Supplementary Information

Enhanced Dielectric Properties with a Significantly Reduced Loss Tangent in (Mg^{2+}, Al^{3+}) Co–Doped $CaCu_3Ti_4O_{12}$ Ceramics: DFT and Experimental Investigations

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Table 1S Electrical factors calculated from modulus spectroscopy of the CCTO sample.

T (°C)	T (K)	1000/T (1/K)	f_{max}	w_{max}	M''_{max}	$2M''_{max}$	C_{gb} (F/m)	R_{gb} (Ω)	R_{gb} (Ω·cm)
30.0	303.0	3.3	177.8	1116.8	1.31E-05	2.62E-05	6.07E-09	1.48E+05	2.65E+05
40.0	313.0	3.2	374.7	2354.3	1.33E-05	2.67E-05	5.97E-09	7.11E+04	1.28E+05
50.0	323.0	3.1	697.6	4382.9	1.36E-05	2.71E-05	5.87E-09	3.89E+04	6.99E+04
60.0	333.0	3.0	1470.5	9239.4	1.38E-05	2.75E-05	5.78E-09	1.87E+04	3.36E+04
70.0	343.0	2.9	2737.5	17200.4	1.40E-05	2.79E-05	5.70E-09	1.02E+04	1.83E+04
80.0	353.0	2.8	4500.7	28278.5	1.43E-05	2.85E-05	5.58E-09	6.34E+03	1.14E+04
90.0	363.0	2.8	8378.7	52644.6	1.46E-05	2.92E-05	5.46E-09	3.48E+03	6.25E+03
100.0	373.0	2.7	13775.0	86550.9	1.50E-05	3.01E-05	5.29E-09	2.18E+03	3.93E+03
110.0	383.0	2.6	29038.1	182451.8	1.65E-05	3.29E-05	4.83E-09	1.13E+03	2.04E+03
30.0	303.0	3.3	177.8	1116.8	1.31E-05	2.62E-05	6.07E-09	1.48E+05	2.65E+05

Table 2S Electrical factors calculated from modulus spectroscopy of the Mg05Al05 sample.

T (°C)	T (K)	1000/T (1/K)	f_{max}	w_{max}	M''_{max}	$2M''_{max}$	C_{gb} (F/m)	R_{gb} (Ω)	R_{gb} (Ω·cm)
90.0	363.0	2.8	45.3	284.6	6.44E-06	1.29E-05	1.19E-08	2.95E+05	5.12E+05
100.0	373.0	2.7	84.3	529.8	6.50E-06	1.30E-05	1.18E-08	1.60E+05	2.77E+05
110.0	383.0	2.6	177.8	1116.8	6.56E-06	1.31E-05	1.17E-08	7.67E+04	1.33E+05
120.0	393.0	2.5	330.9	2079.2	6.64E-06	1.33E-05	1.15E-08	4.17E+04	7.22E+04
130.0	403.0	2.5	544.0	3418.3	6.75E-06	1.35E-05	1.14E-08	2.57E+04	4.46E+04
140.0	413.0	2.4	1012.8	6363.6	6.91E-06	1.38E-05	1.11E-08	1.42E+04	2.45E+04
150.0	423.0	2.4	1665.1	10462.2	7.14E-06	1.43E-05	1.07E-08	8.91E+03	1.54E+04
160.0	433.0	2.3	3099.8	19476.9	7.47E-06	1.49E-05	1.03E-08	5.00E+03	8.66E+03
170.0	443.0	2.3	5096.3	32021.1	7.81E-06	1.56E-05	9.82E-09	3.18E+03	5.51E+03
180.0	453.0	2.2	9487.5	59612.0	8.07E-06	1.61E-05	9.50E-09	1.77E+03	3.06E+03

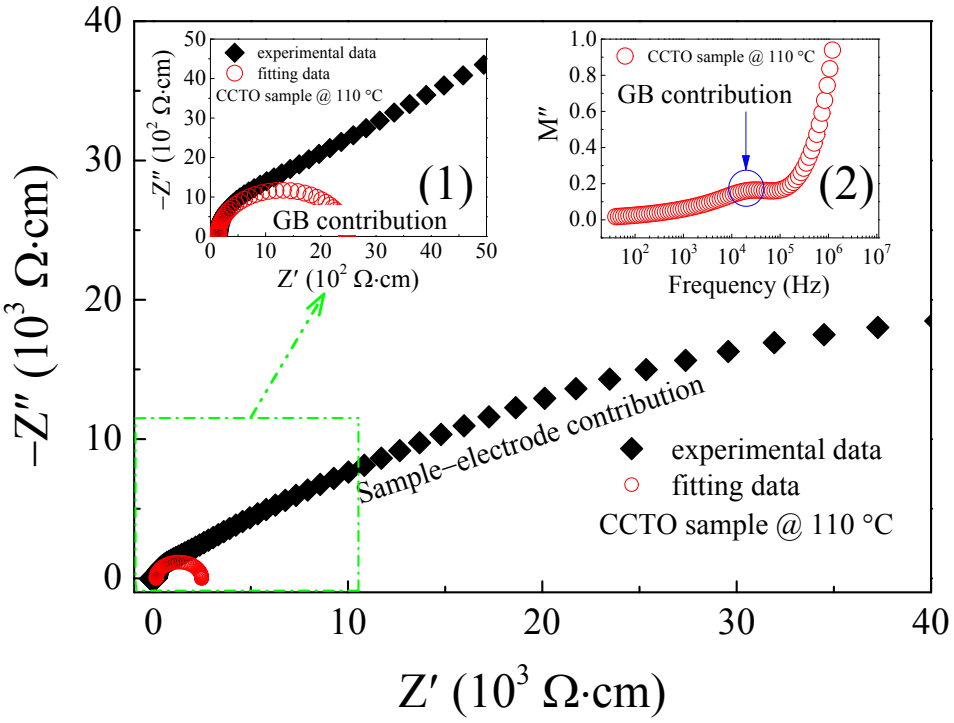

Fig. 1S The Z* plot at 110 °C of the CCTO sample. Insets (1) and (2) show the enlarged scale of the Z* plot and frequency dependence of M″ of this sample, respectively.

Fig. 1S and its inset (1) show the Z* plot at 110 °C of the CCTO sample, including influences of GB (red symbol) and sample–electrode contributions. This figure unveils that influence of a sample–electrode contact has much more dominant than that of GBs. As shown in inset (2), a small M″–peak showing the dielectric response in a part of GBs, it was found that the influence of a sample–electrode contact can be dominated in a frequency range below ~10^4 Hz. In a higher frequency than 10^4, the dielectric response

induced by GBs is observed. To compare the influence of co–doping on the grain boundary resistance, the sample–electrode contribution must be removed. Therefore, in this work, the authors have used modulus spectroscopy to estimate the grain boundary resistance of samples. The equation for calculation is given in the manuscript.

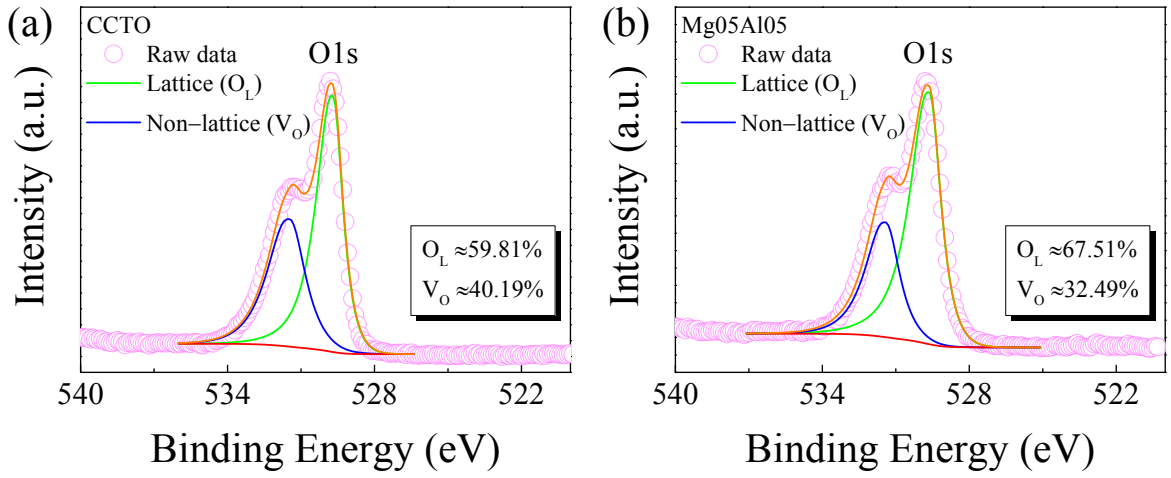

Fig. 2S XPS O1*s* spectra of the CCTO and Mg05Al05 ceramics.

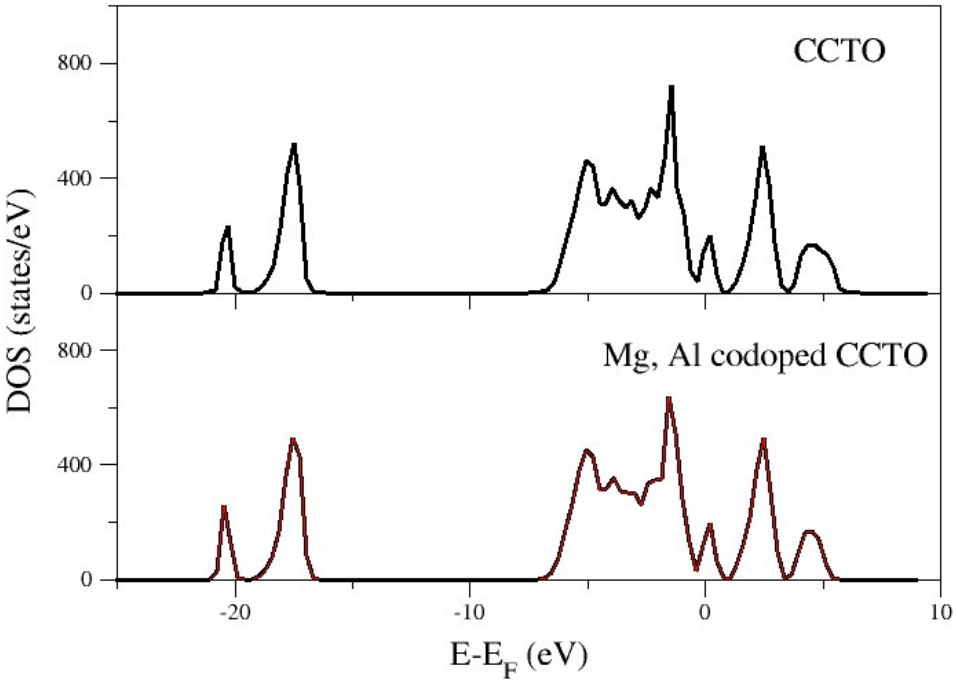

Fig. 3S Total density of states of the CCTO and the Mg and Al codoped CCTO. E_F stands for the Fermi energy.

As clearly presented in Fig. 3S, we also evaluate the optical property related to the energy band theory such as total density of states of CCTO and the Mg^{2+} and Al^{3+} co-doping CCTO. These results were found in Fig. 4s of the supplementary information. It was found from our calculations that the DOS of both structure are almost identical. Therefore, the optical property of the CCTO and Mg05Al05 is indifferent.

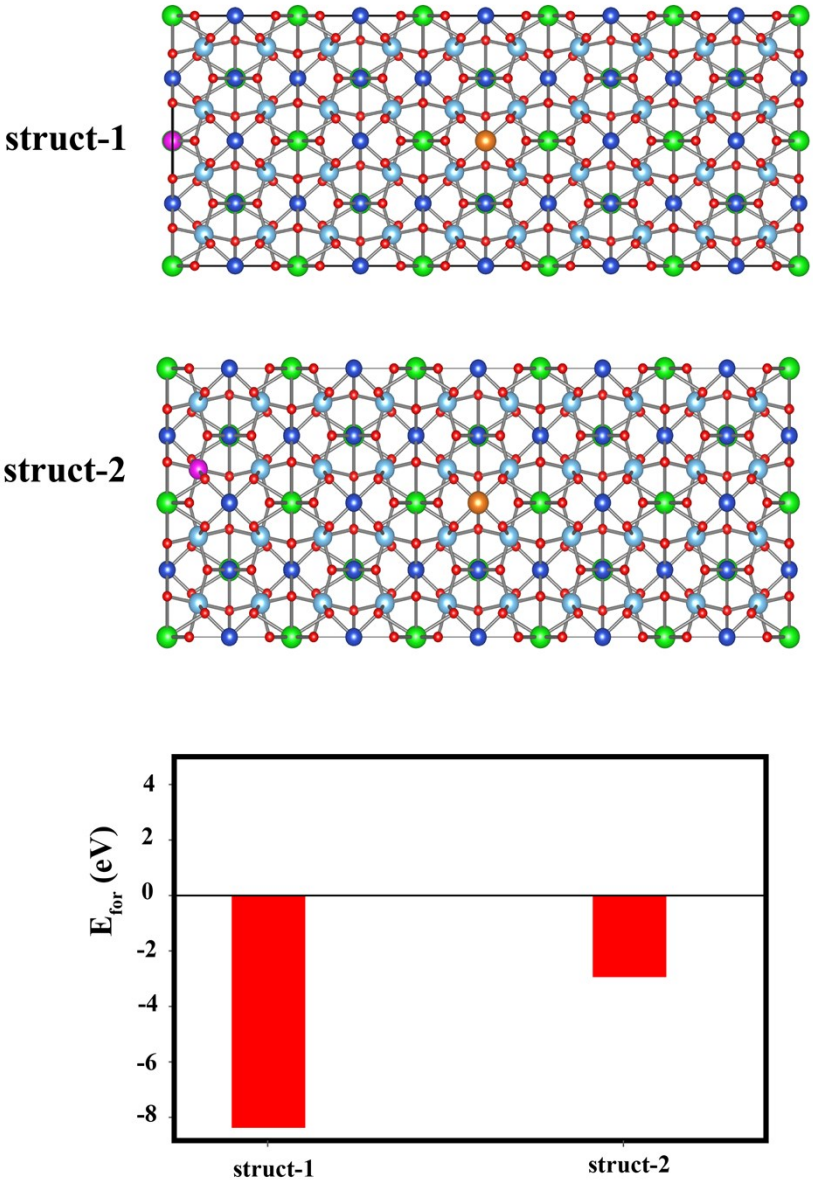

Fig. 4S Formation Energy (E_{for}) of Struct-1 and Struct-2 configurations. For Struct-1, both Mg and Al are substituted at Cu sites. For Struct-2, Mg is replaced at Cu site,

whereas Al is substituted at Ti site. Green, light blue, red, blue, orange and magenta balls are denoted by Ca, Ti, O, Cu, Mg and Al, respectively.

Based on the the ionic radii and coordination numbers, the ionic radius of Mg^{2+} with 4 nearest neighbours is equal to that of Cu^{2+}, namely 0.57 Å. Although, the atomic radius of Ca^{2+} with 6 nearest neighbours (1.0 Å) is larger than that of Mg^{2+}. Hence, Mg^{2+} dopant might substitute at Cu site. Al^{3+} with 4 and 6 nearest neighbours has atomic radius of 0.39 and 0.535 Å, respectively. The atomic radius of Ti^{4+} with 6 nearest neighbours is 0.605 Å which is rather close to the radius of Al^{3+} with 6 nearest neighbours. Consequently, Al^{3+} might be replace at either Cu^{2+} or Ti^{4+} site. Based on this analysis, only two possible configurations are considered. For Struct-1, both Mg and Al are occupied at Cu sites in the CCTO host. Struct-2 represents Cu and Ti sites are replaced by Mg and Al atoms, respectively. As presented in Fig. 4S, it was found from our calcualtions that the formation energies of Struct-1 and Struct-2 are -8.20 and -2.18 eV, respectively. It is well known that a stable structure gives the lowest formation energy. Hence, Struct-1 gives the lowest formation energy. In other words, Mg and Al are likely to be occupied at Cu sites simultaneously.