Supporting Informations for

High temperature Aurivillius piezoelectrics: the effect of (Li, Ln) modification on structure and properties of (Li, Ln)$_{0.06}$(Na, Bi)$_{0.44}$Bi$_2$Nb$_2$O$_9$ (Ln = Ce, Nd, La and Y)

Changbai Long, Huiqing Fan * and Mengmeng Li

State Key Laboratory of Solidification Processing, School of Materials Science and Engineering,

Northwestern Polytechnical University, Xi'an 710072, PR China

Corresponding Author

*** E-mail:** *hqfan3@163.com* **and** *longchangbai@126.com*. **Tel.:** *+86 29 88494463*; **fax:** *+86 29 88492642*.

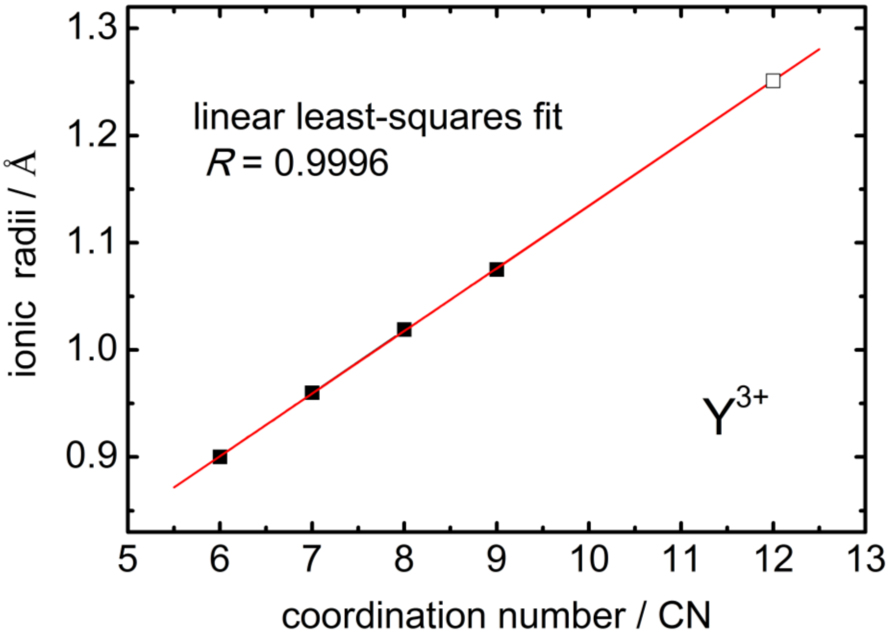

Fig. S1. A good linear fitting for different coordination number (CN) Y^{3+} radius (the solid symbols: the reported data, the hollow symbol: fitting data, the line: fitting line).

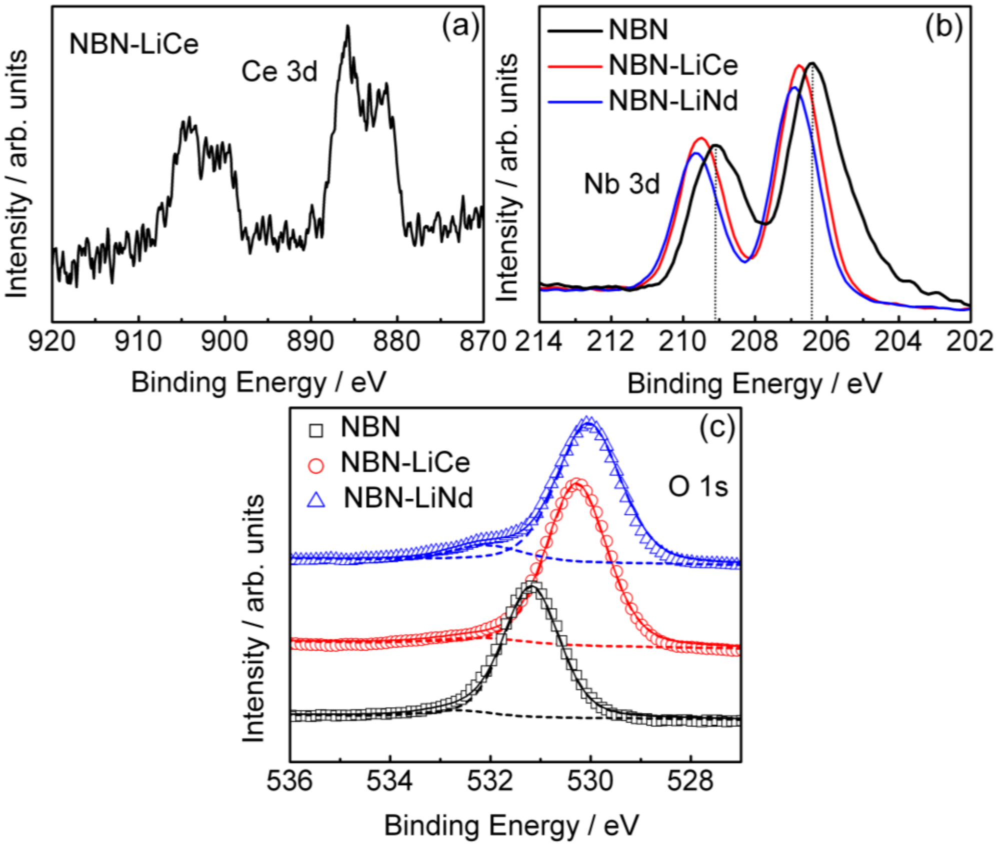

Fig. S2 XPS of the NBN, NBN-LiCe and NBN-LiNd ceramics after 1 min sputtered. (a) Ce 3d spectrum of the NBN-LiCe. (b) Nb 3d spectra of the the NBN, NBN-LiCe and NBN-LiNd. (c) O 1s spectra of the NBN, NBN-LiCe and NBN-LiNd, with two fitting peaks by Gauss-Lorentz method. (the symbols are experimental data, the solid lines are fitting spectra, and the dotted lines are fitting peaks).

In Fig. S2(a), the 5/2 and 3/2 spin-orbit double doublet components of the Ce 3d spectrum locate at 881.3 eV and 899.6 eV (lower peak of each doublet), respectively, which are equivalent to those of Ce_2O_3. (**Ref. 1 and 2**) It further confirms that Ce with (+3) valent state occupies the A site. In Fig. S2(b), the doublet peaks of the Nb 3d spectrum of NBN-LiNd locate at higher binding energies than those of the NBN and NBN-LiCe. It suggests that the valent state of Nb ion in NBN-LiNd should be more higher than those in the NBN and NBN-LiCe, and there are the fewer oxygen vacancies around NbO_6 octahedra in NBN-LiNd. In Fig. S2(c), the first fitting peak at low binding energy side corresponds to the Nb-O bond and the second is ascribed to the oxygen attached to bismuth. (**Ref. 3**) It is observed that the two peaks of NBN-LiNd and NBN-LiCe both shift into lower energies, as compared to those of NBN. This suggests that the oxygen ions in NBN-LiNd and NBN-LiCe from the stronger Nb-O bond and the weaker Bi-O bond both carry higher effective negative charge than those in NBN. Among them, the NBN-LiNd could have the fewer oxygen deficiencies in the lattice positions due to the higher electronegativity of its oxygen ions.

Reference:

1 X. M. Wang, X. Q. Zeng, G. S. Wu, S. S. Yao, Y. J. Lai. *J. Alloys Comp*., 2008, **456**, 384-389.

2 F. Zhang, P. Wang, J. Koberstein, S. Khalid, S. Chan. *Surface Science*, 2004, **563**, 74-82.

3 C. Jovalekic, M. Pavlovic, P. Osmokrovic and Lj. Atanasoska, *Appl. Phys. Lett*., 1998, **72** (9), 1051-1053.

Table S1 Lattice parameters, cell volume and density for the NBN and NBN-LiLn ceramics. The lattice parameters and cell volume of NBN and NBN-LiNd were derived from the Rietveld refinement results. For evolution of lattice parameters of other samples, powder XRD data of them were collected in the 2θ range 10–130° with a step size of 0.02°, the entire run lasting about 2 h. The theoretical density was determined by using the obtained lattice parameters, and the experimental density was measured by the Archimedes method.

composition	a (Å)	b (Å)	c (Å)	V (Å^3)	experimental density (g/cm^3)	theoretical density (g/cm^3)	Relative density (%)
NBN	5.48888(9)	5.46110(9)	24.9512(4)	747.922(20)	7.147	7.671	93.2
NBN-LiCe	5.48162(5)	5.46157(5)	24.91470(23)	745.903(13)	7.176	7.646	93.9
NBN-LiNd	5.48666(9)	5.46046(8)	24.9122(4)	746.363(19)	7.511	7.642	98.3
NBN-LiLa	5.48725(6)	5.46187(6)	24.91537(23)	746.730(13)	7.377	7.637	96.6
NBN-LiY	5.48546(8)	5.45798(8)	24.91551(31)	745.959(18)	7.215	7.619	94.7