



Fig. S. (a) X-ray diffraction curves of LNO samples with different concentration of Tm<sup>3+</sup>; (b) The magnified XRD diffraction peaks inside figure; XPS scans of (c) Li 1s and (d) Nb 3d core-levels measured from LNO samples with different concentration of Tm<sup>3+</sup>.

We've carried out another series of experiments, in which the Tm<sub>2</sub>O<sub>3</sub> were doped with different concentration. The samples were heat treated at 690°C for 3h as well. And the XRD patterns of these samples are shown in the Supplementary figure (a) and (b). According to the figures, it's obvious that the XRD diffraction peaks move to the smaller angle gradually with the increasing concentration of Tm<sup>3+</sup>, which represents for the incorporation of the dopants into the LiNbO<sub>3</sub> lattice.

And to verify the embedding mode of Tm<sup>3+</sup> ion inside LiNbO<sub>3</sub> lattice, structural XPS analysis is also provided. It is seen that the core-level peaks of Li 1s and Nb 3d in the LNO-Tm samples present a uniform shift toward the lower binding energies compared with the LNO sample, representing the variation of chemical microenvironment around these two type of ions after the doping of Tm. These results

indicate that such differences in terms of binding energy are stemmed from a Fermi level shift. And combining with the XRD results, it can be verified that the embedding mode of Tm is the substitution for both Nb and Li sites.