

## Unexpected redox behavior of high surface alumina containing highly dispersed cerium cations

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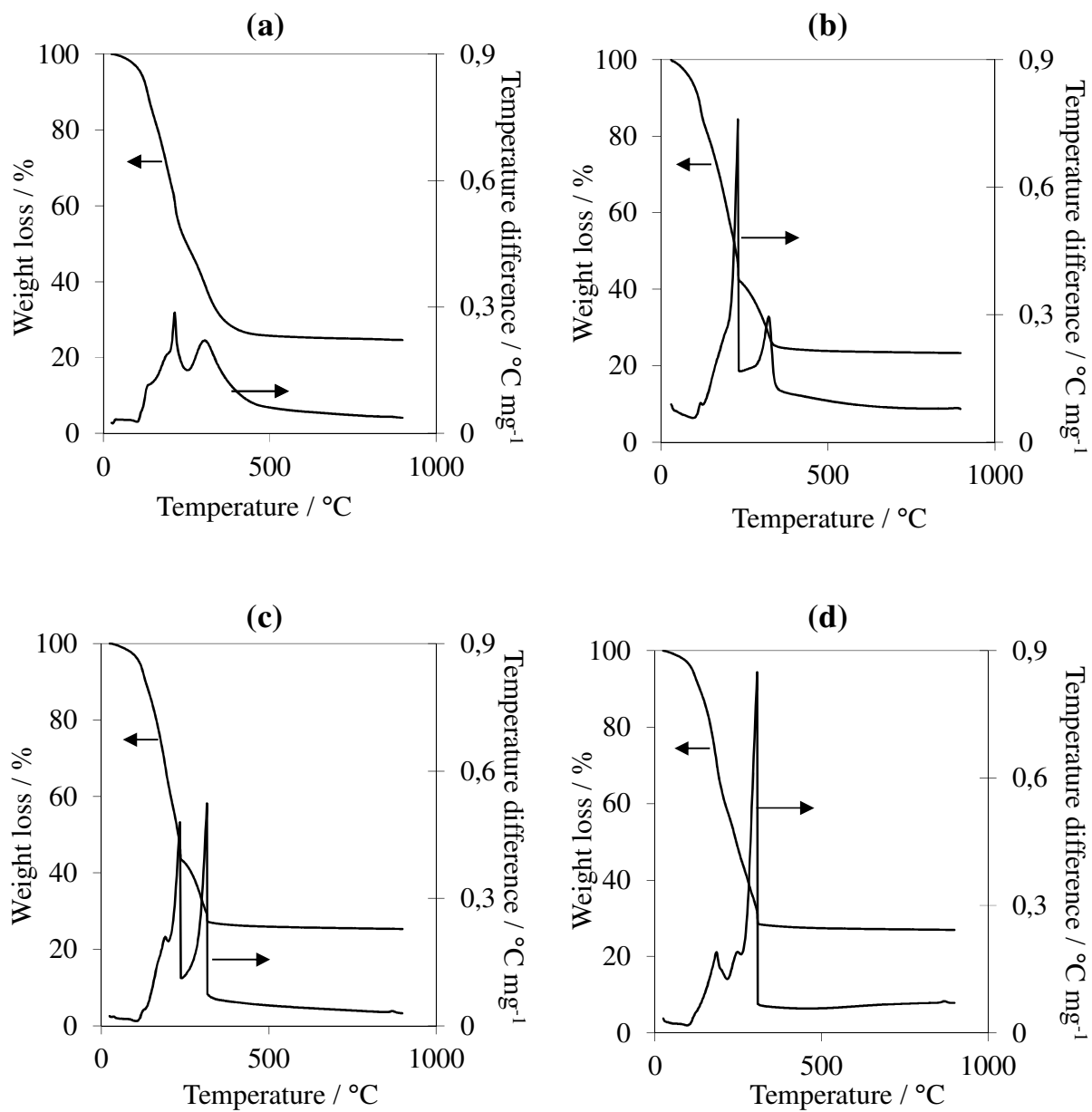
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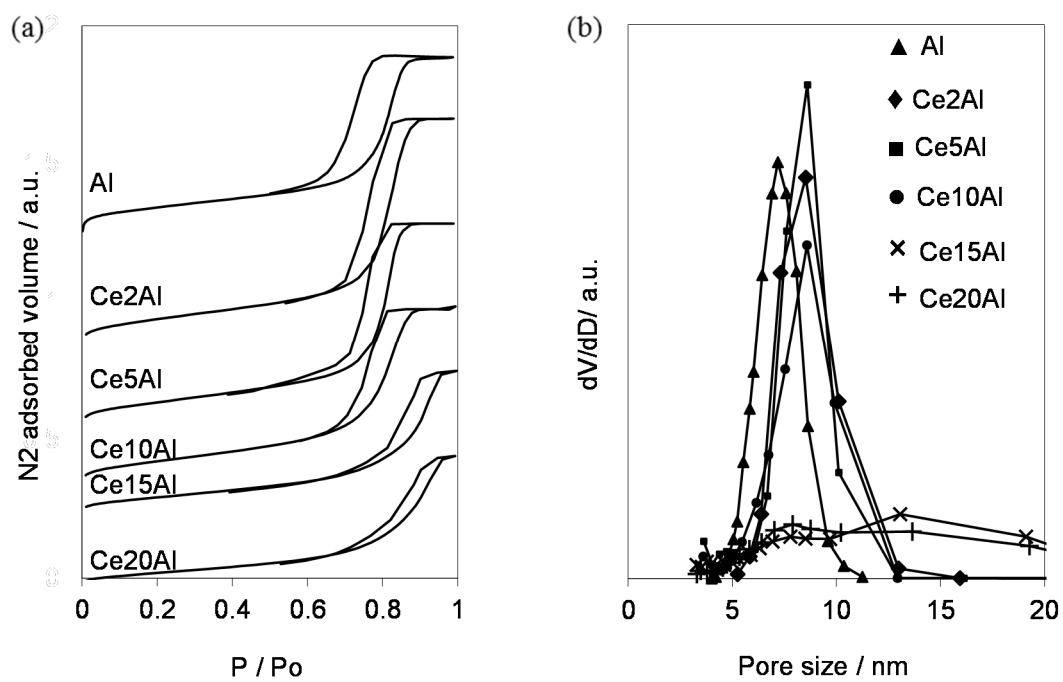
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## SUPPORTING INFORMATION

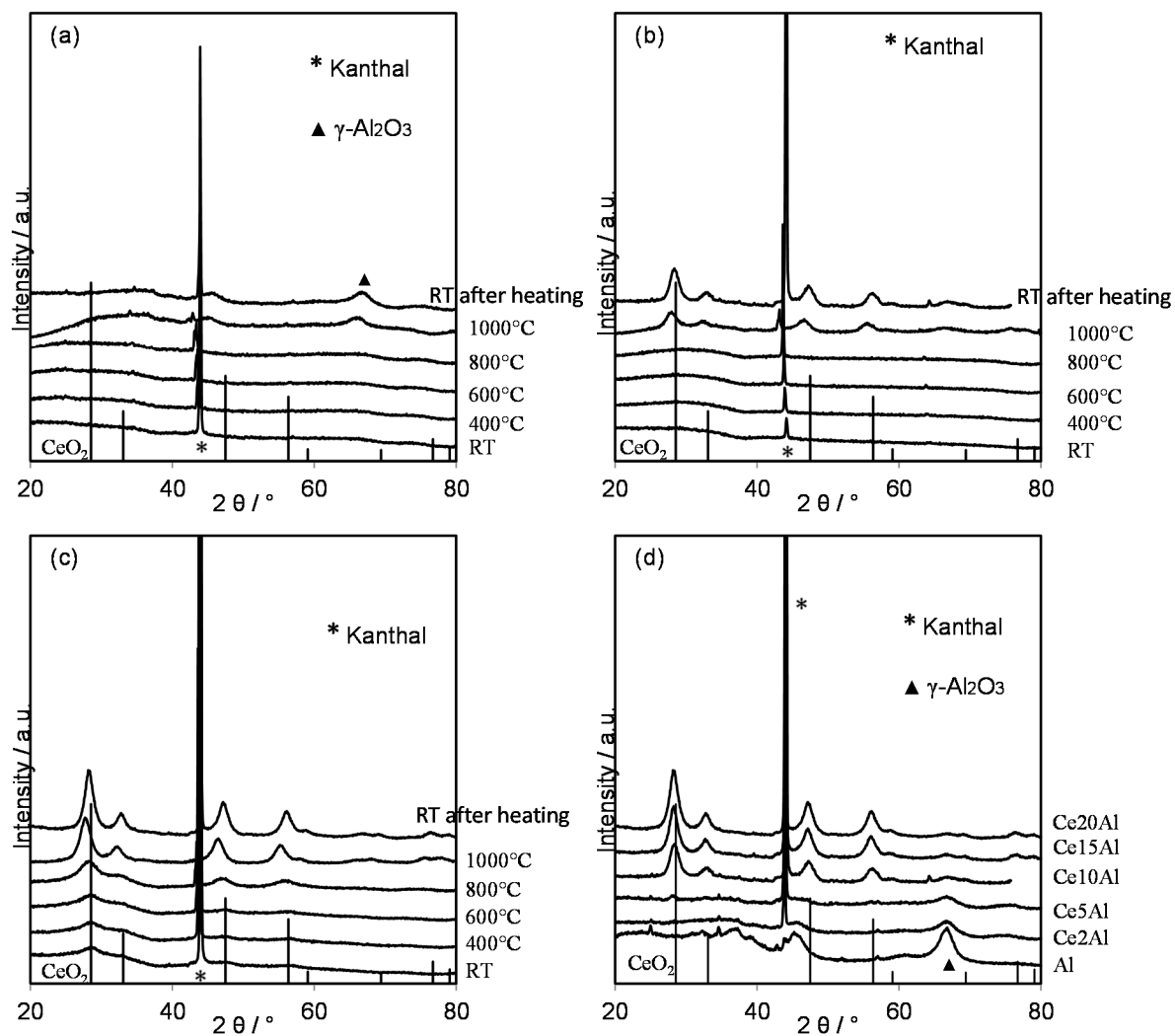
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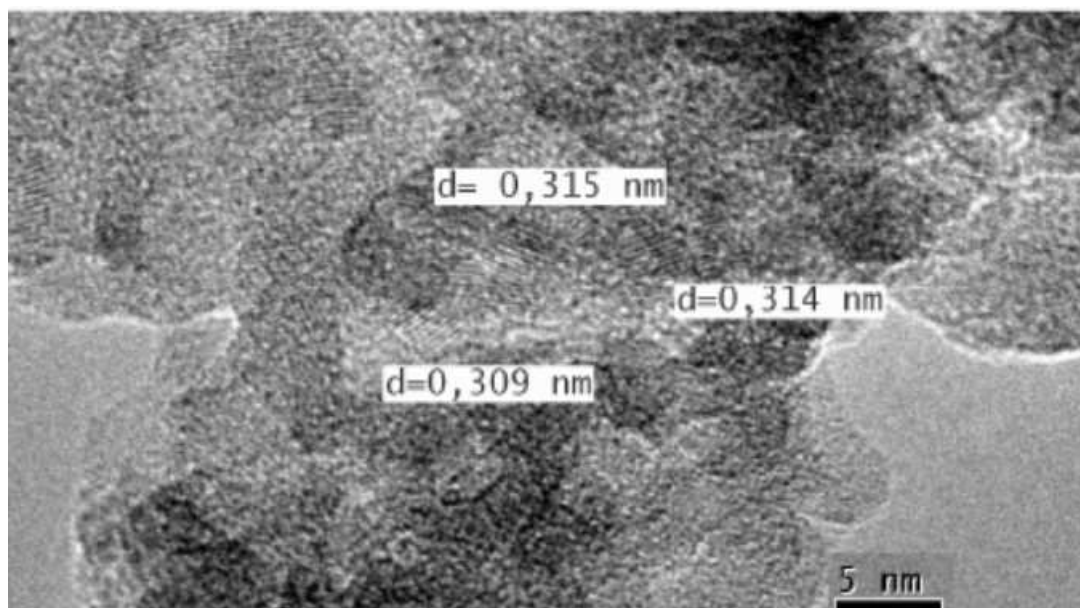
**Figure S1.** TG-DTA profiles for the as-synthesized samples (a) Al, (b) Ce<sub>2</sub>Al, (c) Ce<sub>10</sub>Al and (d) Ce<sub>20</sub>Al.



**Figure S2.** N<sub>2</sub> adsorption-desorption curves (a) and corresponding BJH desorption pore size distribution (b) obtained over the solids after calcination at 600 °C.

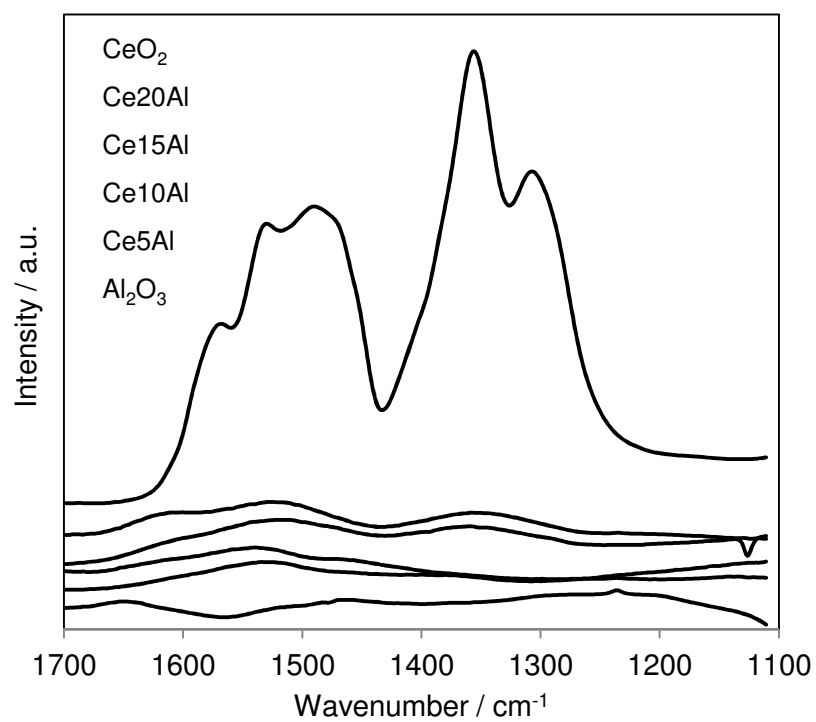


**Figure S3.** X-ray diffraction patterns recorded under air atmosphere on 20 – 80° region at: RT, 400, 600, 800, 1000 °C and RT after heating; for the samples: (a) Ce<sub>2</sub>Al; (b) Ce<sub>10</sub>Al; (c) Ce<sub>20</sub>Al; and all the samples heated up to 1000 °C and cooled down to RT.

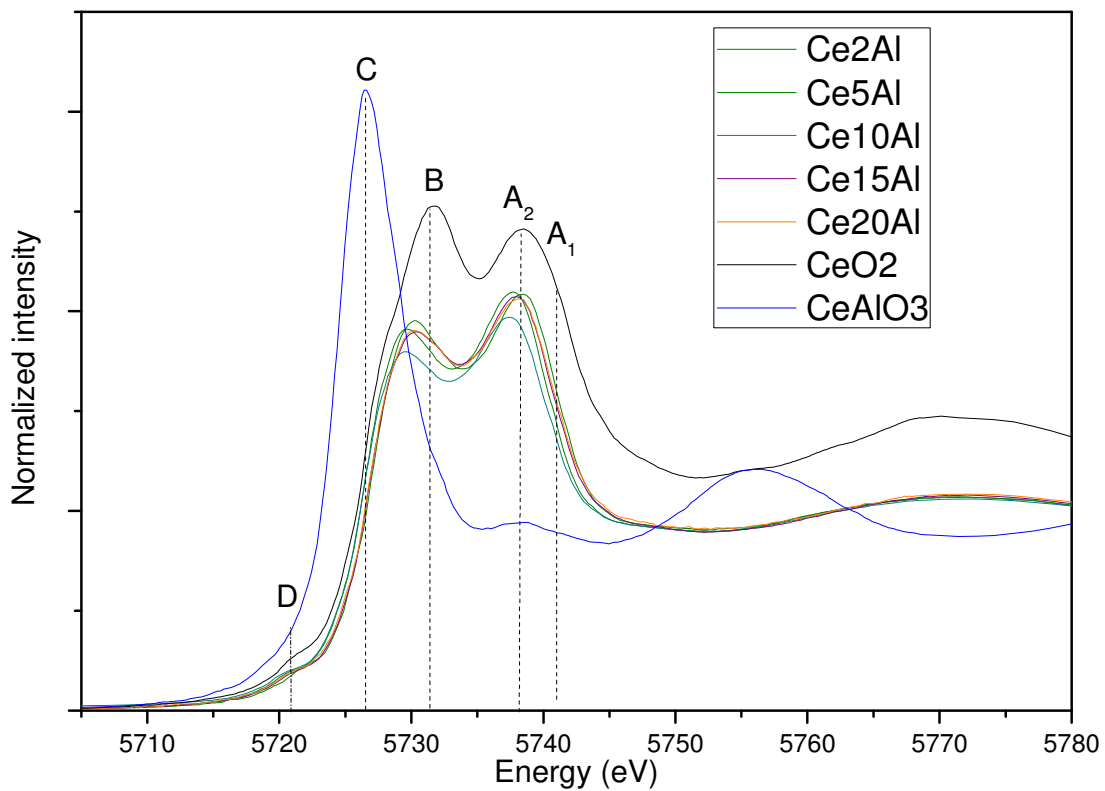


**Figure S4.** TEM picture of Ce<sub>20</sub>Al sample

The mean interplanar spacing measured on some particles matched the distance between two consecutive planes expected for the fluorite cubic phase of cerium dioxide (~0.31 nm).

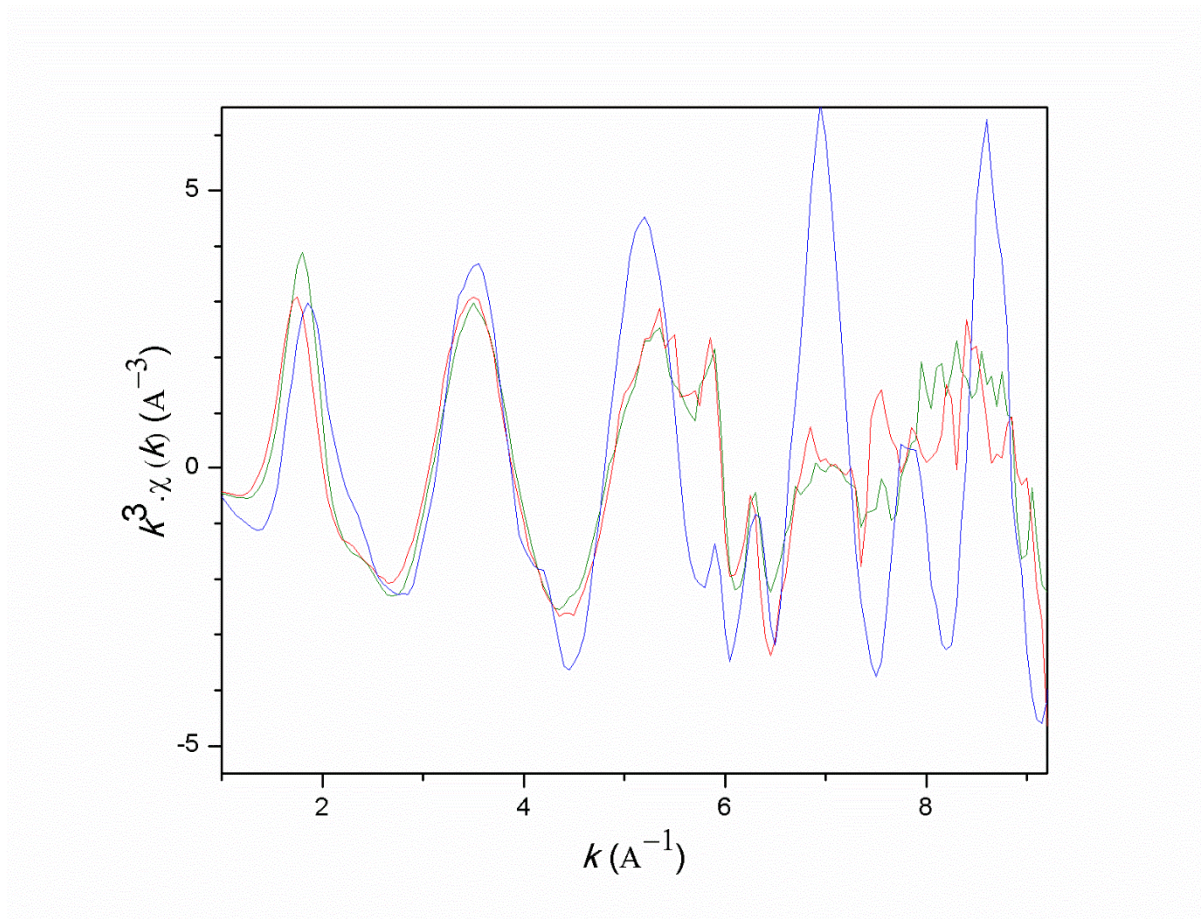


**Figure S5.** FTIR subtraction spectra collected after CO<sub>2</sub> adsorption at RT and desorption under secondary vacuum at 150 °C.

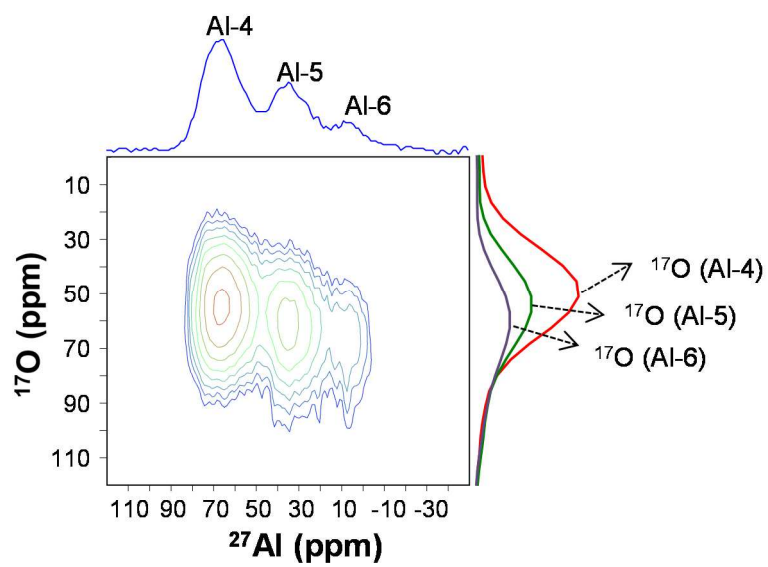


**Figure S6.** Ce L<sub>3</sub> edge XANES spectra of CeO<sub>2</sub>, CeAlO<sub>3</sub> and CeXAl samples at RT. The peaks contributions A<sub>1</sub>, A<sub>2</sub>, B, C and D were assigned as explained in reference [1].





**Figure S7.** EXAFS  $k^3$ -weighted oscillations for Ce10Al (green line), Ce20Al (red line) and CeO<sub>2</sub>. (blue line)



**Figure S8.**  $^{27}\text{Al}$ - $^{17}\text{O}$  heteronuclear correlation spectra of  $^{17}\text{O}$ -exchanged Al sample

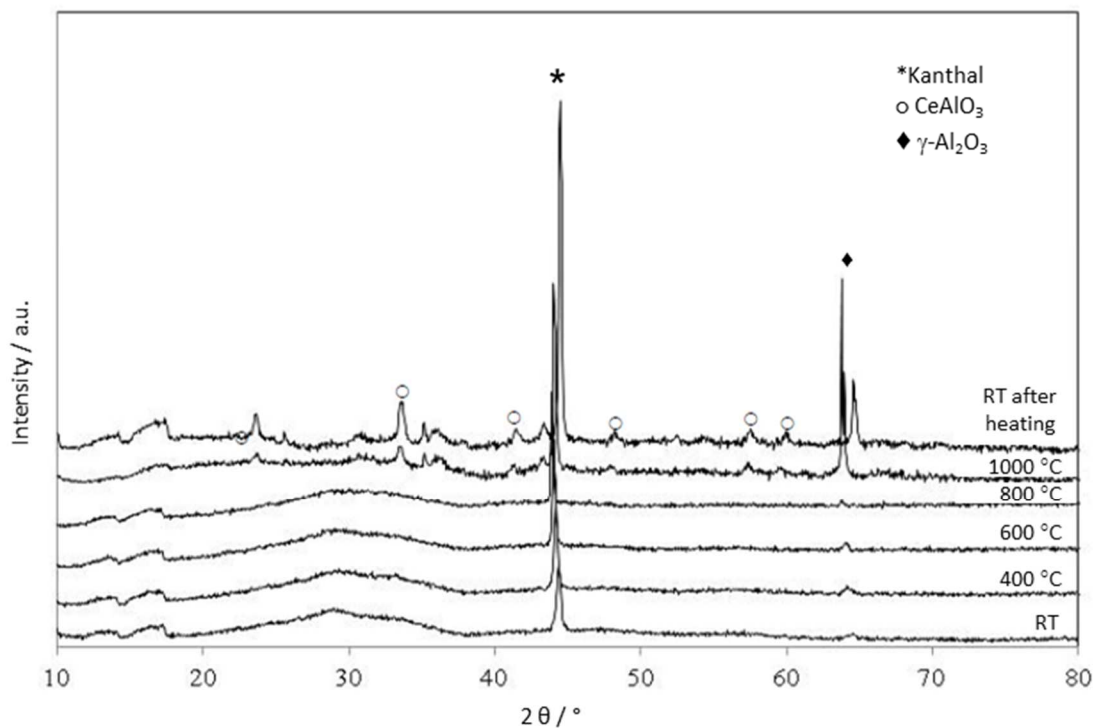


Figure S 9. X-ray diffraction patterns recorded under hydrogen atmosphere on 20 – 80° region at: RT, 400, 600, 800, 1000 °C and RT after heating over Ce15Al sample.

#### Reference

- (1) Nachimuthu, P.; Shih, W.-C.; Liu, R.-S.; Jang, L.-Y.; Chen, J.-M. *J. Solid State Chem.* **2000**, *149* (2), 408–413.