Electrical conductivity of low-doped ceria-based ceramics

Igor V. Zagaynov*, Sergey V. Fedorov, Olga S. Antonova

A.A. Baikov Institute of Metallurgy and Materials Science, Moscow, Russia

*Corresponding author: igorscience@gmail.com

Material and methods

The $Ce(NO_3)_3 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, $SnCl_2 \cdot 6H_2O$, $ZrO(NO_3)_2 \cdot 7H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, Pr_6O_{11}, and $TiCl_4$ (Acros Organics) compounds were used as initial salts. Appropriate amounts of salts were dissolved in concentrated nitric acid (68%) to achieve a salt concentration of 0.667 M. After dissolving the salts, this mixture was added to distilled water to obtain a final concentration of 0.1 M. Subsequently, co-precipitation was carried out by adding 2.5 M KOH solution up to pH 11. Ultrasonic processing (35 kHz, 150 W) was used during all processes at 30 °C under stirring. The resulting precipitates were filtered, washed with a distilled water-ethanol solution (H_2O/C_2H_5OH=9 vol.), dried at 150 °C for 12 h, and calcined in static air by heating at a rate of 4 °C/min from room temperature to 500 °C and kept at 500 °C for 1 h in a muffle furnace [Ceram. Int. 50 (2024) 14513-14519; Chem. Eng. J. 489 (2024) 151340].

The as-obtained powders were pressed into pellets (with 5 wt.% binder from a 5 wt.% aqueous solution of polyvinyl alcohol) with 10 mm in diameter and 2 mm in thickness at 200 MPa and then were sintered at 1000 °C for 4 h in air with a heating rate of 4°C/min. Symmetric cells for the impedance studies (Elins Z-350M impedance meter, the frequency ranges from 0.1 Hz to 4 MHz at the amplitude of AC signal of 30 mV) were prepared by deposition (brushing) of platinum paste onto both sides of the electrolyte pellets, drying at 150 °C for 1 h and annealing at 900 °C for 4 h in air. A platinum wire was used as current collector [Process. Appl. Ceram. 13 (2019) 244-249]. The grain (bulk) and grain boundary contributions to the total conductivity were evaluated using AC impedance spectroscopy. The impedance response was modelled using a series resistor and inductor for the contact leads and a resistor in parallel with a constant phase element (CPE) for each of the grain/grain boundary/electrode responses, which were connected in series. To separate the ionic contribution from total conductivity, Wagner's polarization technique with an electrical loader (Solartron 1285A Potentiostat) was used to calculate the ionic transport number by imposing an external fixed DC voltage (1.5 V) across the electrolyte (DC current was monitored as a function of time on application of a fixed DC voltage across the symmetric C|electrolyte|C cell).

Powders and ceramics were characterized by:

Powder X-ray diffraction data (XRD) were collected at room temperature (DRON-3M, Russia) with CuK_α radiation. The average size of the crystallite size (crystalline domains) (d_{XRD}) was made by applying the Scherrer equation to the full-width at half maximum after accounting for instrumental broadening using germanium as reference; d_{XRD} was calculated not on a separate peak, but was on all planes during the fitting of the spectrum (more details in the Supplementary). Quantitative phase analysis was calculated by the Rietveld method

Scanning electron microscopy (SEM) analyses of the materials were carried out under a Tescan VEGA II electron microscope with energy dispersive analyzer INCA Energy 300.

Thermogravimetry (TG-DSC) was carried out under air flow with Netzsch STA449F3. The samples were heated to 1300°C at the rate of 10°C/min in air. An empty alumina crucible served as a reference.

The relative density of ceramics was determined by hydrostatic weighing; liquid - distilled water. Relative density was calculated as the ratio of densities determined by hydrostatic weighing (ρ_h), ISO 18754:2020 // GOST 24409-80, and XRD based cell parameter (ρ_{XRD}); for comparison, geometric density data (ρ_g) have been added to Table S1. The pycnometric density was measured with an accuracy of ± 0.03% using an Ultrapyc 1200e gas pycnometer (Quantachrome) in an atmosphere of high-purity helium in a purge mode in a constant gas flow. The cell calibration V_c=10 cm^3 was performed using a stainless-steel calibration sphere with a known volume of the sphere V_s=7.0699 cm^3. The determination of the density is based on the Archimedes displacement principle.

Table S1. Main characteristics of sintered ceramics for measurements.

No	Sample	Pellets for measurement (diameter*height, mm)	ρ_g, g/cm^3
0	CeO_2	8.23*1.28	6.2
Cu1	$Cu_{0.01}Ce_{0.99}O_2$	7.96*1.74	6.4
Mn1	$Mn_{0.01}Ce_{0.99}O_2$	8.60*1.23	5.2
Bi1	$Bi_{0.01}Ce_{0.99}O_2$	8.80*1.28	6.1 (6.7*)
Ti1	$Ti_{0.01}Ce_{0.99}O_2$	8.05*1.38	6.6
Zr1	$Zr_{0.01}Ce_{0.99}O_2$	8.43*1.53	5.5
Sm1	$Sm_{0.01}Ce_{0.99}O_2$	8.98*1.72	4.9
Ni1	$Ni_{0.01}Ce_{0.99}O_2$	8.93*1.73	4.4
Co1	$Co_{0.01}Ce_{0.99}O_2$	7.92*1.29	6.5
Sn1	$Sn_{0.01}Ce_{0.99}O_2$	8.27*1.34	5.1
Nd1	$Nd_{0.01}Ce_{0.99}O_2$	8.72*1.39	5.5 (6.2*)
Gd1	$Gd_{0.01}Ce_{0.99}O_2$	9.14*0.89	4.9
Fe1	$Fe_{0.01}Ce_{0.99}O_2$	8.84*1.16	5.1
Pr1	$Pr_{0.01}Ce_{0.99}O_2$	9.10*1.39	4.5

* - density determined by helium pycnometry.

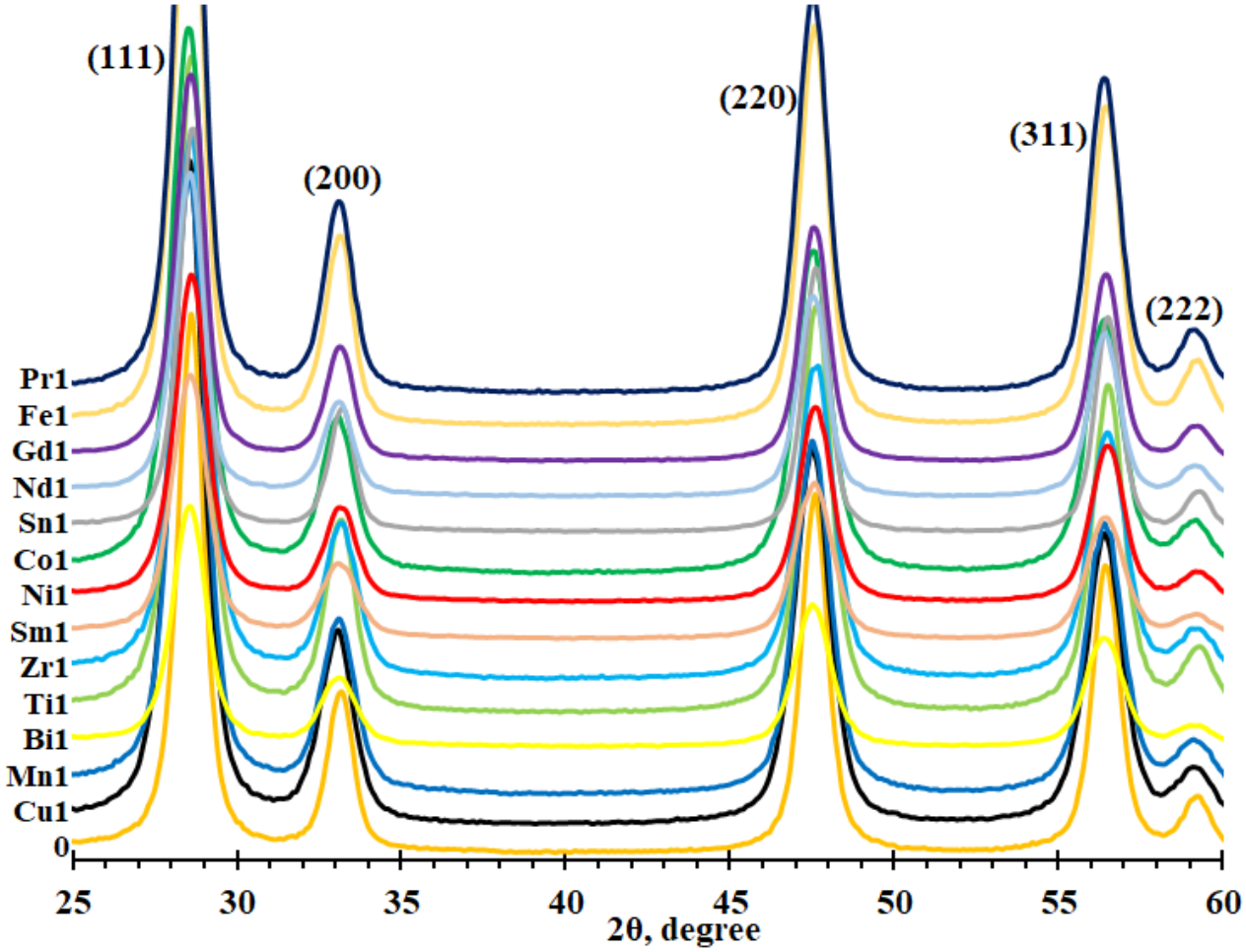


Figure S1. XRD patterns of the calcined materials at 500 °C.

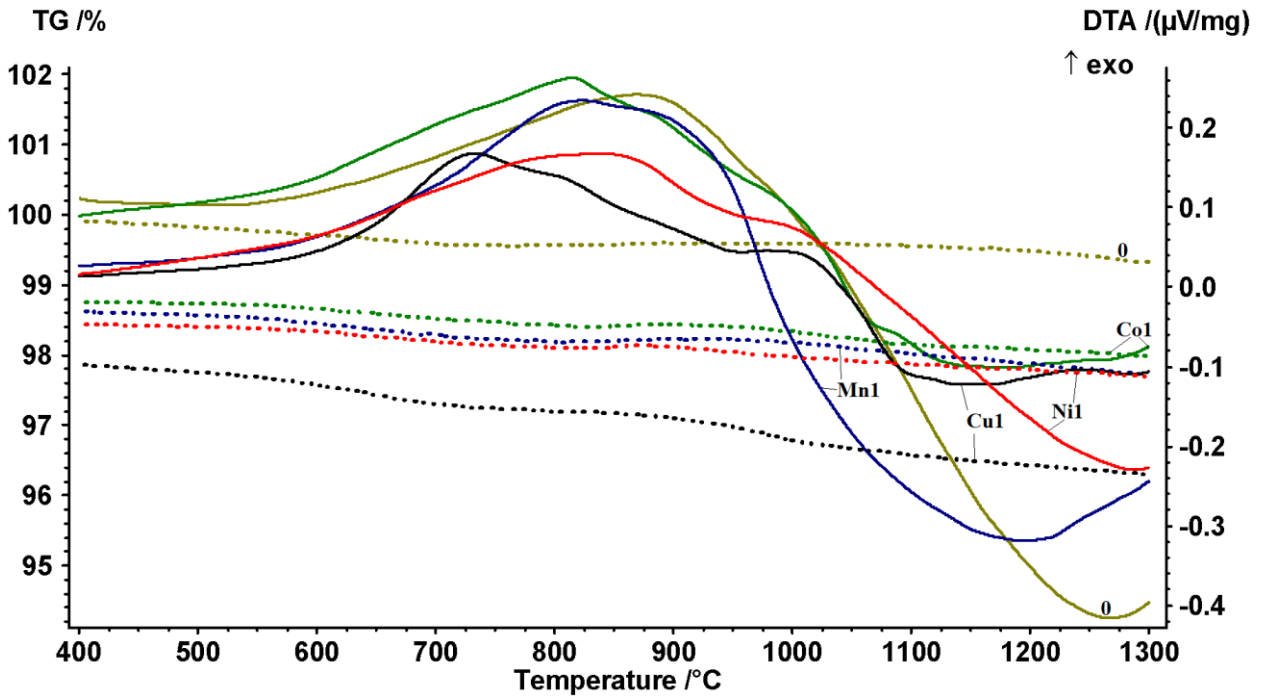


Figure S2. TG-DTA curves of powders 0, Cu1 (black), Mn1 (blue), Ni1 (red), and Co1 (green). TG (dotted line), DTA (solid line).

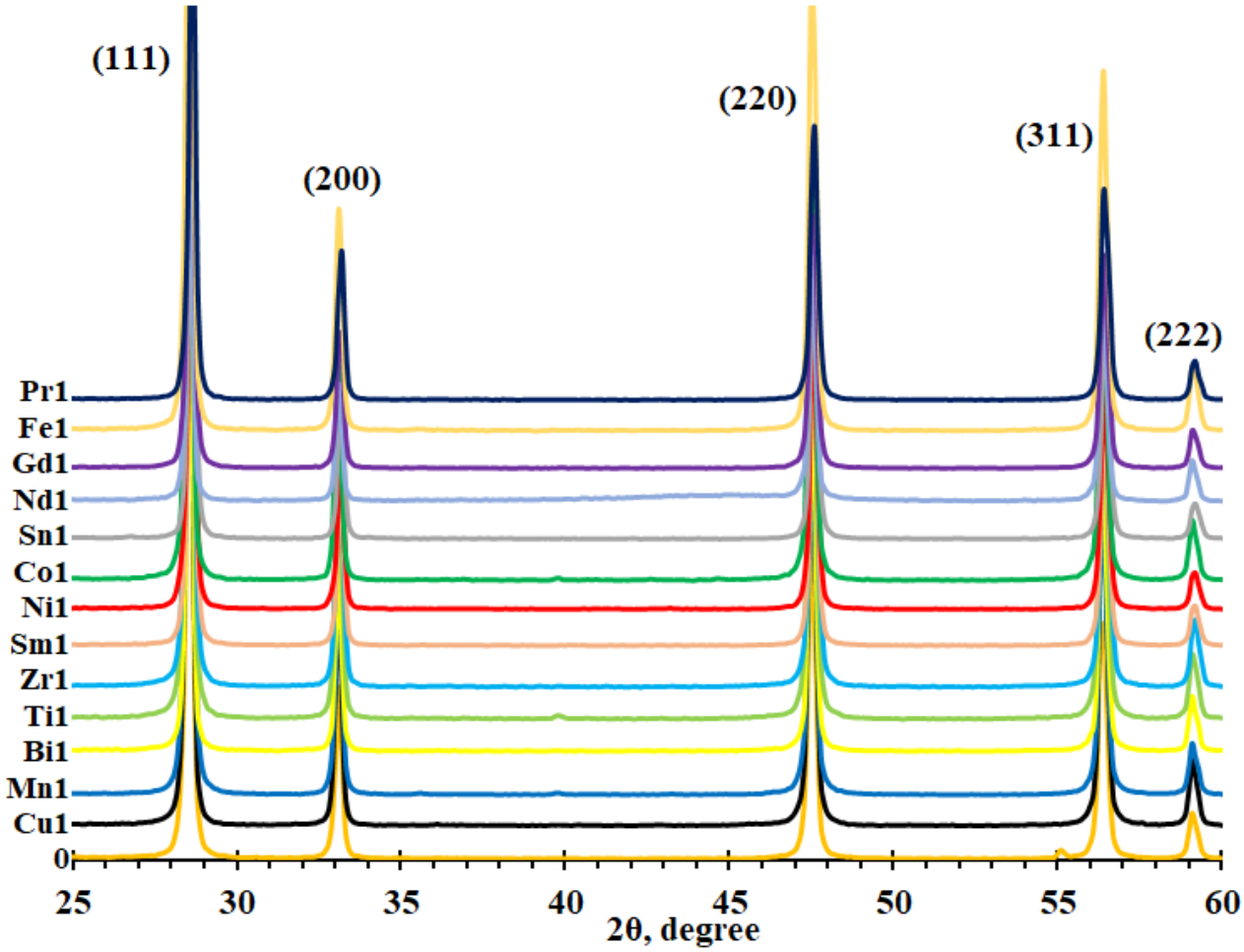


Figure S3. XRD patterns of the sintered ceramics at 1000 °C.

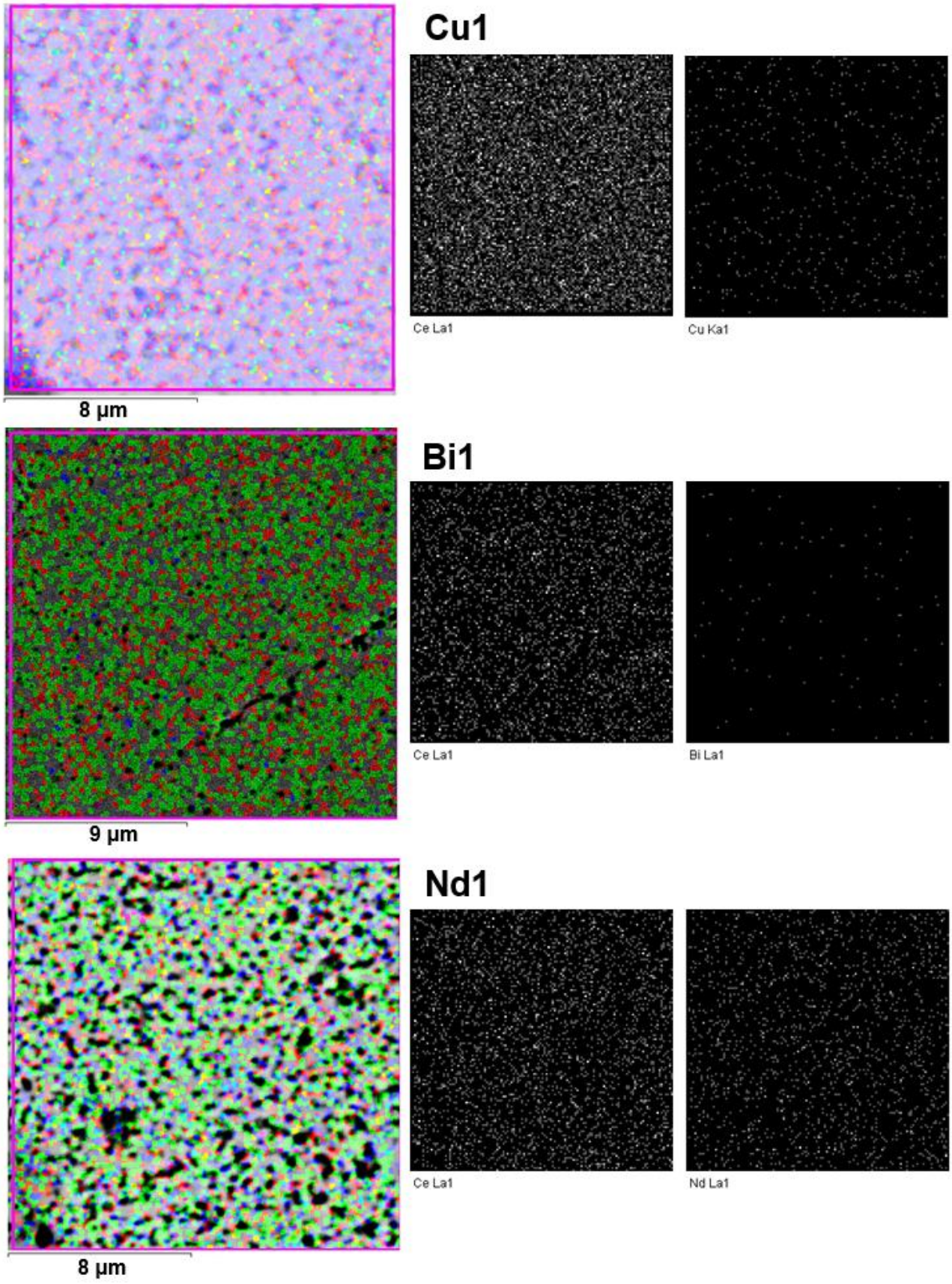
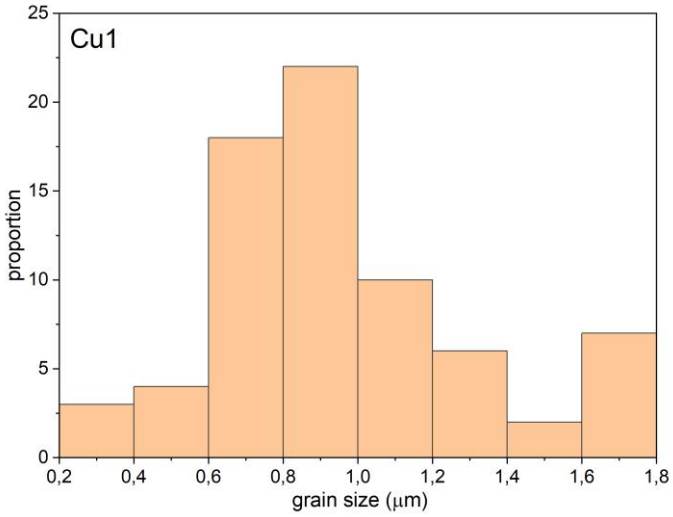
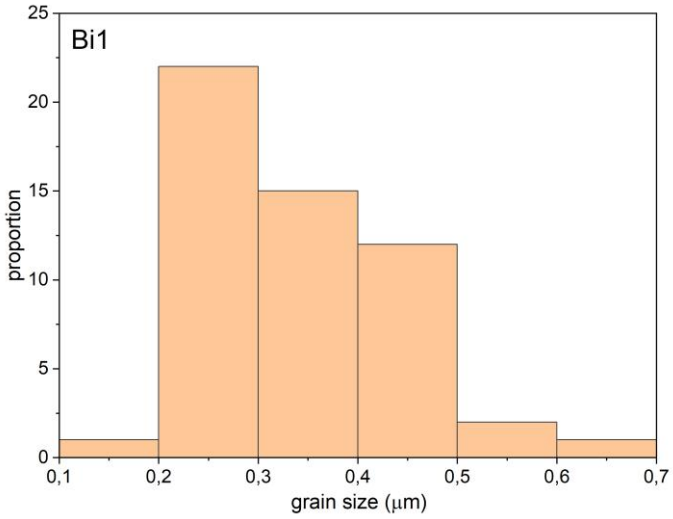


Figure S4. SEM-EDS mapping of ceramics Cu1, Bi1, and Nd1 (Red – O).





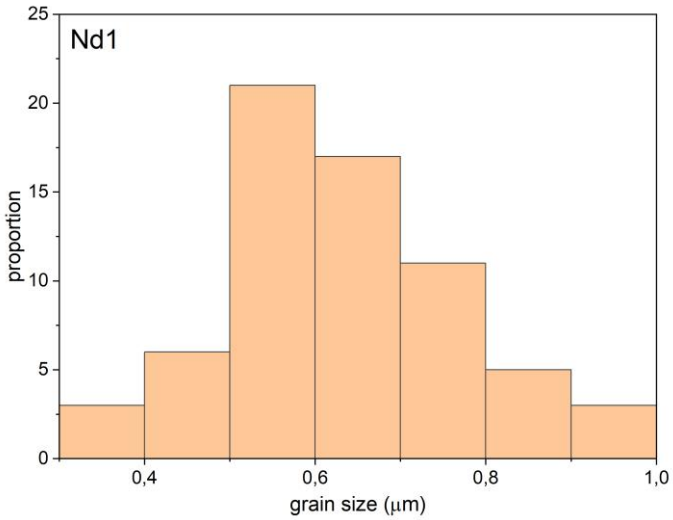


Figure S5. Grain size distribution.

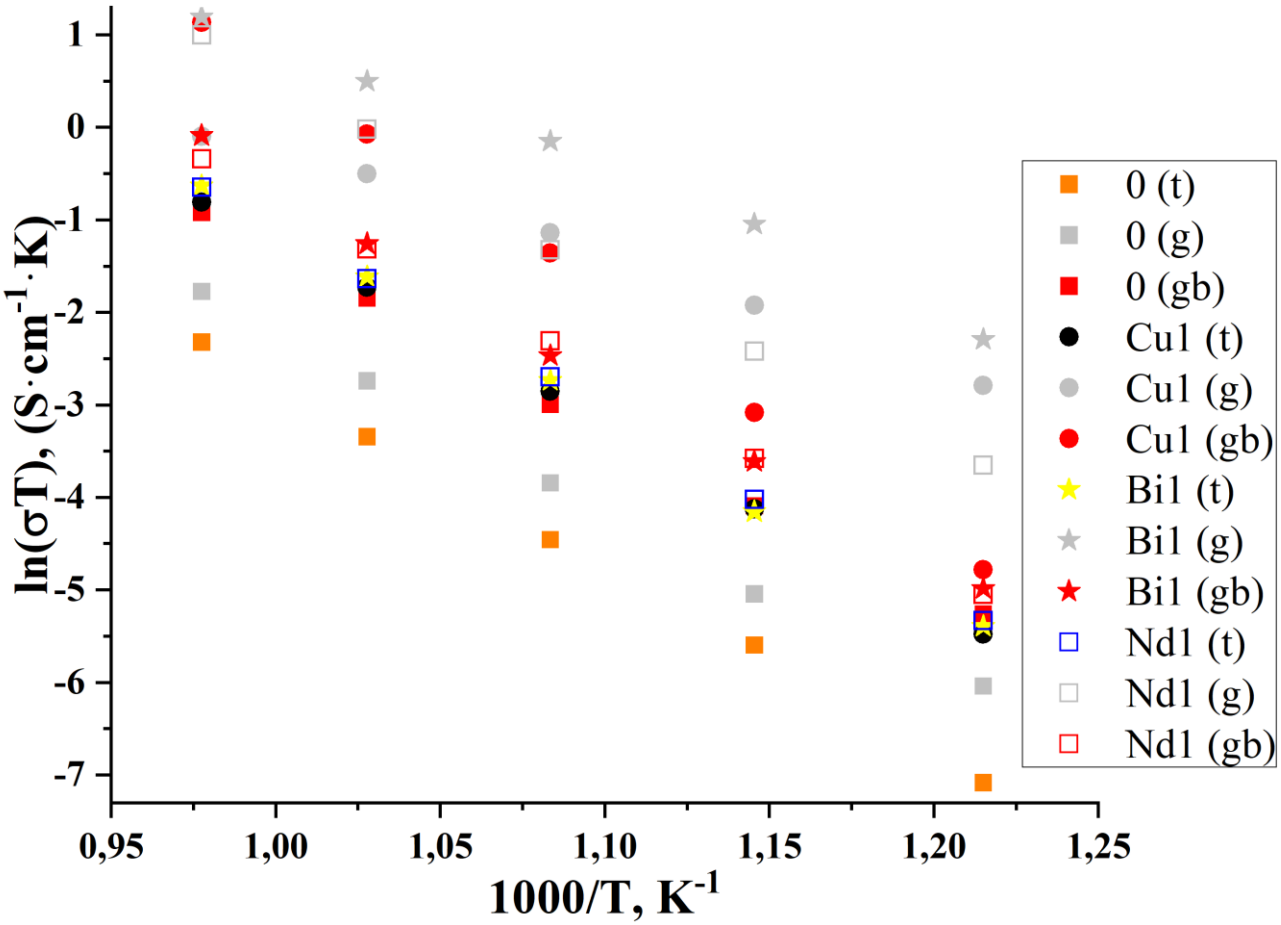


Figure S6. Arrhenius plots of conductivity: total (t, see Fig. 3) grain (g, gray), grain boundary (gb, red).

Table S2. The activation energy, E_a (eV), for total, grain, and grain boundary conductivity.

No	Sample	total	grain	grain boundary
0	CeO_2	1.68	1.6	1.6
Cu1	$Cu_{0.01}Ce_{0.99}O_2$	1.72	1.0	2.1
Bi1	$Bi_{0.01}Ce_{0.99}O_2$	1.74	1.2	1.8
Nd1	$Nd_{0.01}Ce_{0.99}O_2$	1.73	1.7	1.7