Preliminary experimental characterization of the ambient humidity response of Bi$_3$TiNbO$_9$

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Abstract. A preliminary electrical characterization of Bi$_3$TiNbO$_9$ pellets, prepared by mechanochemical activation shows a nearly exponential conductivity increase over 4 orders of magnitude from dry ambient to dew point of 10 °C, at 23 °C ambient temperature; or 5 order of magnitude in thick films over interdigitated electrodes. Relaxation currents, following bias stress, respond also, at a lower sensitivity level. Under different DP on either electrode, the lower DP value controls the overall current, which flows through the bulk, not through the mantle of the cylindrical pellets. Repetitive cycling does not deteriorate the response to the ambient humidity.

1. Introduction
The Aurivillius phase of Bi$_3$TiNbO$_9$ (BTN), has received much attention, due to its high temperature ferroelectric and piezoelectric properties [1]. The synthesis of this material, 500 °C below the sintering temperature required by the traditional solid state reaction route was achieved by mechanochemical activation by A. Castro et. al. [2], using mechanochemical activation. In that work, after milling for up to 370 h in a low energy ball mill., a fluorite-like, metastable phase appeared, also, by heating at 370 °C. An early electrical study of that phase revealed its sharp sensitivity to ambient humidity [3].

In this work, the salient characteristics of BTN, prepared by high energy milling, are described, towards its application in resistive low humidity sensors.

2. Experimental
Powder samples of nominal composition 3Bi$_2$O$_3$ : Nb$_2$O$_5$ : 2TiO$_2$ were prepared from analytical grade powders by mechanochemical activation in a SPEX 8000 automatic mill, with tungsten carbide vial and hardened steel balls, for 24 h. The balls to powder mass ratio was set at 10:1.

Pellets were shaped by uniaxial pressing at pressure from 25 to 1830 MPa. Then sintered at 480 °C for 12 h, the sintered pellets were lightly sanded with 400X sand paper, dusted off by Ar gun, and coated with 10 nm thick Pt electrodes by magnetron sputtering (base pressure of 10$^{-5}$ mbar).

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pressure of $10^{-5}$ mbar). Simple centered circle electrodes, as well as circle plus guard rings, were used to probe the current path through the pellets.

A simple controlled humidity chamber was used for testing the response of pellets with simple electrodes. Pellets with guard ring were used to probe for the current path: either through the bulk or the mantle of the cylindrical pellets. A dual-chamber with independent flux and humidity regulations over either face of the pellet was development to test for possible current asymmetries related to dry or humid ambients on the cathode or anode.

BTN thick films were prepared with AREMCO ceramabind 643 as a binder on interdigitated Pt electrodes on alumina. The thick films were dried at 200°C during 2 h and then sintered at 480°C for 12 h.

Current-voltage and pulsed voltage current-time measurements was made using a Keithley 237 electrometer, at room temperature (23 °C). For measurements at variable ambient humidity, the latter was controlled by passing the moisture saturated carrier gas through a condenser block at the desired dew point (DP) temperature (down to dew point of 1°C). Lower dew point values, were prepared by mixing dry and low humidity gas flows. The resulting humidity was monitored by a chilled mirror hygrometer after passage through the pellet testing chambers.

3. Results and Discussion

The conductance of BTN pellets in vacuum is thermally activated and, at 107 °C, it reaches the value of $3.1 \times 10^{-4}$ ohm$^{-1}$ m$^{-1}$ after a 51 h settling time.

Conductivity measurements at fixed bias and variable DP, result in an exponential increase (from nearly $10^{-3}$ to $10^{2}$ pS/cm) ($\approx 4.1 \exp(0.1749 \text{ (DP}/°C)$) over the DP range of -40 to +10 °C, at ambient temperature of 23 °C. This, nearly maximum, sensibility is achieved at the cost of a slow response (1 to 3 min), in the less dense pellets. Other samples, pressed at 1830 MPa display ~2 orders of magnitude response over this DP range, with response transient below 30 s.

Upon removal of the bias, the relaxation current follows DP cycling in a similar manner, albeit at a lower sensitivity level, as the current during application of the bias.

The response to humidity may be caused by some reaction, such as the surface dissociation of water. Henceforth, the current may be controlled by the polarity of the electrode which is exposed to the wet gas flux. This has been tested in a dual chamber, with results as shown in Fig. 1. Most notably, the current is seen to drop (more than one order of magnitude, in this particular case), whenever either electrode is exposed to dry ambient. Indeed, the current due to just one dry electrode is essentially the same as that with both electrodes in dry ambient. The current level is seen to overshoot upon returning to humidity, above the value it had just before the previous drop due to going into a dry ambient. This is pointed out by the “$I_{m}$” and arrow in Fig. 1, an it is a feature which appears also during relaxation, after bias stress.

The current path, through either the inner porous bulk or the mantle of the pellet, was tested using guarded electrodes, as shown in Fig. 2. There, the inset shows the electrodes configuration, where “V” stands for the (100 V) bias source, “A” stands for the electrometer, and “G” stands for the guard line, which is kept at the same bias as the electrometer line. This configuration applies to the stages “1” and “4”. In stage “3”, the positions of the “A” and “G” lines are
exchanged. In stage “2”, the electrometer line goes to the guard ring, and the guard line is disconnected.

The current levels during the opposite stages “1” and “3” indicate that the current flows through the bulk of the (porous) pellet, the side of the pellet, exposed to the humid ambient, being of no particular import.

Preliminary measurements of a (~ 80 µm) thick film on the interdigitated Au electrodes display a larger and faster response than in the case of the pellets. As shown in Fig. 3, the current goes through excursions in excess of 5 orders of magnitude upon cycling from dry to DP of 10 °C ambients.

The response of BTN to ambient humidity, so far observed, presents the promise of this material for sensors in the low humidity range.

As regards the response mechanism, the numerical solution of a carrier diffusion model has been proposed [4], mostly to model the current overshoot which is pointed out in Fig. 1. The model assumes the diffusion of a charge carrier in the self-consistent electric field, considering an external bias and the space charge field of the carrier density. Limited qualitative agreement is achieved with the general features of the relaxation current, its overshoot behavior, in particular, and with results of the asymmetric dual-chamber tests.

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