Supplementary information: S1

A comparative variation of Raman active modes at two different temperature conditions are listed in the table S1. The values exhibit a significant shift for ν_2, ν_3, ν_5 and ν_6 modes towards lower wave-number (or lower frequency) region, whereas ν_1 and ν_4 modes are shift towards higher wave-number (or higher frequency) direction. Due to the heat treatment the iodine vacancy was created and the vacancies are occupied by oxygen that forms stronger bismuth-oxygen (Bi-O) bond, which alters the BiI_6 octahedra network, as a consequence the modes ν_1 and ν_4 are shifted. The presence of O^{2-} ion in the lattice makes a weaker the I-I interaction of the iodine molecule (I_2) surrounding the tri-iodide (I^{3-}) and on the longer poly-iodide [I-I….I_3…I-I]$_n$ chains, as result the frequency shift was observed for ν_2, ν_3, ν_5 and ν_6 modes. Broadening effect is more prominent for ν_5 and ν_6 modes that can be related to the compositional disorder in presence of O^{2-} ion in the lattice.

Table S1: Raman active modes (cm^{-1}) of BiI_3 material, measured at 30 ^{0}C and 60 ^{0}C.

Modes	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Raman shift (cm^{-1}) @ 30 ^{0}C	65.0	93.5	123.2	145.5	245.6	315.2
Raman shift (cm^{-1}) @ 60 ^{0}C	67.1	91.2	122.2	149.6	232.4	313.5

Figure: S1

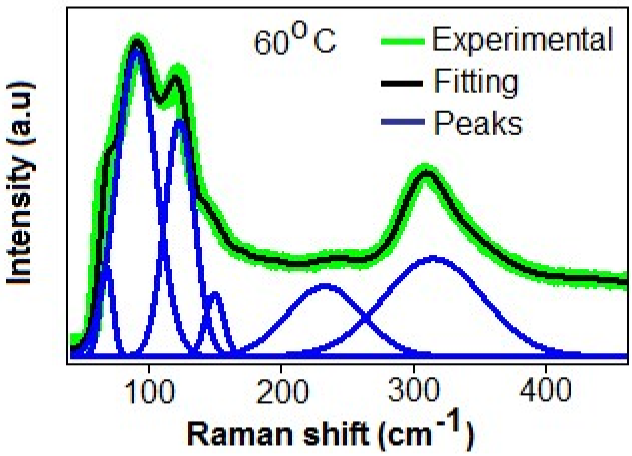

Figure S1: Deconvoluted Raman spectra @ 60 ^{0}C of bismuth iodide.

Supplementary information: S2

The variation of capacitance value with respect to the applied bias that can be expressed by the following relations [ref]:

$$C^{-2} = \frac{2\left(V_d + V\right)}{\left(q\varepsilon\varepsilon_0 A^2 N_d\right)} \tag{1}$$

$$\frac{d(C^{-2})}{dV} = \frac{2}{(q\varepsilon\varepsilon_0 A^2 N_d)} \tag{2}$$

Where V_d is the diffusion potential extracted from the intercept of C^{-2} vs. V plot on the V axis, q is the electronic charge, ε is the dielectric constant of the material, ε_0 is the dielectric constant of the vacuum, A is the contact area and N_d is the carrier concentration of the material.

Supplementary information: S3

The complex electric modulus (M^*) spectra were extracted from the complex dielectric constant (ε^*) by using the following relations:

$$M^* = {}^{1}/_{(\varepsilon^*)} = M' + jM'' \tag{4}$$

$$M' = \left({}^{\varepsilon'}/_{\varepsilon'^2 + \varepsilon''^2}\right),\quad M'' = \left({}^{\varepsilon''}/_{\varepsilon'^2 + \varepsilon''^2}\right) \tag{5}$$

Where, M′ and M″ are the real and imaginary part of electric modulus and ε′ and ε″ are the real and imaginary part of dielectric constant respectively.