Supporting Information

Understanding the electronic properties of BaTiO$_3$ and Er doped BaTiO$_3$ through confocal scanning microscopy and XPS: Role of oxygen vacancy

P1. Histogram of grain size from AFM

![Histogram of grain size from AFM](image)

Fig. R1 Grain size distribution histogram obtained from the AFM of the (a) BT and (b) BTE thin films.

P2. Nature of one-photon excitation (1PE) and two-photons excitation (2PE)

The SCFM provides an explicit definition of the fluorescence from the electronically excited states of the thin films. An important requirement that contributes in the contrast of the fluorescence image is to obtain a significant signal-to-noise ratio (SNR).$^1$ Although the scanning speed is important, another factor that optimizes the excitation efficiency (associated with a greater amount of fluorescence photons) is the used laser line.$^{1,2}$
The presence and the absence of the rare earth (Erbium) ions, in perovskite structures suggest the use of one-photon excitation (1PE) and two-photons excitation (2PE) in order to improve the excitation efficiency. The **1PE SCFM** implies the use of mainly the visible excitation energies (3.18 to 1.77 eV), where the one-photon fluorescence involves the excitation from the electronic ground state to an excited state by a single photon, and the energy released by the single photon is slightly less than the excitation photon, as shown in the schematic representation in Fig. R2(a). In **2PE SCFM**, the excitation energies remain between 1.55 to 1.24 eV, where two photon fluorescence process involves the excitation from the electronic ground state to an excited state due to the simultaneous excitation/absorption by the two-photons, where the energy released by a single photon is slightly larger than the excitation photon, as shown in the schematic representation in Fig. R2(b).

**P3. Statistical information of the emission from SCFM**

To obtain greater statistical details about how the calculated values deviate from the deconvolution of the emission spectra for each region (expressed here in terms of the emission wavelengths) for the respective BT and BTE thin films, box plots are represented in the Fig. R3. Fig. R3 compares the distribution of the emission (from the deconvolution of the emission spectra) at 2.11, 2.27, 2.40, 2.47 and 2.08, 2.22, 2.31, 2.41, 2.43, 2.59 eV, for the thin BT and BTE film, respectively, where the mean of 1PE and 2PE was obtained for both the thin films.
For thin BT film in the Fig. R3(a-c), the statistical data showed clearly that a tendency towards stability exist at 2.27 and 2.40 eV while a greater variability in the position of the emission band also exist around 2.11 and 2.47 eV for 1PE and 2PE. This variability is associated with the increase of the dispersion, particularly at 2.40 eV, which indicates that the changes in the color are not only linked to the emission intensity, but also to the shift of the emission bands. The variability behavior observed for the BT film might be attributed to the dynamic self-trapping processes as is mentioned before. The intensity variations (from the deconvolution) of the peaks which correspond to the yellow and blue color in thin BT film showed an order, which is following: $I_{P1}^{P1} < I_{P1}^{P1} < I_{P1}^{P1}$ and $I_{P4}^{P4} < I_{P4}^{P4}$~$I_{P4}^{P4}$. In case of 2PE the results can suggest that, for the intensity P1 (yellow) and P4 (blue), the functionalization of the BT surface has a characteristic of hole-extraction better than the 1PE. Such intensity can be regarded as an indirect marker for the excitons produced in this film.

For the BTE film, six peaks are observed with 1PE while three peaks are observed with 2PE, shown in the Fig. R3(d-f). Clearly the thin BTE film showed a greater variability of P1* obtained with 1PE than with 2PE, which indicate the possible effect of the excitation on the emission of the rare earth ions. Contrary to that observed in the BT film, the BTE film does not show significant variability in the emission of 1PE and 2PE. However, the yellow emission band dispersion observed with 2PE, is significantly lower when compared to 1PE. The statistical data observed clearly shows that the peak at 2.11eV (excited energy 1.55 eV), that correspond to the yellow color, showed a strong drop in its average intensity. This significant decrease is attributed to the high cooperative effect between the Erbium ions which is associated to the non-radioactive process of the P1* level, when compared to the excitation energies at 3.06, 1.57 and 1.27 eV. The intensity variations (from the deconvolution) of the peaks that correspond to the yellow and green colors in thin BTE film showed an order, which is following: $I_{P1}^{P1} < I_{P1}^{P1} < I_{P1}^{P1} < I_{P1}^{P1}$, and $I_{P4}^{P4} < I_{P4}^{P4} < I_{P4}^{P4}$~$I_{P4}^{P4}$. 

Fig. R3 Statistical box plot of the average intensity values as a function of the deconvolution of the emission spectra of thin films BT (a-c) and BTE (d-g). The box plot denotes median (centre line), mean value (dots), 25th (bottom edge of the box), 75th (top edge of the box), 95th (upper whisker) and 5th (lower whisker) percentiles. The sample size in each column is 10 devices. The red star denotes the efficiency of the champion cell.

1. References
