Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

A comparative 2 and 4-probe DC and 2-Probe AC electrical conductivity of novel co-doped $Ce_{0.9-x}RE_xMo_{0.1}O_{2.1-0.5x}$ (RE = Y, Sm, Gd; x = 0.2, 0.3)

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Table S1 The band gap from the diffuse reflectance spectra

Table S2 Fitting parameters of the impedance for $Ce_{0.6}RE_{0.3}Mo_{0.1}O_{1.95}$ (M = Sm, Gd) in air at 350 ^oC.

Table S3 Fitting parameters of the impedance for $Ce_{0.6}RE_{0.3}Mo_{0.1}O_{1.95}$ (RE = Sm, Gd) in air at 550 and 650 ^oC.

Table S4 Fitting parameters of the impedance for $Ce_{0.6}RE_{0.3}Mo_{0.1}O_{1.95}$ (RE = Sm, Gd) in air at 750 ^oC.

Fig. S1 PXRD patterns of (a) $Ce_{0.7}Sm_{0.2}Mo_{0.1}O_2$ (b) $Ce_{0.7}Gd_{0.2}Mo_{0.1}O_2$ and (c) $Ce_{0.7}Y_{0.2}Mo_{0.1}O_2$ prepared in air at elevated temperatures.

Fig. S2 Diffuse reflectance spectra of as prepared $Ce_{0.7}Gd_{0.2}Mo_{0.1}O_2$ and $Ce_{0.6}Gd_{0.3}Mo_{0.1}O_{1.95}$. For comparison, the starting materials are also given. Band value was estimated as described in ref. (65).

Fig. S3 FTIR spectra of as prepared $Ce_{0.7}Gd_{0.2}Mo_{0.1}O_2$ and $Ce_{0.6}Gd_{0.3}Mo_{0.1}O_{1.95}$. For comparison, the starting materials are also given.

Fig. S4 Scanning electron microscopy (SEM) images (10 μm) of as-prepared $Ce_{0.7}RE_{0.2}Mo_{0.1}O_2$ (a) = Sm; (b) = Gd and (c) = Y. Insets show the diagram at 20 μm. Their corresponding EDX images are given in (d) –(f).

Fig. S5 Typical AC resistivity plots of $Ce_{0.7}Gd_{0.2}Mo_{0.1}O_2$ and $Ce_{0.6}Gd_{0.3}Mo_{0.1}O_2$ at 350 ^oC in (a) air and (b) wet H_2. Insets show the expanded view.

Fig. S6 Arrhenius plots for bulk electrical conductivity of (a) $Ce_{0.7}Sm_{0.2}Mo_{0.1}O_2$ (b) $Ce_{0.7}Gd_{0.2}Mo_{0.1}O_2$ and (c) $Ce_{0.7}Y_{0.2}Mo_{0.1}O_2$ in air and wet H_2 determined by 2-probe electrical measurements using Pt electrodes. About four to five orders of magnitude higher electrical conductivity was observed in wet H_2. For comparison, 4-probe DC electrical conductivity data in wet H_2 was included.

Fig. S7 Powder X-ray diffraction patterns of (a) $Ce_{0.7}Sm_{0.2}Mo_{0.1}O_2$ (b) $Ce_{0.7}Gd_{0.2}Mo_{0.1}O_2$ and (c) $Ce_{0.7}Y_{0.2}Mo_{0.1}O_2$ after AC impedance measurement up to 700^oC in wet H_2.

Fig. S8 Powder X-ray diffraction patterns of (a) $Ce_{0.6}Sm_{0.3}Mo_{0.1}O_{1.95}$ (b) $Ce_{0.6}Gd_{0.3}Mo_{0.1}O_{1.95}$ and (c) $Ce_{0.6}Y_{0.3}Mo_{0.1}O_{1.95}$ after AC impedance measurement up to 700^oC in wet H_2.

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Fig. S9 (a) Typical variation of electrical current as a function of time of $Ce_{0.6}Gd_{0.3}Mo_{0.1}O_{1.95}$ in wet H_2 at 450 °C for the 2- probe DC measurement with the applied potential of 0.1 V and 0.4 V. It demonstrates that an initial transient current converges on a steady-state current for an applied bias of 0.1 and 0.4 V at 450 °C. For clarity, we have shown both current and time in the log scale. A steady state current was observed within 1 Sec. In (b), we show the variation of voltage as a function of time for $Ce_{0.6}Gd_{0.3}Mo_{0.1}O_{1.95}$ in wet H_2 at 450 °C using the 4-probe DC measurement. A similar behavior was observed for the Sm and Y compounds.

Fig. S10 PXRD patterns showing the chemical stability of $Ce_{0.7}Sm_{0.2}Mo_{0.1}O_2$ with YSZ after sintering the reaction mixture (1:1 weight ratio) at (a) 1000°C, (b) 900°C and (c) 800°C in wet H_2 for 24 h. For comparison, (d) the mixture of $Ce_{0.7}Sm_{0.2}Mo_{0.1}O_2$ with YSZ, (e) the starting materials YSZ powders and (f) as-prepared $Ce_{0.7}Sm_{0.2}Mo_{0.1}O_2$ are shown. New phases due to Mo (JCPDS Card No 42- 1120) and $Zr_{0.4}Ce_{0.6}O_2$ (JCPDS Card No. 38-1439) are marked with * and #, respectively.

Table S1 Estimated band gap from the diffuse reflectance spectra

Composition	Eg (eV)	Literature values Eg (eV)
CeO_2	3.31	Present work
		3.31,[60] 3.1,[61] 3.55,[62] 3.19-(bulk)[63] 3.15,[64] 3.35[65]
$Ce_{0.7}Gd_{0.2}Mo_{0.1}O_2$	3.07	Present work
$Ce_{0.6}Gd_{0.3}Mo_{0.1}O_{1.95}$	3.09	Present work
MoO_3	3.15	Present work
		3.15 (polycrystalline thin film), [66] 3.0-3.4 (amorphous film), [67]
		2.9 (bulk), [68] 3.05,[69] 3.16 (amorphous film),[70] 3.27 (crystalline film)[70]

Table S2 Fitting parameters of the impedance for $Ce_{0.6}RE_{0.3}Mo_{0.1}O_{1.95}$ (M = Sm, Gd) in air at 350 ^{o}C.

		Q1 (F)			Q2 (F)			Q3 (F)
Compound	R1 (Ω)	n1	C1(F)	R2 (Ω)	n2	C2 (F)	[a]R3 (Ω)	n3
$Ce_{0.6}Sm_{0.3}Mo_{0.1}O_{1.95}$	6.73×10^{3}	6.09×10^{-10}	1.84×10^{-11}	1.69×10^{5}	1.40×10^{-7}	4.87×10^{-8}	2.77×10^{12}	5.79×10^{-5}
		0.78			0.78			0.26
$Ce_{0.6}Gd_{0.3}Mo_{0.1}O_{1.95}$	1.10×10^{4}	1.76×10^{-9}	2.59×10^{-11}	1.38×10^{5}	2.15×10^{-7}	5.85×10^{-8}	3.22×10^{14}	1.11×10^{-4}
		0.72			0.73			0.38

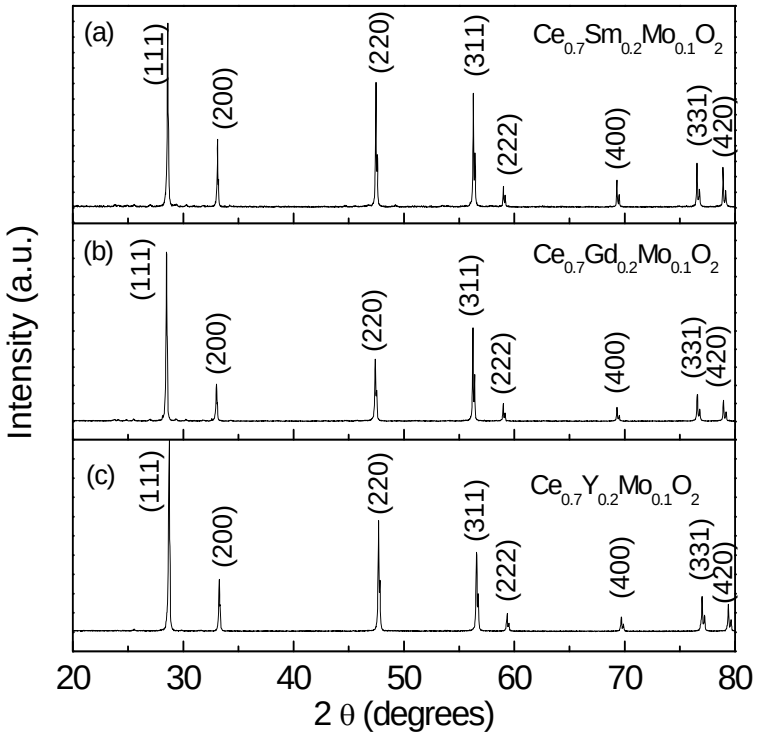
[a]Extrapolated value**.**

Table S3 Fitting parameters of the impedance for $Ce_{0.6}RE_{0.3}Mo_{0.1}O_{1.95}$ (RE = Sm, Gd) in air at 550 and 650 ^{o}C.

				Q2 (F)			Q3 (F)			Q4 (F)	
Compound	T (^{o}C)	R1 (Ω)	R2 (Ω)	n2	C2(F)	R3 (Ω)	n3	C3(F)	R4 (Ω)	n4	C4(F)
$Ce_{0.6}Sm_{0.3}Mo_{0.1}O_{1.95}$	550	1.84×10^{2}	3.60×10^{2}	1.06×10^{-6}	1.06×10^{-6}	1.52×10^{3}	2.14×10^{-5}	2.73×10^{-7}	7.38×10^{3}	2.46×10^{-3}	2.40×10^{-2}
				1.00			0.44			0.56	
	650	61.48	89.85	1.41×10^{-6}	8.79×10^{-7}	1.44×10^{2}	2.46×10^{-4}	8.33×10^{-7}	3.79×10^{2}	9.68×10^{-3}	2.69×10^{-2}
				0.95			0.37			0.56	
$Ce_{0.6}Gd_{0.3}Mo_{0.1}O_{1.95}$	550	2.31×10^{2}	3.25×10^{2}	2.02×10^{-6}	2.02×10^{-6}	1.18×10^{3}	2.26×10^{-5}	2.24×10^{-7}	7.33×10^{3}	1.78×10^{-3}	9.86×10^{-3}
				1.00			0.44			0.60	
	650	66.96	75.76	1.89×10^{-6}	1.07×10^{-6}	121.4	1.87×10^{-4}	6.40×10^{-7}	4.55×10^{2}	5.74×10^{-3}	1.26×10^{-2}
				0.94			0.40			0.55	

Table S4 Fitting parameters of the impedance for $Ce_{0.6}RE_{0.3}Mo_{0.1}O_{1.95}$ (RE = Sm, Gd) in air at 750 ^{o}C.

			Q2 (F)			Q3 (F)	
Compound	R1 (Ω)	R2 (Ω)	n2	C2(F)	R3 (Ω)	n3	C3(F)
$Ce_{0.6}Sm_{0.3}Mo_{0.1}O_{1.95}$	31.61	30.33	6.11×10^{-6}	5.41×10^{-7}	40.54	2.78×10^{-2}	3.41×10^{-2}
			0.78			0.37	
$Ce_{0.6}Gd_{0.3}Mo_{0.1}O_{1.95}$	32.76	29.81	9.94×10^{-6}	6.63×10^{-7}	41.95	1.51×10^{-2}	9.21×10^{-3}
			0.75			0.48	



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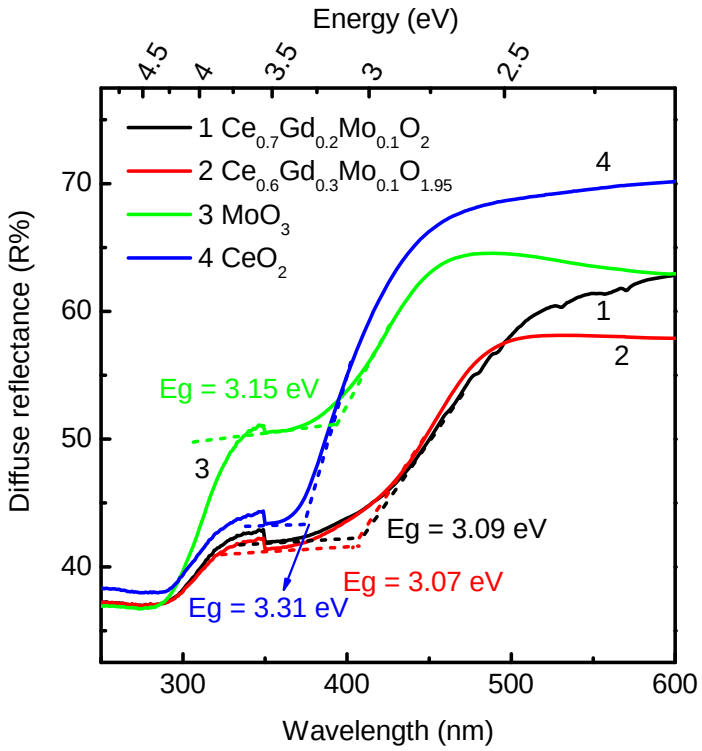

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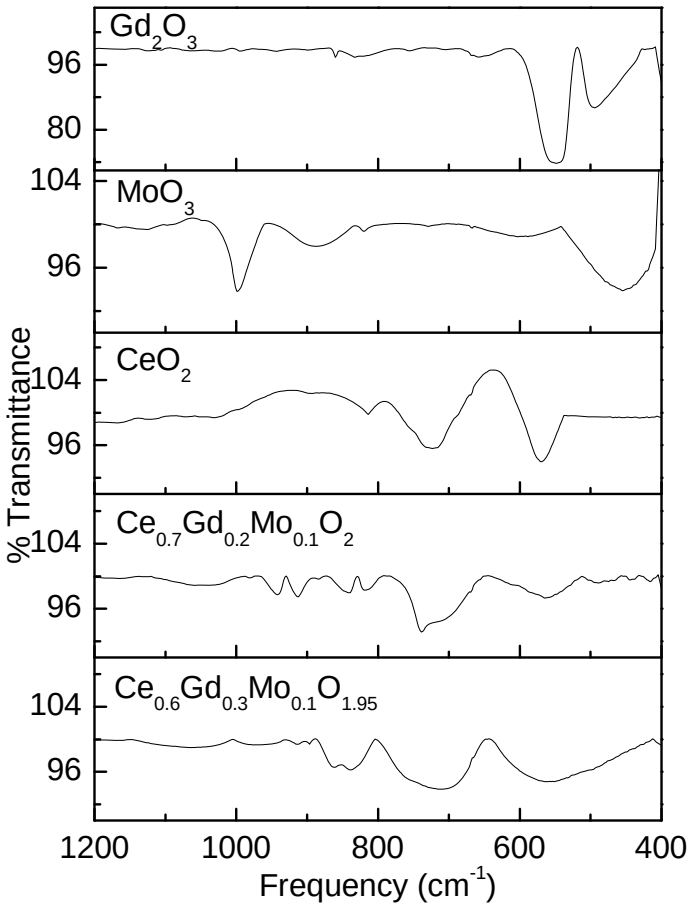

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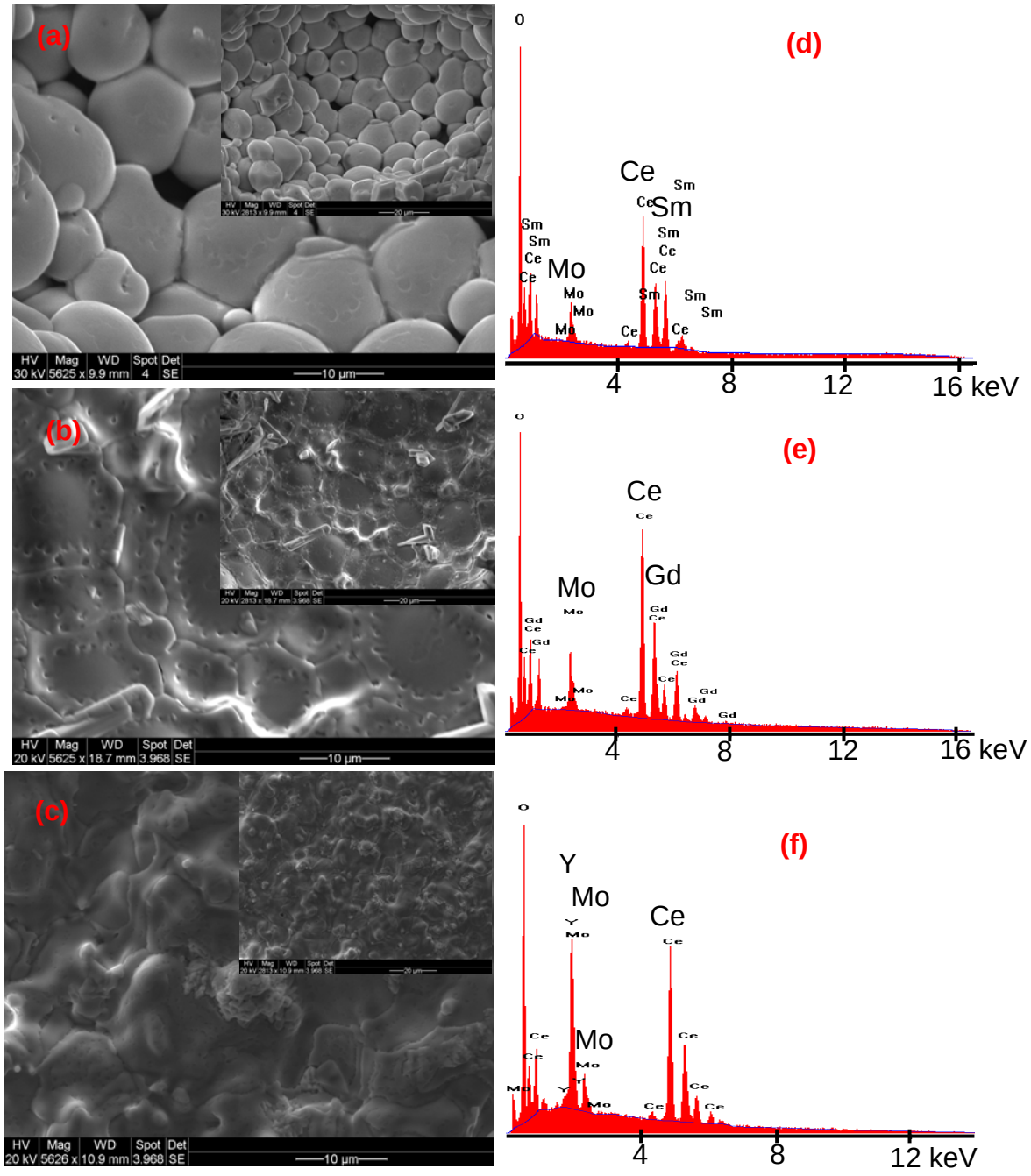

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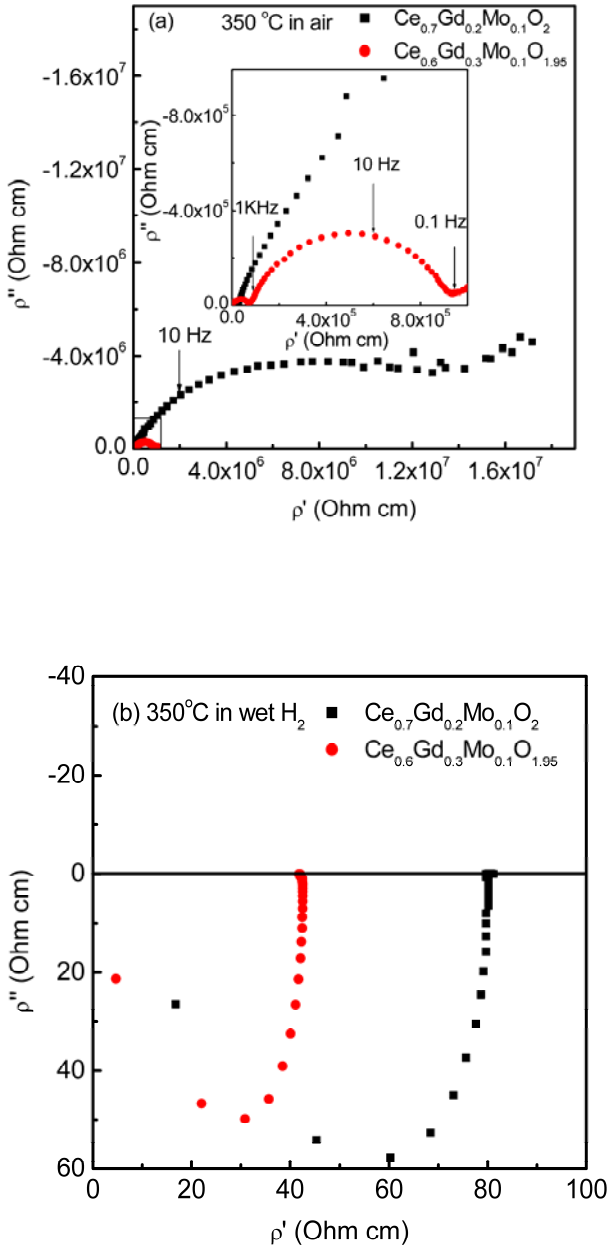

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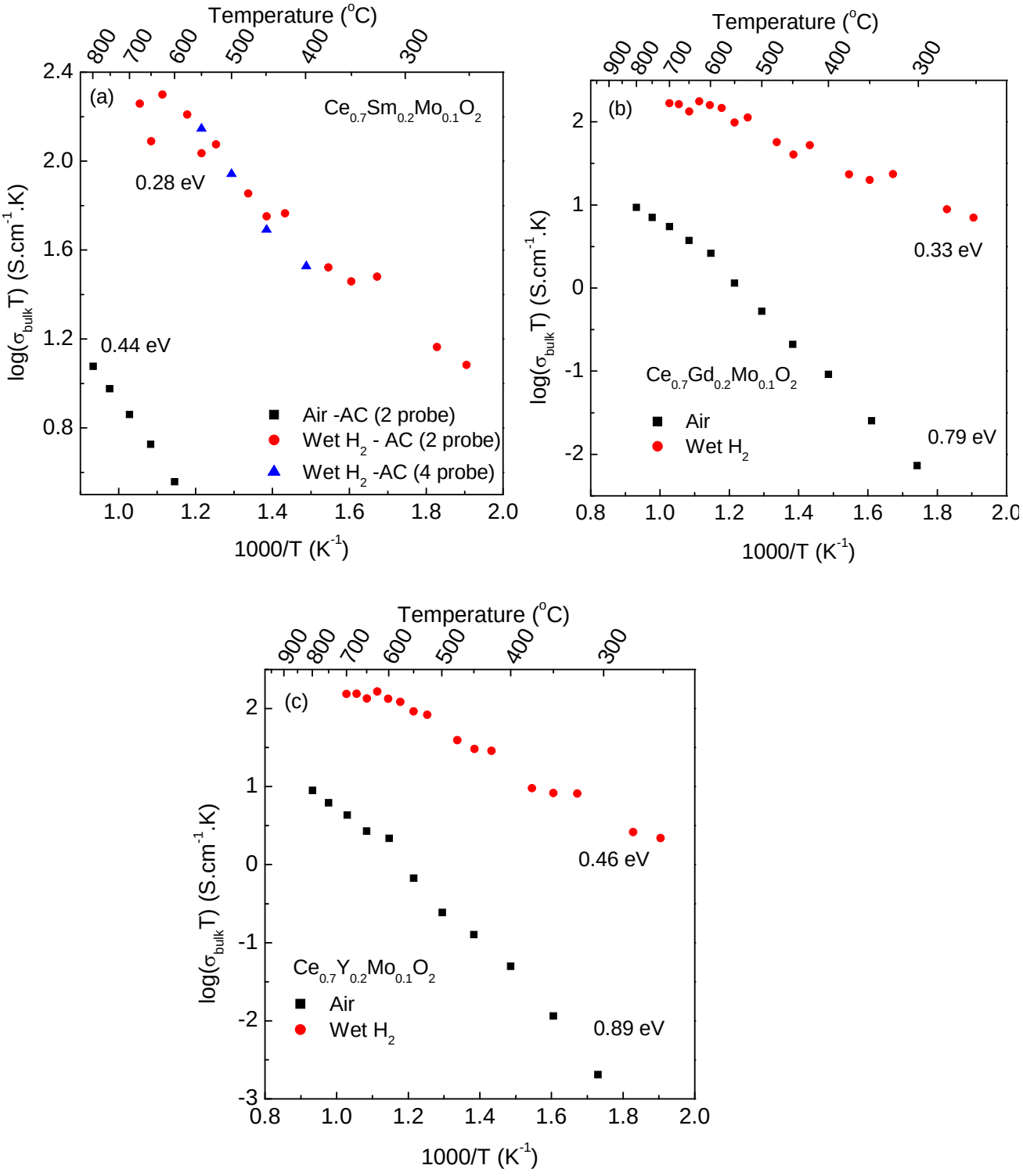

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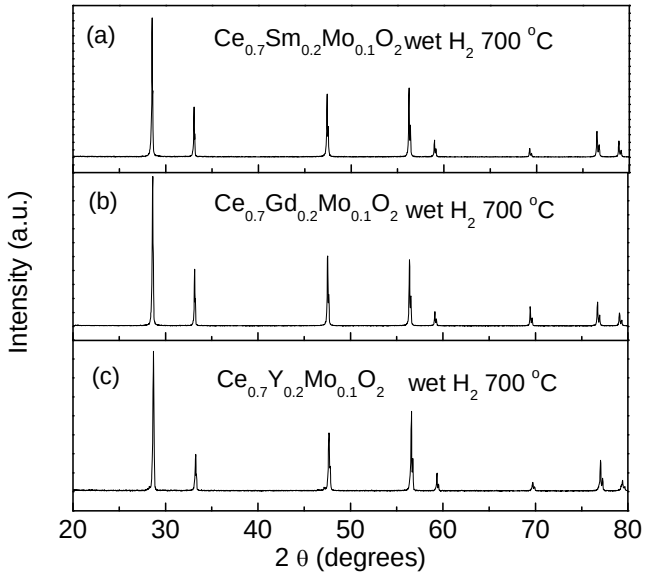

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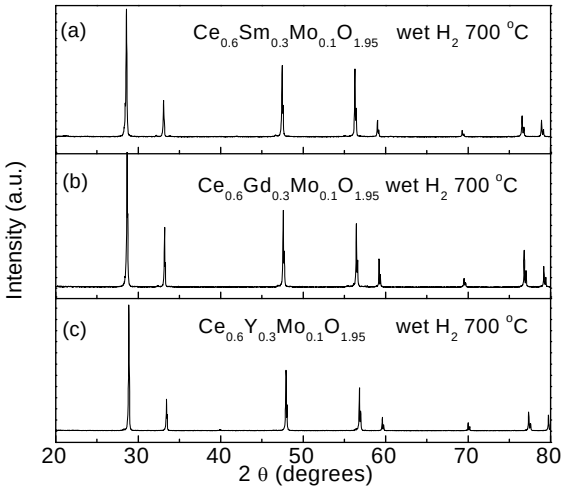

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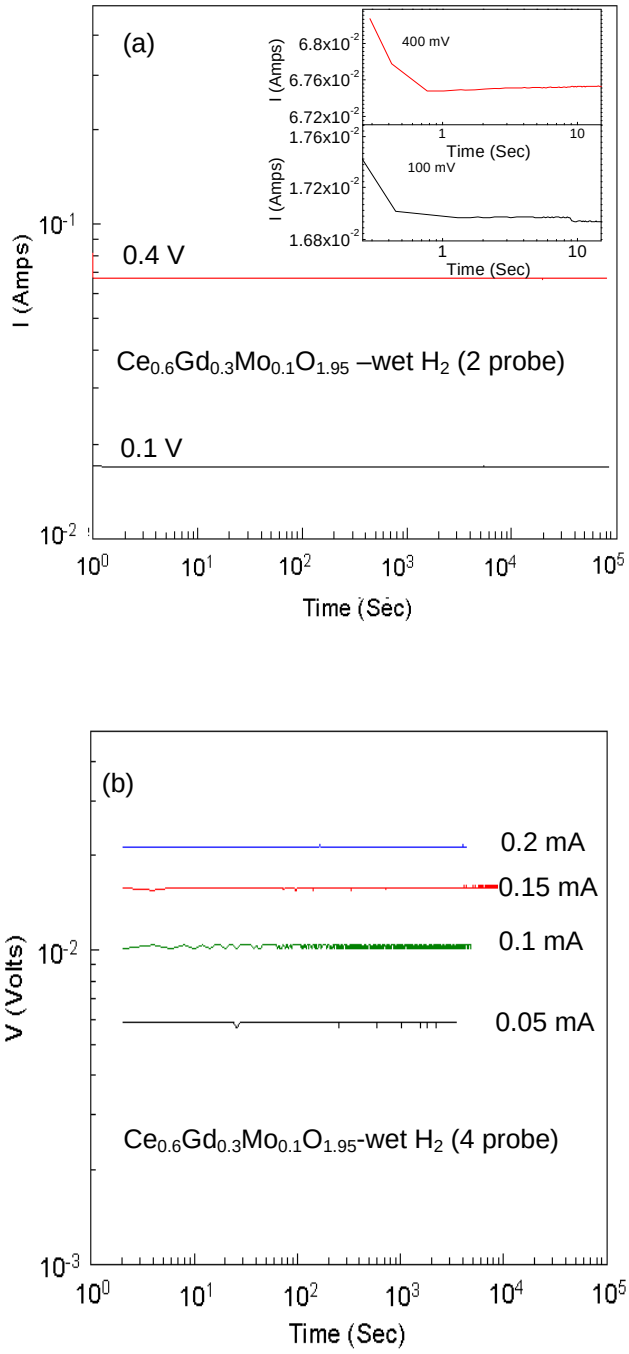

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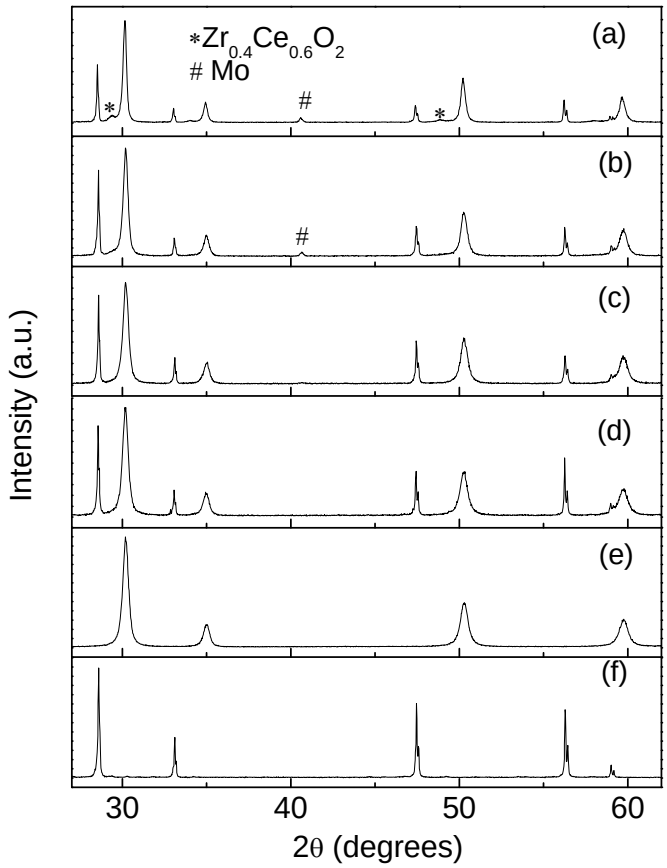

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