SUPPLEMENTARY INFORMATION

Extended investigation of the conductive characteristics of monoclinic tungstates with a $Bi_{3.24}Ln_2W_{0.76}O_{10.14}$ (*Ln* = La, Pr or Nd) composition

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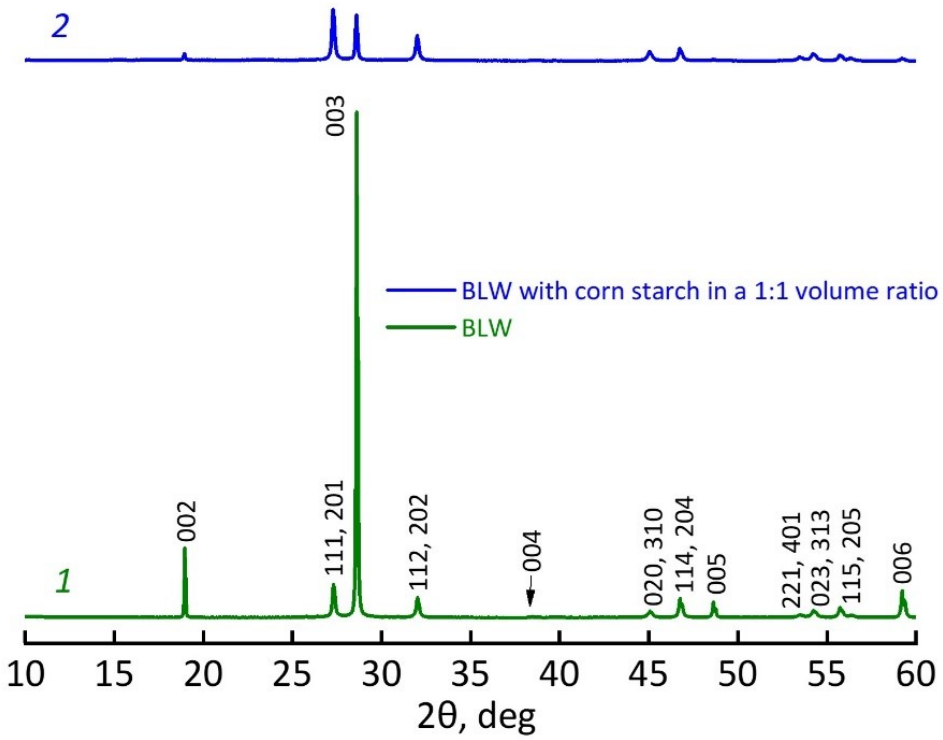

Fig. S1. Powder XRD patterns of (1) $Bi_{3.24}La_2W_{0.76}O_{10.14}$ (BLW) ceramics and (2) the $Bi_{3.24}La_2W_{0.76}O_{10.14}$ (BLW) sample powder mixed with corn starch in a 1:1 volume ratio.

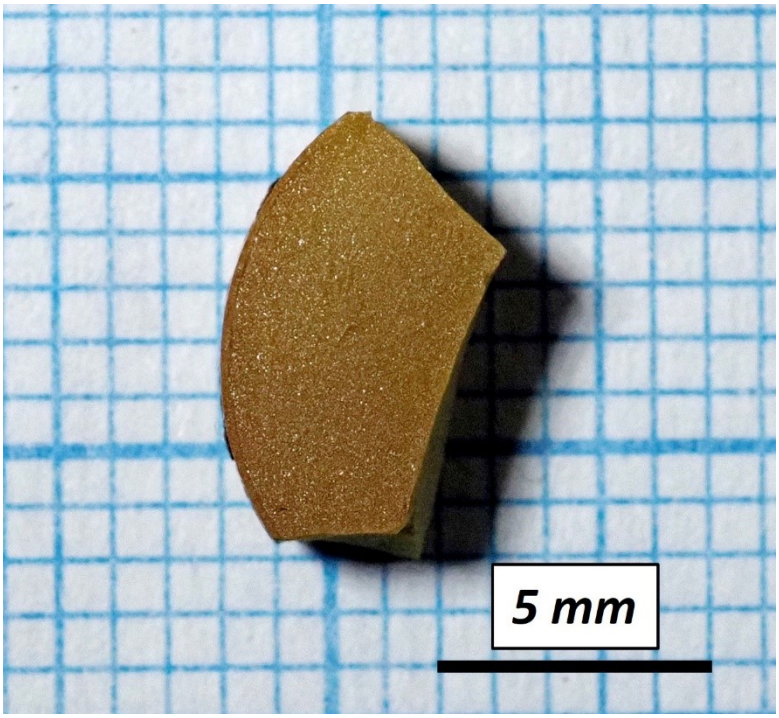

Fig. S2. Photograph of $Bi_{3.24}Pr_2W_{0.76}O_{10.14}$ (BPW) ceramics in daylight.

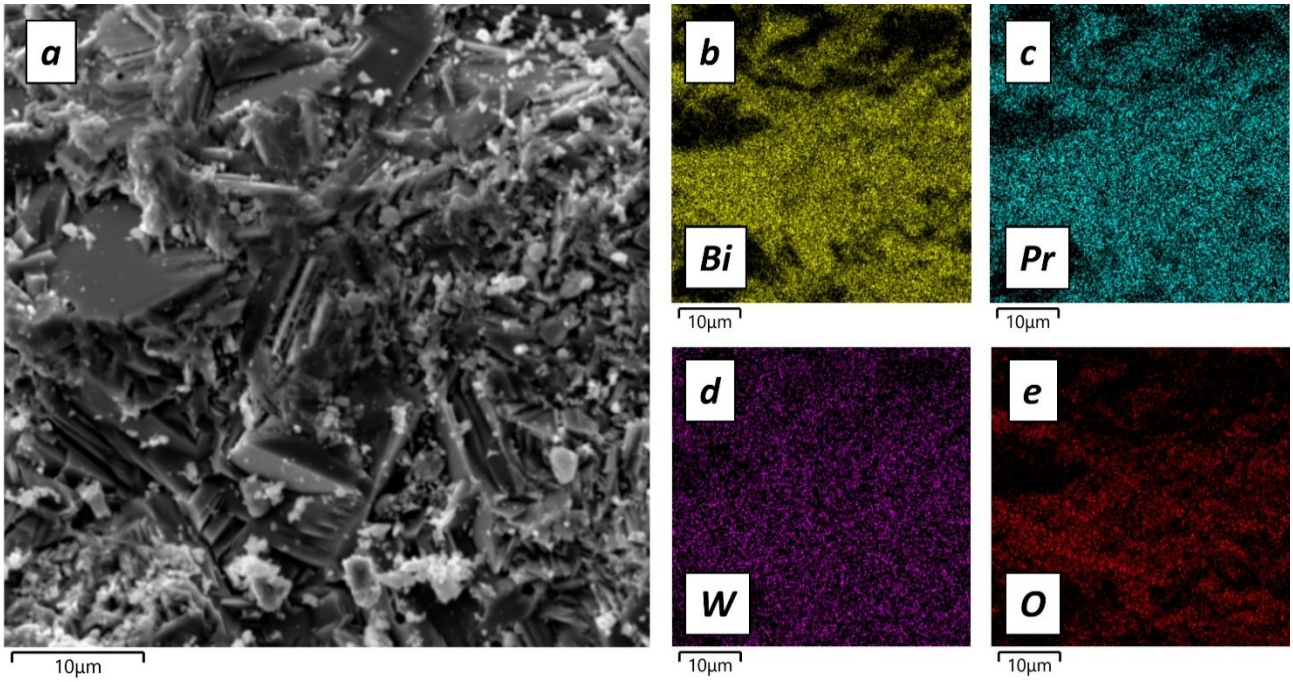

Fig. S3. (a) The BPW ceramics SEM micrograph, test area; (b) Bi element mapping; (c) Pr element mapping; (d) W element mapping; (e) O element mapping.

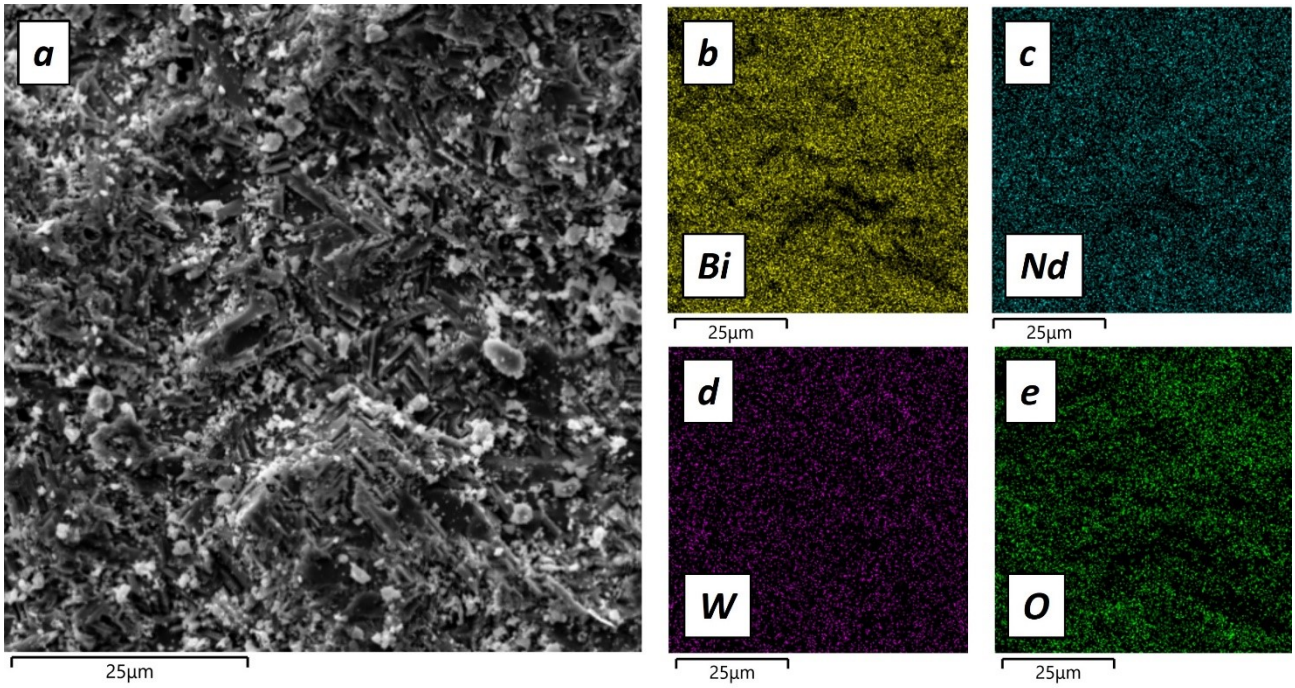

Fig. S4. (a) The BNW ceramics SEM micrograph, test area; (b) Bi element mapping; (c) Nd element mapping; (d) W element mapping; (e) O element mapping.

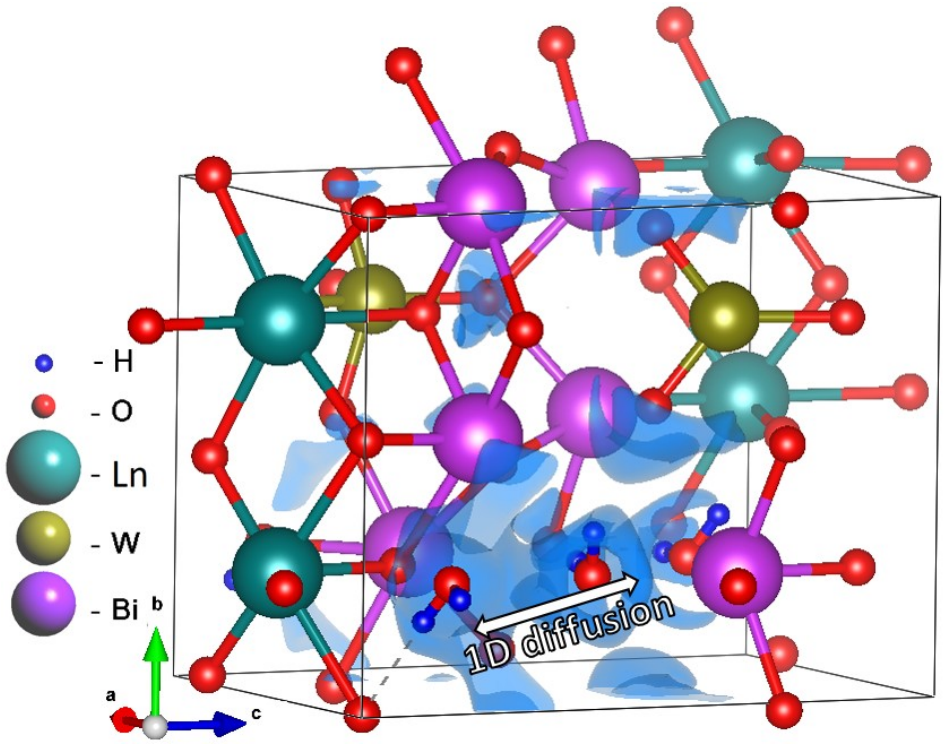

Fig. S5. Proton migrations from the BVSE approach in the $Bi_{3.24}Ln_2W_{0.76}O_{10.14}$ (*Ln* = La, Pr or Nd) with 1.5 maximum possible water molecules (0.75 per formula unit).

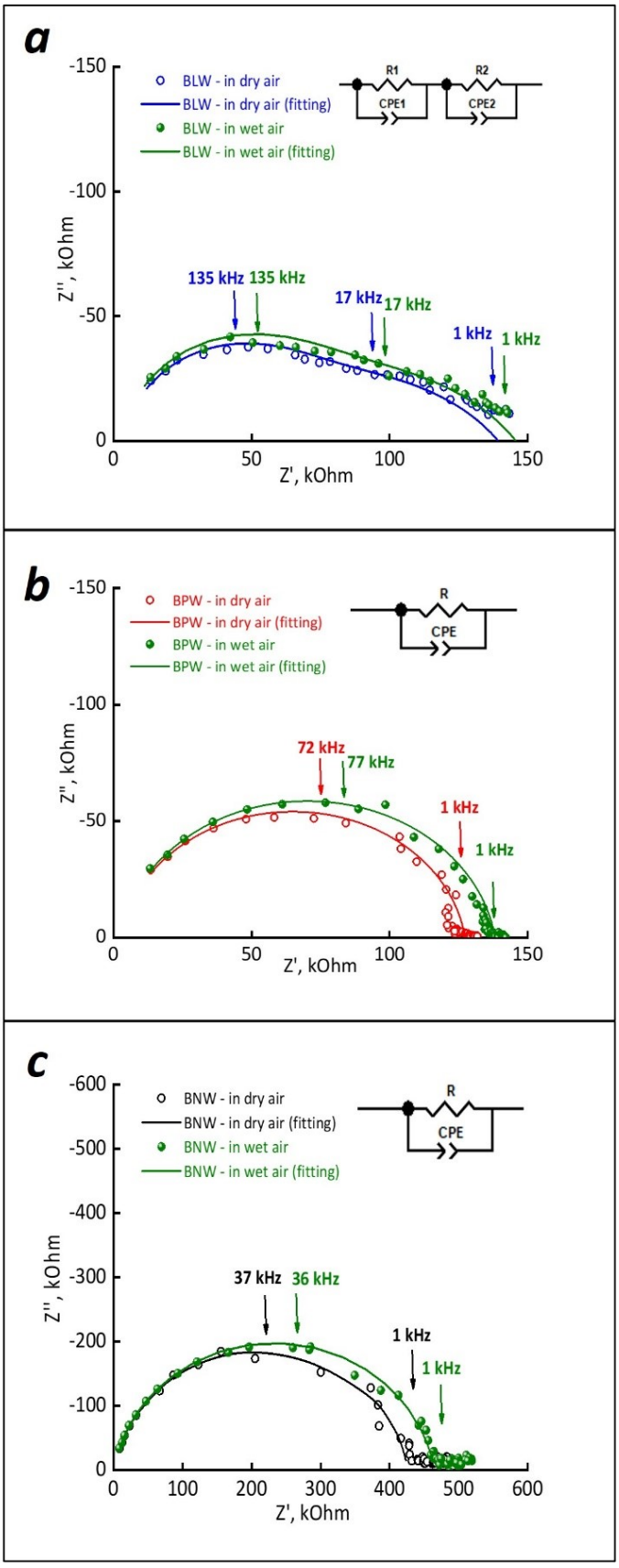

Figure S6. Impedance hodographs of the (a) $Bi_{3.24}La_2W_{0.76}O_{10.14}$ (BLW), (b) $Bi_{3.24}Pr_2W_{0.76}O_{10.14}$ (BPW) and (c) $Bi_{3.24}Nd_2W_{0.76}O_{10.14}$ (BNW) ceramics in a dry and humid atmosphere at 450 °C.

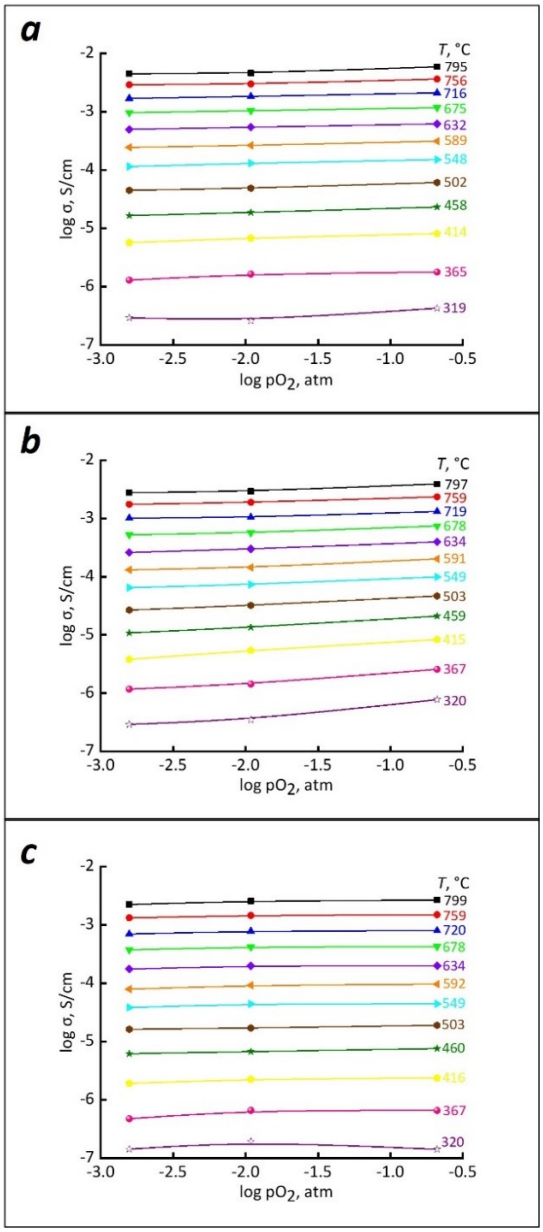

Fig. S7. Total conductivity oxygen partial pressure $p(O_2)$ dependences of the (a) $Bi_{3.24}La_2W_{0.76}O_{10.14}$ (BLW), (b) $Bi_{3.24}Pr_2W_{0.76}O_{10.14}$ (BPW) and (c) $Bi_{3.24}Nd_2W_{0.76}O_{10.14}$ (BNW) ceramics.

Table S1. Equivalent circuit fit parameters for the complex impedance plots of the BLW, BPW, BNW samples in a dry and wet atmosphere at 450 °C.

Sample	Bulk			Grain boundary		
	R1, Ohm×10^6	*CPE1*, T×10^{-11}	*CPE1*, P	*R2*, Ohm×10^6	*CPE2*, T×10^{-8}	*CPE2*, P
BLW (dry air)	0.05±0.01	1.78±0.05	1.01±0.01	0.09±0.01	1.30±0.05	0.56±0.01
BLW (wet air)	0.05±0.01	1.75±0.05	1.01±0.01	0.09±0.01	0.94±0.05	0.60±0.01
BPW (dry air)	0.13±0.01	3.37±0.05	0.91±0.01	-	-	-
BPW (wet air)	0.14±0.01	3.47±0.05	0.91±0.01	-	-	-
BNW (dry air)	0.42±0.01	2.96±0.05	0.92±0.01	-	-	-
BNW (wet air)	0.47±0.01	3.93±0.05	0.90±0.01	-	-	-