Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information for

A candidate for lead-free ultrahigh-temperature piezoelectrics: excellent electro-mechanical properties of Aurivillius oxides, $Ca_{1-5x}Li_{2x}Nd_{2x}\square_xBi_2Nb_{2-2x}Sc_xW_xO_{9-1.5x}$

Changbai Long ∗, Huiqing Fan ∗, Mengmeng Li, Pengrong Ren and Yu Cai

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.

Table S1 Lattice parameters (*a*, *b* and *c*) and cell volume (*V*) of the CBNO-LiNd-ScW-*x* ceramics. The lattice parameters and cell volume of the CBNO-LiNd-ScW-0.01 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.

CBNO-LiNd-ScW-*x*	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
x = 0	5.47866(15)	5.43716(15)	24.8781(5)	741.077(33)
x = 0.01	5.47656(10)	5.43861(10)	24.86232(28)	740.521(21)
x = 0.02	5.47464(11)	5.43988(12)	24.85525(30)	740.224(23)
x = 0.03	5.47238(9)	5.44188(9)	24.85162(25)	740.083(19)
x = 0.04	5.47224(13)	5.44255(14)	24.84546(34)	739.971(27)

Table S2 Selected bond lengths (Å) and bond angles (°) for the CBNO-LiNd-ScW-0.01

Bond lengths (Å) or angles (°)			
Ca1/Bi1/Li1/Nd1-O		Nb/Sc/W-O	
A1-O1	3.025(32)×1	Nb-O1	2.130(5) ×1
	2.482(32) ×1	Nb-O2	1.844(10) ×1
	2.384(33) ×1	Nb-O4	2.139(25) ×1
	3.106(33) ×1	Nb-O4	1.853(25) ×1
A1-O4	2.594(22) ×2	Nb-O5	2.163(19) ×1
	2.538(21) ×2	Nb-O5	1.742(20) ×1
A1-O5	3.224(17) ×2		
	2.528(14) ×2		
Bi2/Ca2/Nd2-O		B-O1-B,	155.9(12)
Bi2/A2-O2	2.505(14) ×1	B = Nb/Sc/W	
	3.392(15) ×1		
	2.694(18) ×1		
	3.227(19) ×1		
Bi2/A2-O3	2.33(4) ×1		
	2.20(4) ×1		
	2.25(5) ×1		
	2.43(5) ×1		

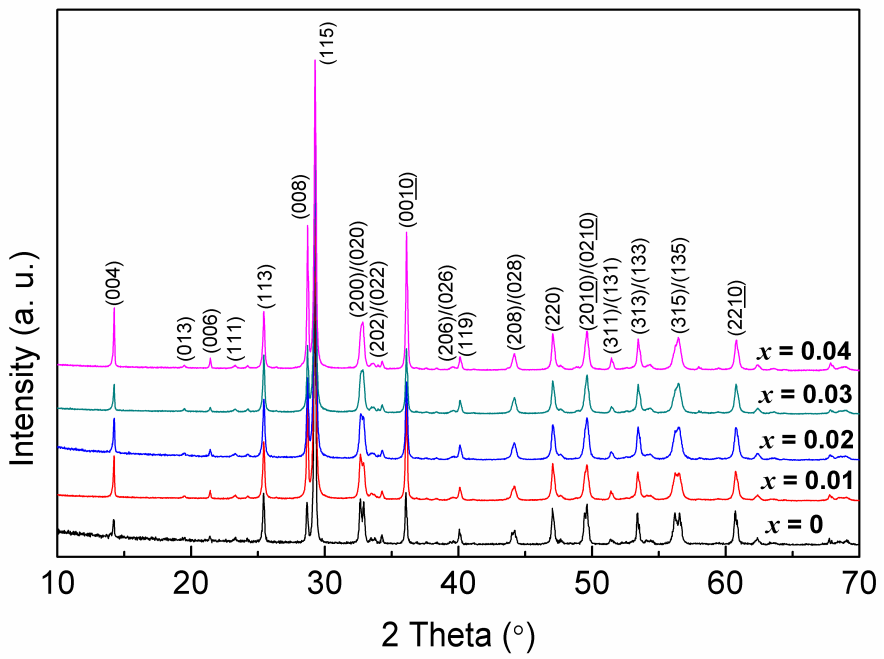

Fig. S1 Powder XRD patterns of the CBNO-LiNd-ScW-*x* (*x* = 0, 0.01, 0.02, 0.03, 0.04) ceramics.

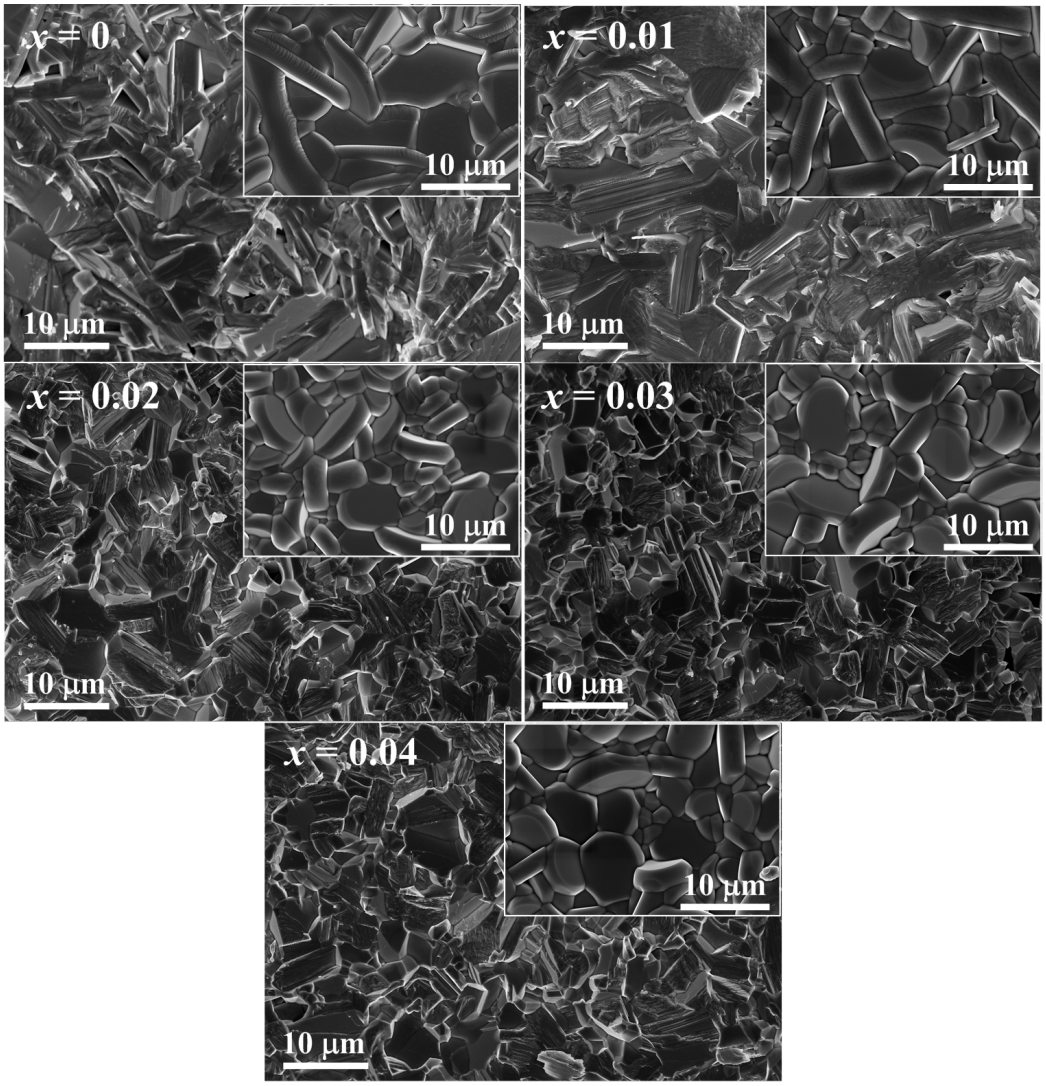

Fig. S2 Cross-section SEM images of the prepared CBNO-LiNd-ScW-*x* (*x* = 0, 0.01, 0.02, 0.03, 0.04) ceramics, with corresponding surface morphologies as insets.

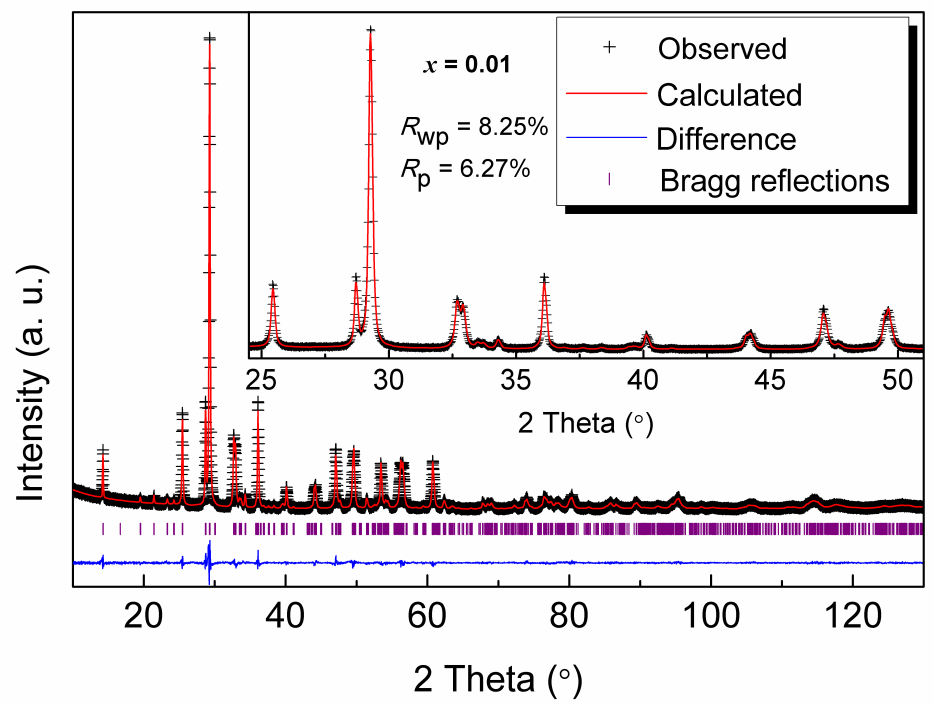

Fig. S3 Rietveld refinement for the CBNO-LiNd-ScW-0.01 at room temperature, with an inset showing a regionally enlarged drawing.

XRD Rietveld refinement for the CBNO-LiNd-ScW-0.01 was carried out with $A2_1am$ space group at room temperature, by using the GSAS-EXPGUI program (**Ref. 1** and **2**). The XRD data were collected in 2θ range of 10-130° with a step size of 0.02° and a step time of 10 s. The coordinates of $CaBi_2Nb_2O_9$ reported by Blake, *et al*. (**Ref. 36 in text)** were used as an initial model, where Li (2%) and Nd (2%) occupied the Ca (4a) site, and Sc (1%) and W (1%) occupied the Nb (8b) site, as well as the existence of a small amount of Ca vacancies (1%). Also, the *x* coordinate of the cation site (8b) in the $(Bi_2O_2)^{2+}$ layers was fixed in the refinement process, in order to define the origin of the polar axis. The A-site Li/Nd substitution could be considered be an isovalent modification, while the replacement of B-site Nb by Sc/W was an acceptor substitution. Another, the existence of the A-site vacancies was an acceptor modification. Therefore, there should be some oxygen vacancies produced due to charge neutrality restriction. Explanatorily, the initial refinement with the release of the occupancies of the oxygen atoms could not achieve convergence, and the occupancy for some site was far from 1, even higher than 1. Thus, we simply considered that the oxygen loss at each site was equivalent, and their occupancies were 0.998333 with the aim of balance the chemical charge in CBNO-LiNd-ScW-0.01. In addition, the occupancy of light Li atom at A site was not refined and fixed to be 2% according to the idealised addition during synthesis.

Reference:

1 A. C. Larson, R. B. Von Dreele, *General Structure Analysis System (GSAS)*; LANL Report LAUR 86-748Los Alamos National Laboratory: Los Alamos, NM, 2000.

2 B. H. Toby, *J. Appl. Crystallogr.*, 2001, **34**, 210-213.

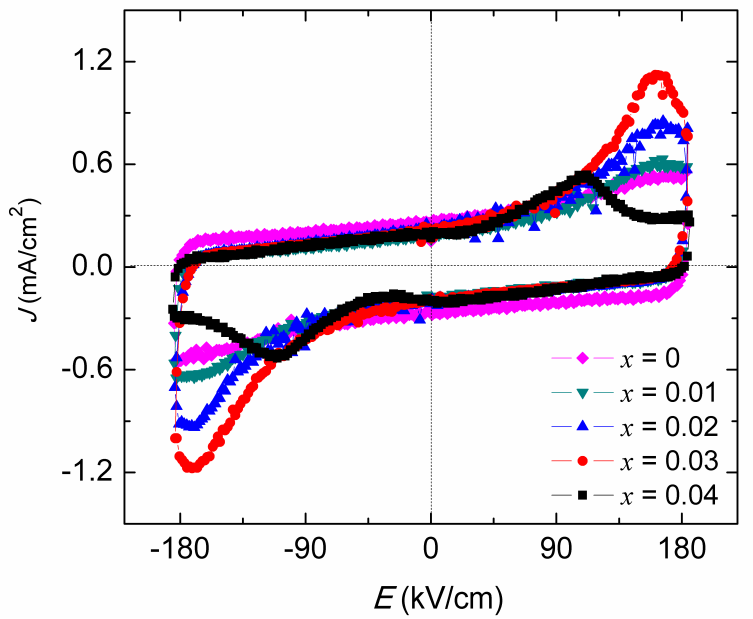

Fig. S4 Current density hysteresis (*J*-*E*) loops of the CBNO-LiNd-ScW-*x* (*x* = 0, 0.01, 0.02, 0.03, 0.04) ceramics.

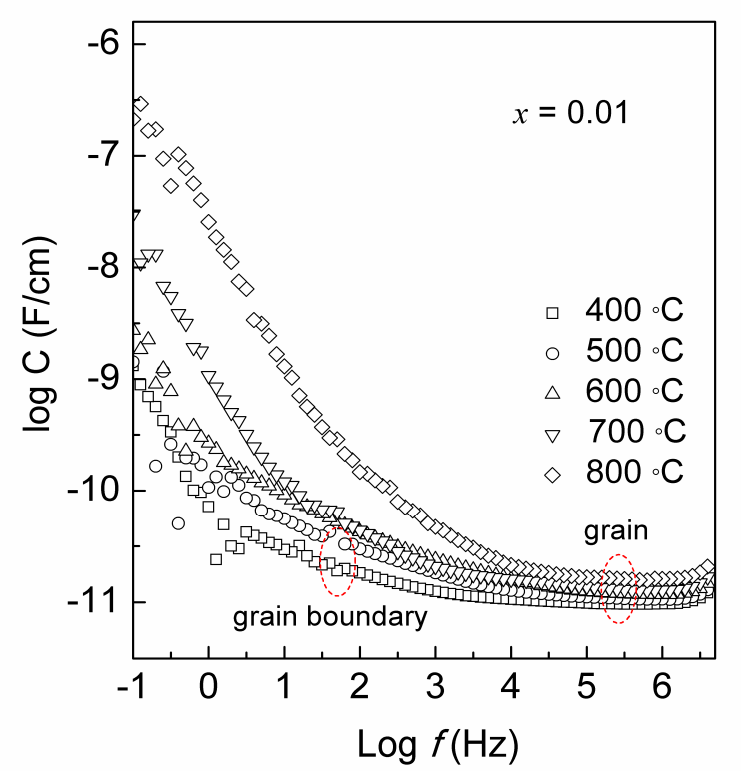

Fig. S5 Capacitance spectroscopic plots of the CBNO-LiNd-ScW-0.01 sample with Pt electrode over 400-800 °C.

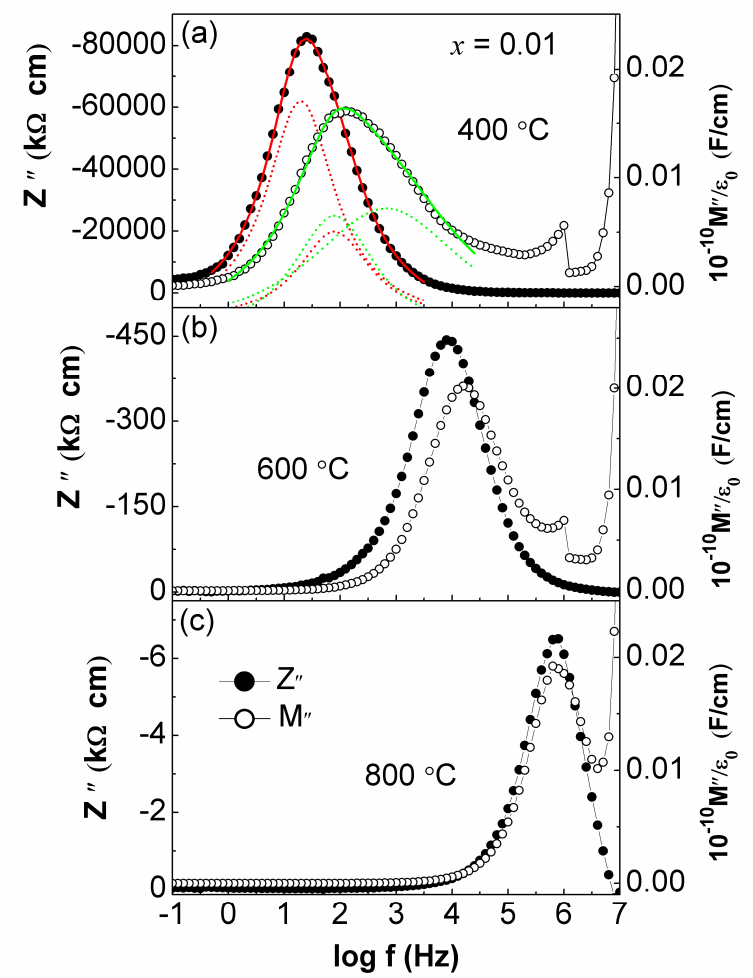

Fig. S6 (a) 400 °C, (b) 600 °C and (c) 800 °C impedance and complex modulus spectroscopic plots of the CBNO-LiNd-ScW-0.01 sample. The symbols were experimental data, the solid lines were fitting spectra, and the dotted lines were fitting peaks (the lower-frequency peak was ascribed to the effect of grain boundary while the higher-frequency peak was in response to the grain).