected in the Brazilian Coastal Tablelands region, dispersed and submitted to the physical fraction separation process. Clay fractions were powdered, dried and sieved in a 53 mm mesh sieve. The clay fraction analyses were carried out in a diffractometer XRD Rigaku, model Ultima IV, with CuKα radiation, step by step mode in the $5^\circ \leq 2\theta \leq 80^\circ$ ($0.02^\circ / 5$ s) and refined through the RM using GSAS+EXPGUI. Results revealed that Kaolinites with the highest microdeformation values were those that presented higher degree of isomorphic substitution. Based on these results, it is possible to state that soils with higher degrees of isomorphic substitutions probably corroborate to hardness degree, due to the charge excess between the Kaolinite layers.