

**Figure S1.** Scanning Electron Micrograph taken with backscattered electrons detector of a sample sintered at 1100 °C for 10 h.



Figure S2. pH evolution at room temperature of suspension of 500 mg of  $La_2LiNbO_6$  in 50 ml of water.



**Figure S3.** Dependence on 1/T of the conductivity of La<sub>2</sub>LiNbO<sub>6</sub> sensor.  $\alpha$  point at T = 45°C and RH% =62% delimits the T and RH% regions where the sensor is useful for practical applications (T ≥ 46°C, RH% > 62%).



**Figure S4**. Dependence on frequency of real component of conductivity ( $\sigma$ ') of sample (disk) with the lateral surfaces covered with a paraffin film. The test sample was prepared using a dry pellet of the sample inside a dry box. Tests were carried out at different RH%.



**Figure S5.** Electric response on time at 50 °C and 55 % RH of La<sub>2</sub>LiNbO<sub>6</sub> sample. (a) sensor freshly assembled and (b) after one year of operation. The inset shows the dependence of  $\sigma$ ' measured at 1kHz on time after one year.



**Figure S6.** Shape and size of La<sub>2</sub>LiNbO<sub>6</sub> pellet used to study the electric response on RH%.