The solid electrolyte is one of the most important components for a solid oxide fuel cell (SOFC). The various divalent or trivalent metal ion-doped bismuth-based materials exhibit good ionic conductivity. Therefore, these materials are used as electrolytes in the SOFC. In this paper, the samples of (Bi0.92-*x*Ho0.03Er0.05)2O3 + (ZnO)*x* solutions with a 0 ? *x* ? 0.2 molar ratio are synthesized by the solid state reaction method. The detailed structural and electrical characterizations are investigated by using x-ray diffraction (XRD), alternating current electrochemical impedance spectroscopy, and scanning electron microscopy (SEM). The XRD patterns of all samples are indexed on a monoclinic symmetry with a P21/c space group. In addition, the rietveld parameters are determined by using the FullProf software program. The impedance measurements of the samples are obtained at the 1 Hz to 20 MHz frequency range. The impedance value of the pellets increases with temperature. Based on the impedance results, it is found that the contribution of grain (bulk) is more than a grain boundary in terms of conductivity, which permits the attribution of a grain boundary. The ionic conductivity decreases with an increasing amount of Zn contribution. The value of highest electrical conductivity among all samples is calculated as 0.358 S cm-1 at 800°C for undoped (Bi0.92Ho0.03Er0.05)2O3.