Supporting Information

The Electrical and Structural Characterization of $Ba_3Mo_{1-x}Nb_{1+x}O_{8.5-x/2}$: The relationship between mixed coordination, polyhedral distortion and the ionic conductivity of $Ba_3MoNbO_{8.5}$

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Table S1. Refined atomic parameters, cell parameters and agreement factors from Rietveld refinement of the crystal structures of $Ba_3Mo_{1-x}Nb_{1+x}O_{8.5-x/2}$. The model was refined in the space group $R\bar{3}m$ H. Atom positions are Ba(1) (0, 0, 0), Ba(2) (0, 0, *z*), M(1) (0, 0, *z*), M(2) (0, 0, ½) O(1) (*x*, *y*, *z*), O(2) (½, 0, 0), O(3) (*x, y, z*). U_{ij} indicates anisotropic thermal displacement parameters (in $Å^2$). U_{13} and U_{23} are zero due to the symmetry of the system. O(3) was refined with an isotropic thermal displacement parameter, U_{iso} (in $Å^2$).

			x = 0.0	x = 0.1	x = 0.2	x = 0.3
***a* (Å)**			5.92053 (7)	5.92577 (5)	5.92953 (7)	5.93399 (7)
***c* (Å)**			21.0975 (4)	21.1026 (4)	21.1048 (4)	21.1040 (4)
V ($Å^3$)			640.45 (2)	641.74 (2)	642.62 (2)	643.56 (2)
Atom	**W**	**Parameter**	**x = 0.0**	**x = 0.1**	**x = 0.2**	**x = 0.3**
Ba(1)	**3*a***	***x* = *y* = *z***	0	0	0	0
		Occupancy	1	1	1	1
		U11 = U22 ($Å^2$)	0.0132 (7)	0.0126 (7)	0.0113 (6)	0.0118 (6)
		U33 ($Å^2$)	0.0013 (4)	0.0015 (2)	0.0013 (2)	0.0014 (2)
		U12 ($Å^2$)	0.0066 (8)	0.0063 (7)	0.0056 (8)	0.0041 (8)
Ba(2)	**6*c***	***x* = *y***	0	0	0	0
		z	0.2075 (2)	0.2073 (2)	0.2074 (2)	0.2066 (2)
		Occupancy	1	1	1	1
		U11 = U22 ($Å^2$)	0.0199 (6)	0.0193 (7)	0.0204 (7)	0.0216 (2)
		U33 ($Å^2$)	0.0313 (5)	0.038 (2)	0.032 (2)	0.031 (2)
		U12 ($Å^2$)	0.0099 (6)	0.0097 (5)	0.0102 (5)	0.0108 (5)
M(1)	**6*c***	***x* = *y***	0	0	0	0
		z	0.3987 (1)	0.3987 (1)	0.3989 (1)	0.3988 (1)
		Occupancy	0.914 (2)	0.913 (1)	0.908 (2)	0.899 (1)
		U11 = U22 ($Å^2$)	0.0079 (6)	0.0086 (6)	0.0114 (6)	0.0110 (6)
		U33 ($Å^2$)	0.047 (2)	0.043 (2)	0.046 (2)	0.051 (2)
		U12 ($Å^2$)	0.0039 (3)	0.0043 (3)	0.0057 (3)	0.0055 (3)
M(2)	**3*b***	***x* = *y***	0	0	0	0
		z	0.5	0.5	0.5	0.5
		Occupancy	0.172 (1)	0.174 (1)	0.185 (1)	0.201 (1)
		U11 = U22 ($Å^2$)	0.0079 (6)	0.0086 (6)	0.0114 (6)	0.0110 (6)
		U33 ($Å^2$)	0.047 (2)	0.043 (2)	0.046 (2)	0.051 (2)
		U12 ($Å^2$)	0.0039 (3)	0.0043 (3)	0.0057 (3)	0.0055 (3)
O(1)	**18*h***	***x***	0.1727 (2)	0.1725 (1)	0.1726 (1)	0.1724 (1)
		y	0.8273 (2)	0.8274 (1)	0.8274 (1)	0.8276 (1)
		z	0.10382 (6)	0.10399 (6)	0.10421 (6)	0.10440 (6)
		Occupancy	1	1	1	1
		U11 = U22 ($Å^2$)	0.0206 (5)	0.0203 (4)	0.0219 (5)	0.0206 (5)
		U33 ($Å^2$)	0.0187 (1)	0.0202 (8)	0.0244 (9)	0.0248 (9)
		U12 ($Å^2$)	0.0137 (7)	0.0125 (6)	0.0133 (7)	0.0119 (7)
O(2)	**9*e***	***x***	0.5	0.5	0.5	0.5
		y* = *z	0	0	0	0
		Occupancy	0.500 (4)	0.500 (4)	0.502 (4)	0.502 (4)
		U11 = U22 ($Å^2$)	0.026 (2)	0.027 (1)	0.027 (1)	0.030 (2)

		U33 (Å^2)	0.023 (3)	0.025 (3)	0.027 (3)	0.022 (3)
		U12 (Å^2)	0.0132 (8)	0.0136 (7)	0.0138 (7)	0.0152 (8)
O(3)	**36*i***	***x***	0.082 (1)	0.072 (2)	0.070 (2)	0.067 (2)
		y	0.079 (3)	0.072 (2)	0.071 (3)	0.070 (3)
		z	0.3218 (6)	0.3223 (5)	0.3222 (5)	0.3222 (6)
		Occupancy	0.083 (1)	0.079 (1)	0.074 (1)	0.070 (1)
		Uiso (Å^2)	0.046 (6)	0.026 (5)	0.022 (6)	0.025 (6)
Statistics			**x = 0.00**	**x = 0.10**	**x = 0.20**	**x = 0.30**
χ^2			3.16	3.54	3.05	3.57
R_p (%)			5.47	3.16	2.72	3.16
R_{wp} (%)			6.54	4.00	3.50	4.11

Table S2 Selected bond lengths and angles for $Ba_3Mo_{1-x}Nb_{1+x}O_{8.5-x/2}$ (x = 0.0, 0.1, 0.2, 0.3). Variation of selected atomic bond lengths and angles with x.

Distance (Å)	**x = 0.0**	**x = 0.1**	**x = 0.2**	**x = 0.3**
Ba(1)–O(1)	2.816 (2)	2.829 (1)	2.824 (1)	2.827 (1)
Ba(1)–O(2)	2.96026 (3)	2.96289 (3)	2.96476 (4)	2.96700 (4)
Ba(1)–O(3)	3.01 (2)	2.98 (1)	3.08 (1)	3.09 (1)
	3.48 (2)	3.51 (1)	3.44 (1)	3.44 (1)
	3.84 (1)	3.85 (1)	3.80 (1)	3.79 (1)
Ba(2)–O(1)	2.816 (4)	2.809 (4)	2.808 (4)	2.792 (4)
	2.997 (3)	2.9995 (6)	3.0006 (7)	3.0047 (8)
Ba(2)–O(2)	3.156 (4)	3.167 (3)	3.161 (4)	3.176 (4)
Ba(2)–O(3)	2.45 (1)	2.48 (1)	2.459 (1)	2.474 (1)
M(1)–O(1)	1.835 (2)	1.841 (2)	1.844 (2)	1.848 (2)
M(1)–O(2)	2.196 (2)	2.197 (2)	2.201 (2)	2.201 (2)
M(1)–O(3)	1.70 (1)	1.678 (9)	1.671 (9)	1.660 (10)
M(2)–O(1)	2.114 (2)	2.115 (1)	2.112 (1)	2.112 (2)
Angle (°)	**x = 0.00**	**x = 0.10**	**x = 0.20**	**x = 0.30**
O(1)–M(1)–O(1)	101.97 (3)	101.88 (1)	101.81 (1)	101.75 (1)
O(1)–M(1)–O(2)	85.89 (5)	85.93 (4)	85.98 (5)	86.02 (5)
O(1)–M(1)–O(3)	101.5 (4)	103.3 (4)	103.7 (4)	104.2 (4)
	115.6 (6)	115.3 (5)	115.2 (5)	115.0 (5)
	129.7 (5)	128.9 (4)	128.9 (4)	128.7 (4)
O(2)–M(1)–O(2)	84.73 (1)	84.77 (1)	84.79 (1)	84.82 (1)
O(1)–M(2)–O(1)	84.85 (6)	85.03 (5)	85.19 (6)	85.38 (6)
	95.15 (6)	94.97 (5)	94.81 (6)	94.62 (6)

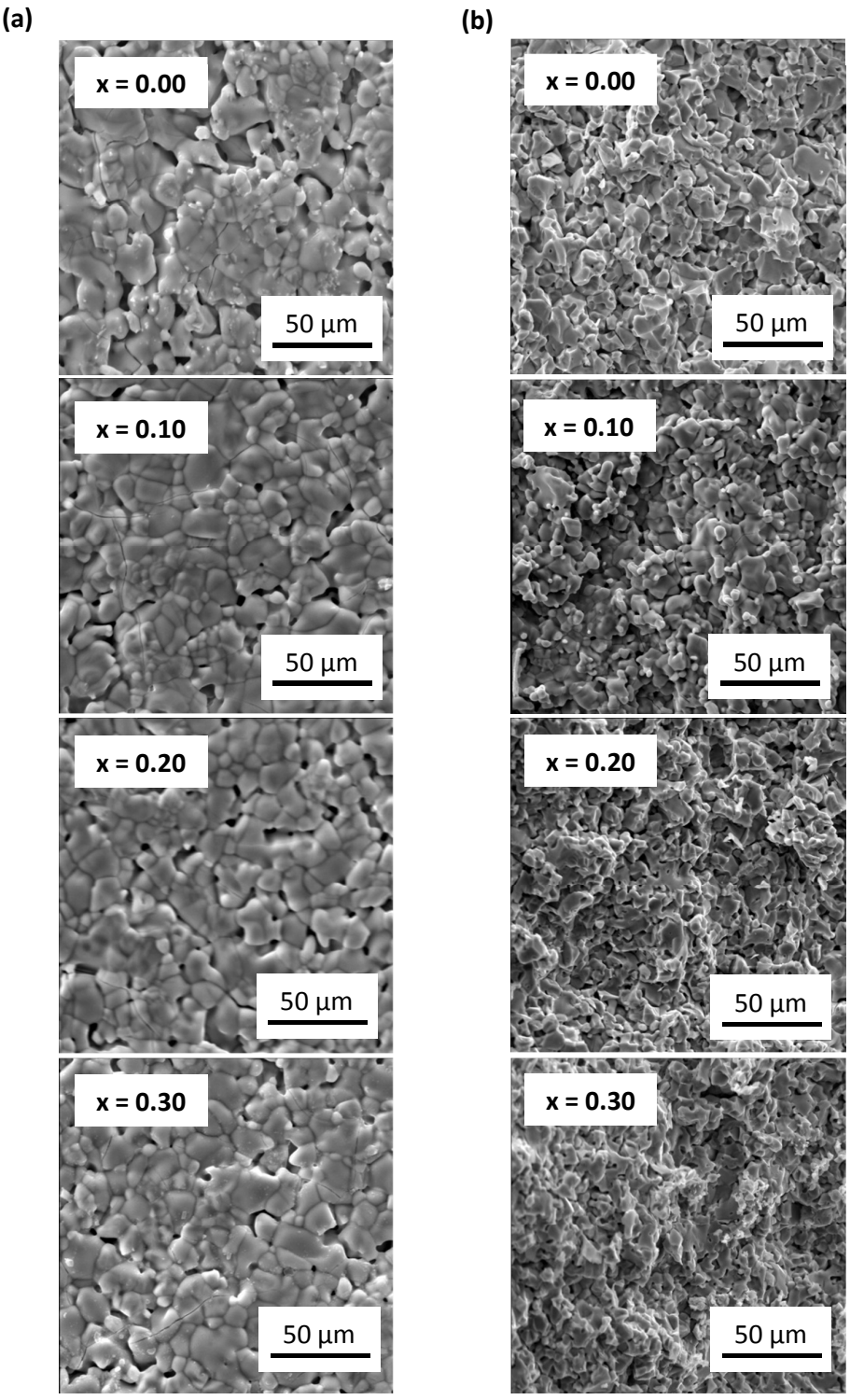

Figure S1. SEM micrographs of the surface **(a)** and section **(b)** of as prepared pellets of $Ba_3Mo_{1-x}Nb_{1+x}O_{8.5-x/2}$ (x = 0.0, 0.1, 0.2, 0.3)**.**

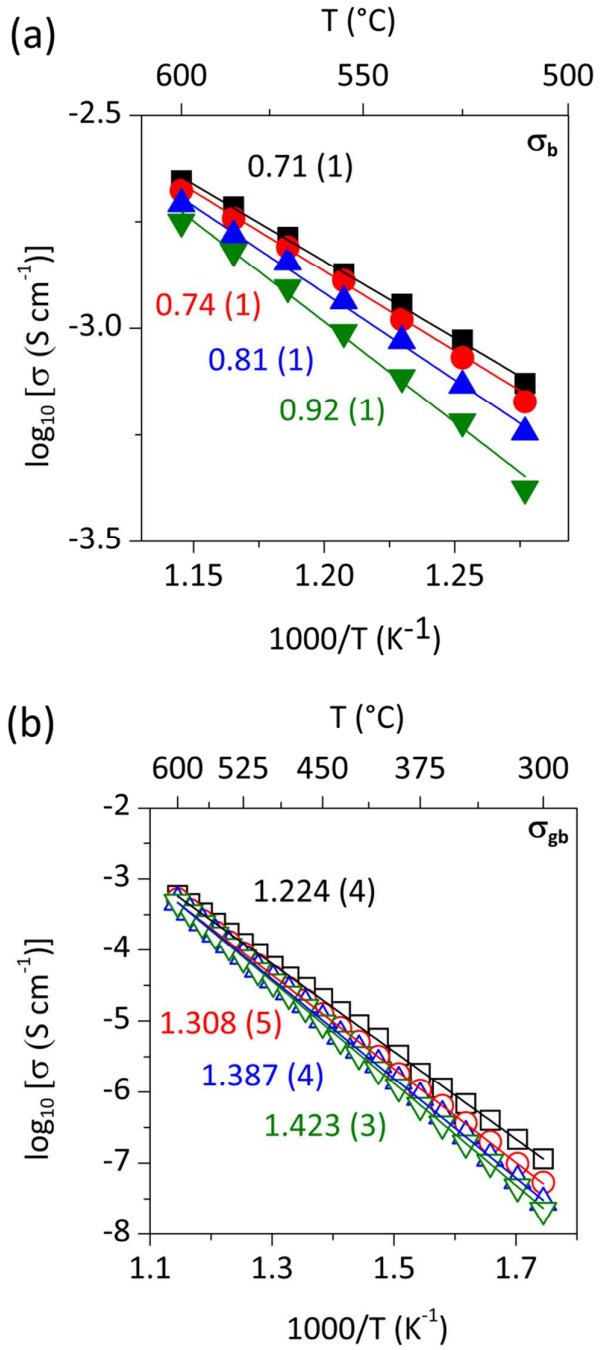

Figure S2. Arrhenius plots of the bulk conductivity above 500 °C **(a)** and of the grain boundary conductivity **(b)** of the Nb-doped samples. Black symbols indicate x = 0.0, red symbols x = 0.1, blue symbols x = 0.2 and green symbols x = 0.3. Lines are the linear fits to the data and the numbers are the calculated activation energies (in eV).

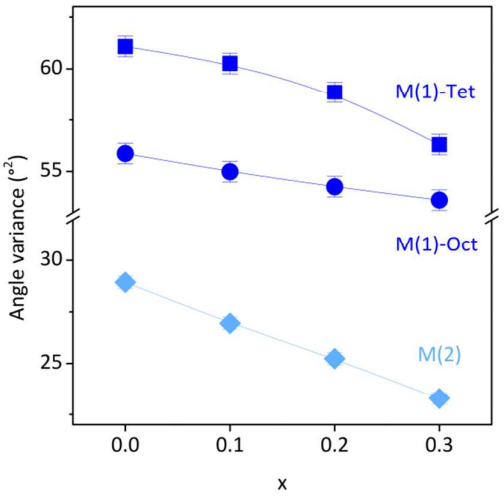

Figure S3 Variation of the angle variance of the $M(1)O_4$ tetrahedra, $M(1)O_6$ octahedra and the $M(2)O_6$ octahedra with x.