Supplemental Materials

Dielectric, Pyroelectric, and Ferroelectric Studies in (1-x)$AgNbO_3$-x$FeNbO_4$ Lead-free Ceramics

Parastoo Moradi[a], Ehsan Taheri-Nassaj[a,] *, Amin Yourdkhani[a], Vasyl Mykhailovych[b,c,d], Andrei Diaconu[b], Aurelian Rotaru[b]

[a] Department of Materials Engineering, Tarbiat Modares University, Tehran, 14115-143, Iran

[b] Faculty of Electrical Engineering and Computer Science & MANSiD Research Center, Stefan cel Mare University, 13 Universitatii St., 720229, Suceava, Romania

[c] Department of General Chemistry and Chemistry of Materials, Yuriy Fedkovych Chernivtsi National University, 2, Kotsiubynskyi St., 58002 Chernivtsi, Ukraine

[d] Physical, Technical and Computer Science Institute, Yuriy Fedkovych Chernivtsi National University, 2, Kotsiubynskyi St., 58002, Chernivtsi, Ukraine

Table S1. Refinement parameters for AN ceramic at 25 °C

Sample		AN
Chemical formula		$AgNbO_3$
Formula weight (g/mol)		248.773
Crystal system		Orthorhombic
Space group		$Pmc2_1$
Unit cell dimensions (Å)		a= 15.66065(38) b= 5.55063(14) c= 5.60524(14)
Volume (Å^3)		487.244(19)
Density (calculated) (g/cm^3)		6.920
$AgNbO_3$ (Wt. Frac)		0.99805(1)
$FeNbO_4$ (Wt. Frac)		0
Ag (Wt. Frac)		0.00195(9)
Chi^2		2.110
Fitted R- factors	R_{wp} (%)	16.03
	R_p (%)	11.57

Table S2. Refinement parameters for ANF005 ceramic at 25 °C

Sample		ANF005
Chemical formula		$AgNbO_3$
Formula weight (g/mol)		248.773
Crystal system		Orthorhombic
Space group		$Pmc2_1$
Unit cell dimensions (Å)		a= 15.64172(68) b= 5.54700(25) c= 5.60189(26)
Volume (Å^3) AN		486.046(37)
Density (calculated) (g/cm^3) AN		6.755
Density (calculated) (g/cm^3) FN		5.622
$AgNbO_3$ (Wt. Frac)		0.92239(39)
$FeNbO_4$ (Wt. Frac)		0.07446(226)
Ag (Wt. Frac)		0.00315(17)
Chi^2		4.196
Fitted R- factors	R_{wp} (%)	23.75
	R_p (%)	17.28

Table S3. Refinement parameters for ANF01 ceramic at 25 °C

Sample		ANF01
Chemical formula		$AgNbO_3$
Formula weight (g/mol)		248.773
Crystal system		Orthorhombic
Space group		$Pmc2_1$
Unit cell dimensions (Å)		a= 15.64202(59) b= 5.54572(22) c= 5.60104(24)
Volume (Å^3) AN		485.869(33)
Density (calculated) (g/cm^3) AN		6.973
Density (calculated) (g/cm^3) FN		5.497
$AgNbO_3$ (Wt. Frac)		0.93596(28)
$FeNbO_4$ (Wt. Frac)		0.06158(202)
Ag (Wt. Frac)		0.00246(16)
Chi^2		3.689
Fitted R- factors	R_{wp} (%)	22.18
	R_p (%)	15.52

Table S4. Refinement parameters for ANF025 ceramic at 25 °C

Sample		ANF025
Chemical formula		$AgNbO_3$
Formula weight (g/mol)		248.773
Crystal system		Orthorhombic
Space group		$Pmc2_1$
Unit cell dimensions (Å)		a= 15.64173(59) b= 5.54641(22) c= 5.60207(24)
Volume (Å^3) AN		486.010(33)
Density (calculated) (g/cm^3) AN		6.844
Density (calculated) (g/cm^3) FN		5.449
$AgNbO_3$ (Wt. Frac)		0.92628(30)
$FeNbO_4$ (Wt. Frac)		0.06956(176)
Ag (Wt. Frac)		0.00417(16)
Chi^2		3.475
Fitted R- factors	R_{wp} (%)	20.15
	R_p (%)	13.54

Table S5. Refinement parameters for ANF05 ceramic at 25 °C

Sample		ANF05
Chemical formula		$AgNbO_3$
Formula weight (g/mol)		248.773
Crystal system		Orthorhombic
Space group		$Pmc2_1$
Unit cell dimensions (Å)		a= 15.64416(64) b= 5.54718(23) c= 5.60014(25)
Volume (Å^3) AN		485.986(36)
Density (calculated) (g/cm^3) AN		6.848
Density (calculated) (g/cm^3) FN		5.470
$AgNbO_3$ (Wt. Frac)		0.89411(46)
$FeNbO_4$ (Wt. Frac)		0.09788(223)
Ag (Wt. Frac)		0.00800(24)
Chi^2		3.939
Fitted R- factors	R_{wp} (%)	21.71
	R_p (%)	14.03

Table S6. Refinement parameters for ANF1 ceramic at 25 °C

Sample		ANF1
Chemical formula		$AgNbO_3$
Formula weight (g/mol)		248.773
Crystal system		Orthorhombic
Space group		$Pmc2_1$
Unit cell dimensions (Å)		a= 15.62553(71) b= 5.54072(25) c= 5.59481(26)
Volume (Å^3) AN		484.380(38)
Density (calculated) (g/cm^3) AN		6.844
Density (calculated) (g/cm^3) FN		5.459
$AgNbO_3$ (Wt. Frac)		0.83871(71)
$FeNbO_4$ (Wt. Frac)		0.14298(244)
Ag (Wt. Frac)		0.01830(32)
Chi^2		4.274
Fitted R- factors	R_{wp} (%)	22.63
	R_p (%)	15.62

Table S7. The relative density with standard error of ANF(x) ceramics

x (%)	**$D_{relative}$ (%)**
0	97.96 ± 0.01
0.5	97.37 ± 0.02
1	97.16 ± 0.03
2.5	96.36 ± 0.02
5	96.86 ± 0.03
10	96.75 ± 0.03

Table S8. The temperature of the phase transitions of ANF(x) ceramics is based on the real parts of the dielectric permittivity-temperature spectrum during heating at 10 kHz

x (%)	T_{M1-M2} (°C)	T_{M2-M3} (°C)	T_{M3-O} (°C)	T_f (°C)
0	71.807	262.74	324.5	184.6
0.5	100.45	307.11	350.85	192.98
1	102.84	306.13	349.14	193.63
2.5	78.178	287.15	325.92	191.02
5	107	326.81	342.79	197.52
10	101.58	-	351.62	193.29

The value of ε_0, e, and A for use in the Mott–Schottky equation is 8.8541×10^{-12} F.m^{-1}, 1.602×10^{-19} C and A = 3.142 10^{-6} m^2, respectively. The value of permittivity and N_D is listed in Table S9.

Table S9. The value of the slope from the line fit in the Mott–Schottky plot, the permittivity and the calculated N_D.

x (%)	Slope ($F^{-2}V^{-1}$)	ε	N_D ($\times 10^{20}$ m^{-3})
0	2.75×10^{18}	256.803	2.02
0.5	1.31×10^{18}	389.198	2.80
1	6.64×10^{17}	399.094	5.39
2.5	5.91×10^{17}	399.248	6.06
5	4.82×10^{15}	526.01	563.48

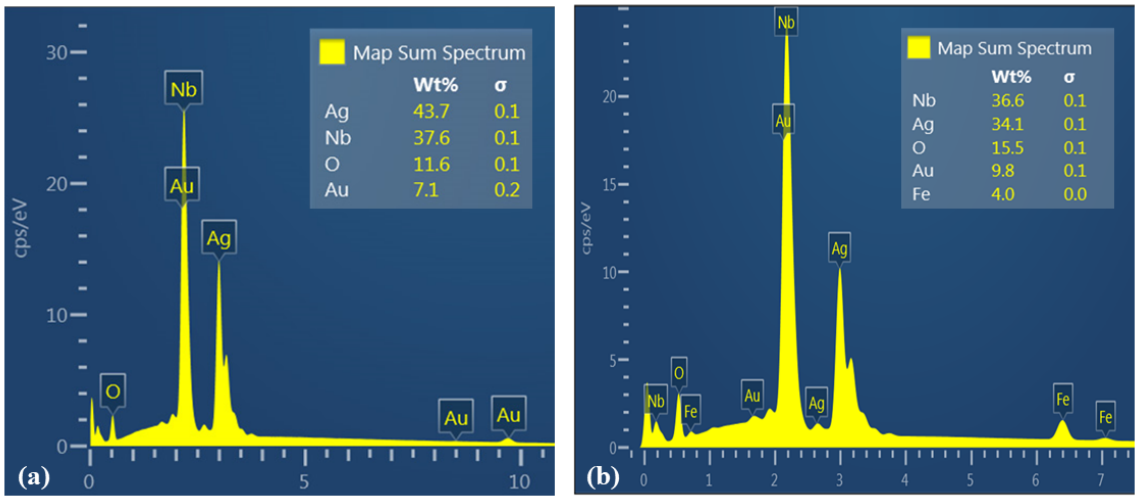

Fig. S1. The EDS spectral analysis of (a) AN and (b) ANF1 ceramics.

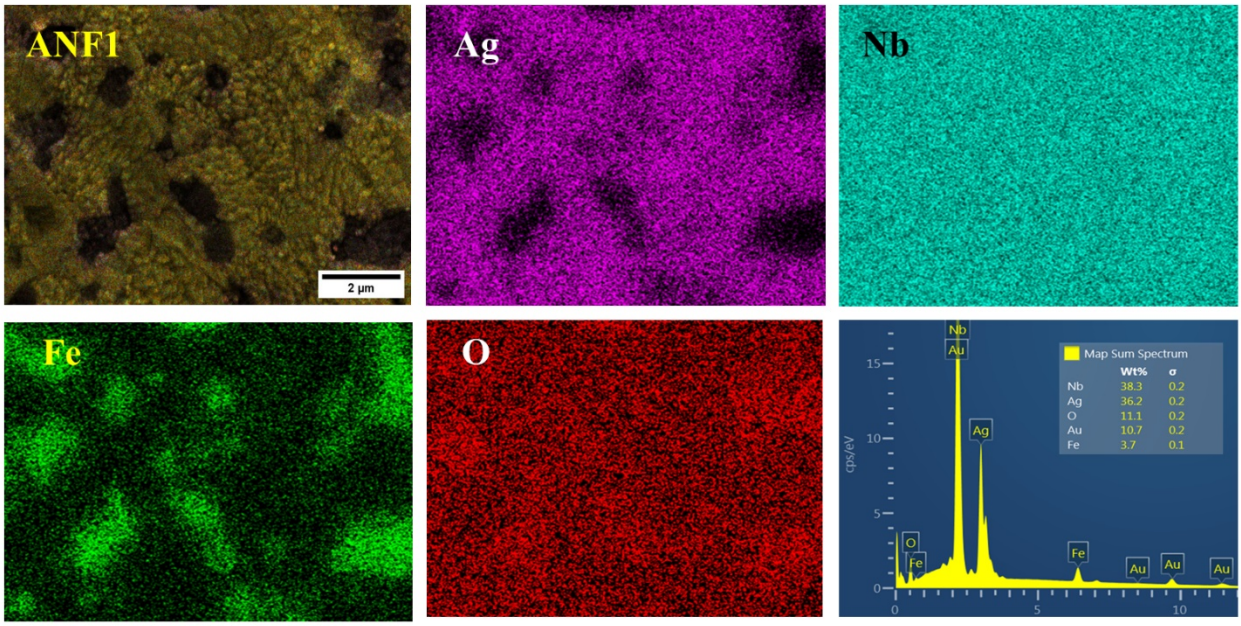

Fig. S2. The EDS maps and spectral analysis of the cross-sectional of ANF1 ceramic.

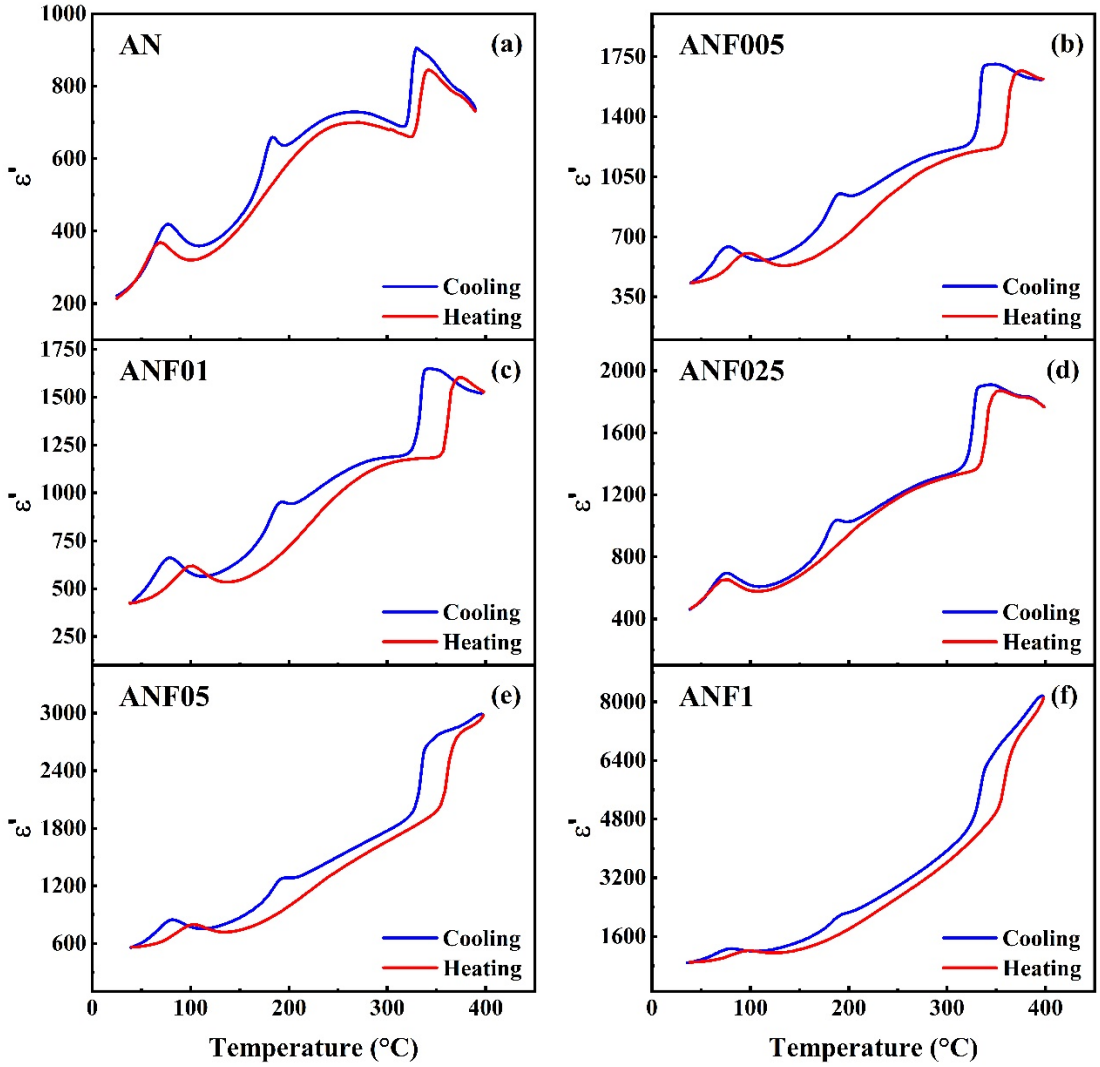

Fig. S3. Temperature dependence of the real (ε′) part of the dielectric permittivity of ANF(x) ceramics at 10 kHz in a heating and cooling cycle.

Fig. S4 shows the Olsen cycle scheme by the black arrows for calculating the energy harvesting of the (1-x)$AgNbO_3$-x$FeNbO_4$ ceramics. As shown, there are four processes in the Olsen cycle: (1) the isothermal process 1 → 2 from a low electric field (E_L) to a high electric field (E_H) at low temperature (T_L), (2) the process 2 → 3 heating the sample from T_L to a high temperature (T_H) at E_H, (3) the isothermal process 3 → 4 involves decreasing from E_H to E_L at T_H, and (4) the process 4 → 1 involves cooling the sample from T_H to T_L at E_L and completes acycle. The area of the closed cycle 1 → 2 → 3 → 4 corresponds to the harvested pyroelectric energy density (W) obtained and can be calculated as follows[1-4]:

$$W = \oint EdP \qquad \text{Eq. 5}$$

The W of (1-x)$AgNbO_3$-x$FeNbO_4$ ceramics was measured between T_L (30 °C) and T_H (100 °C), and electrical fields of 15-20 kV/cm^2.

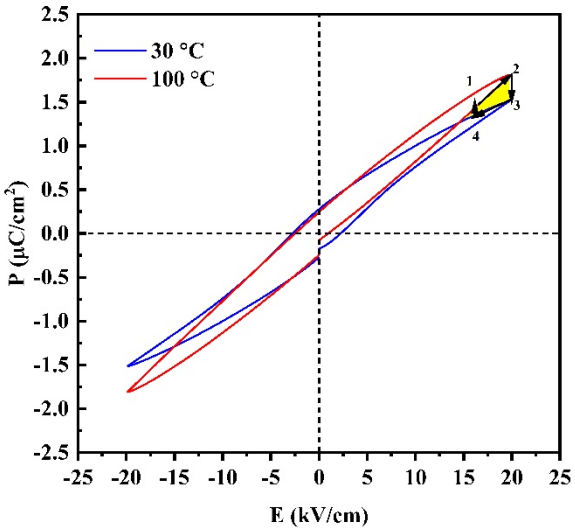

Fig. S4. Olsen cycle diagram of the pyroelectric energy harvesting for the (1-x)$AgNbO_3$-x$FeNbO_4$ ceramics.

1. S. Li, H. Nie, G. Wang, N. Liu, M. Zhou, F. Cao and X. Dong, *Journal of Materials Chemistry C*, 2019, **7**, 4403-4414.
2. R. A. Kishore and S. Priya, *Materials*, 2018, **11**, 1433.
3. A. K. Batra and M. D. Aggarwal, 2013.
4. H. Maiwa, in *Nanoscale Ferroelectric-Multiferroic Materials for Energy Harvesting Applications*, eds. H. Kimura, Z. Cheng and T. Jia, Elsevier, 2019, DOI: https://doi.org/10.1016/B978-0-12-814499-2.00012-8, pp. 217-229.