

Mayenite-Based Electride C₁₂A₇e⁻: A Reactivity and Stability Study – Supplementary Information

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Data Analysis EPR Spectroscopy

EPR spectra were analyzed using OriginPro software. For comparison of different experiments, the measured first derivative of the spectra was integrated to obtain the absorption spectra. The absorption peak was then integrated with a linear background correction. For the comparison of the obtained integrals, they were normalized using eq.(1), where I_N is the normalized integral in a.u., I_{EPR} the integral of the absorption peak in a.u, GA the gain, MA the modulation amplitude, MWP the microwave power and m_{sample} the sample mass.

$$I_N = \frac{I_{EPR}}{(GA \cdot MA \cdot m_{sample} \cdot \sqrt{MWP})} \quad (1)$$

Data Analysis DRUVVis Spectroscopy

DRUVVis spectra were processed according to literature [1–4] using the Kubelka-Munk transformation equation:

$$F(R) = \frac{(1 - R)^2}{2R} \quad (2)$$

with R as reflectance and $F(R)$ as the Kubelka-Munk function. The obtained Kubelka-Munk function is used for an estimation of the electron concentration N_e . For this purpose, relation (3) reported by Matsuishi *et al.* [4] is used is used:

$$N_e = \left[\frac{-(E_{sp} - E_{sp}^0)}{0.119} \right]^{0.782} \quad (3)$$

with N_e as number of electrons in 10^{21} cm^{-3} , E_{sp} the position of the maximum of the absorption peak around 2.8 eV in eV, and $E_{sp}^0 = 2.83 \text{ eV}$ for a $N_e = 1 \cdot 10^{18} \text{ cm}^{-3}$. Spectra were analyzed using OriginPro software. Determination of the maximum position was carried out as follows: 1. smoothing the Kubelka-Munk transformed spectra using a FFT filter 2. calculating the first derivative 3. determining the maximum position from the zero value of the first derivative in the range around $E_{sp} = 2.8 \text{ eV}$. The energy resolution of the measurement was 0.01 eV, the error for the determination of the maximum position is estimated to be $\pm 0.02 \text{ eV}$, which results in an error of the number of electrons.

Photographical Documentation

Photographical documentation of samples was done using a tripod station with an illumination system and a Canon EOS 1000D with an EFS 18-55 mm Image Stabilizer Macro 0.25 m/0.8 ft or an EF 100 mm f/2.8 Macro USM lens.

TEM Experiments

TEM measurements were done with a FEI Osiris TEM. The acceleration voltage was 200 kV. The samples were prepared by dispersing the sample with EtOH between two glass object slides. In this dispersion a graphite-covered Cu net was dipped, which is used as sample holder for the measurement.

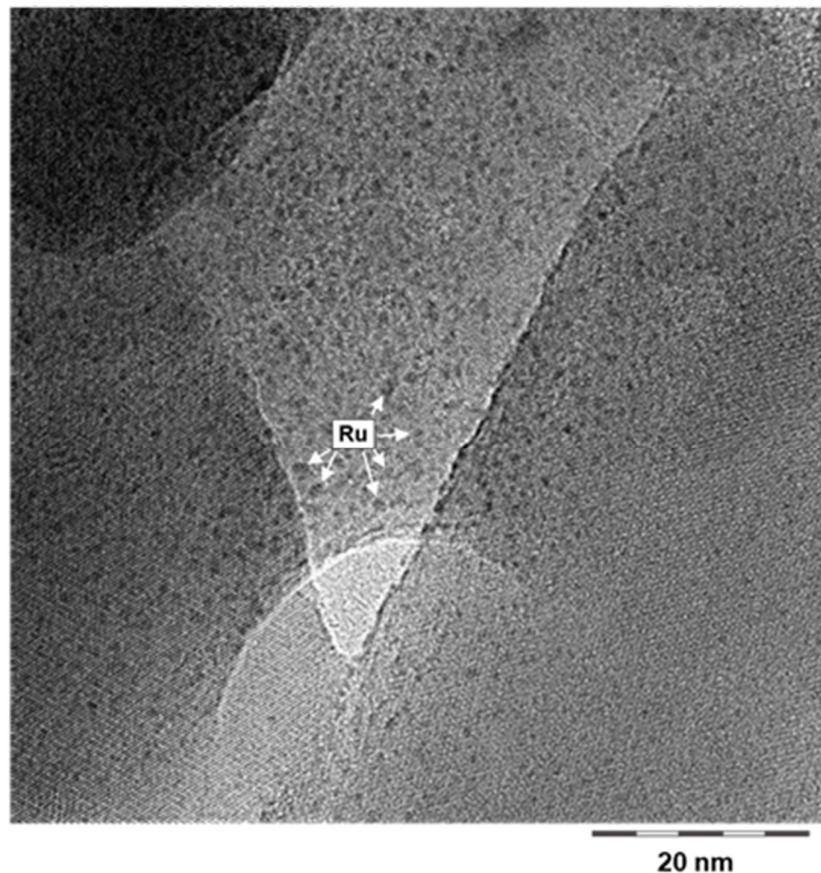


Figure S1. Bright-field TEM measurement of the sample Ru/C12A7e⁻ (20Al) showing Ru nanoparticles with sizes of about 2 nm on the C12A7e⁻ support material.

PXRD after Ru Deposition on C12A7e⁻

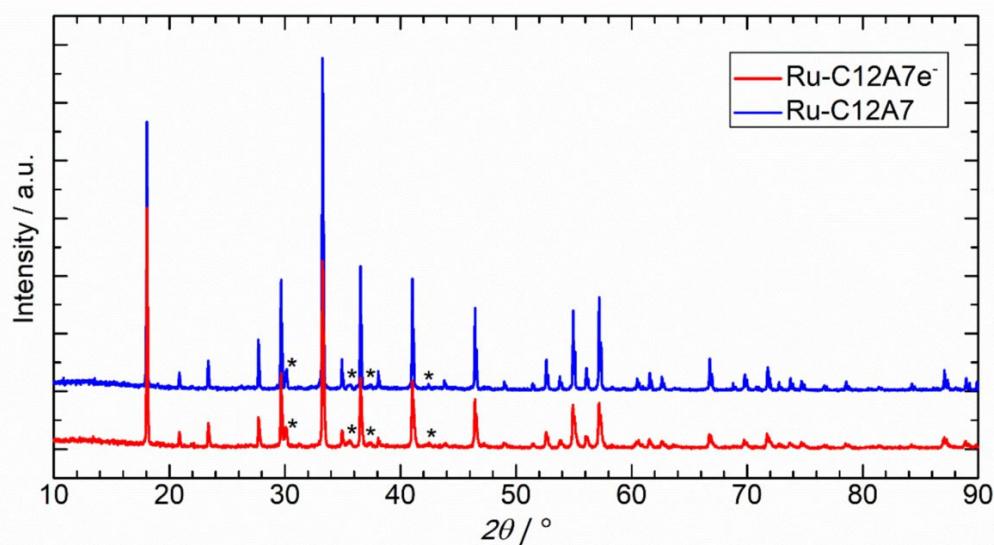


Figure S2. PXRD after Ru deposition on plasma synthesized C12A7e⁻ (3C) (red) and C12A7 (blue) samples showing the presence of the mayenite structure and minor secondary krotite formation (*). No Ru reflections could be observed by PXRD.

Rietveld Refinements of Samples Obtained from Hydrogenation Experiments

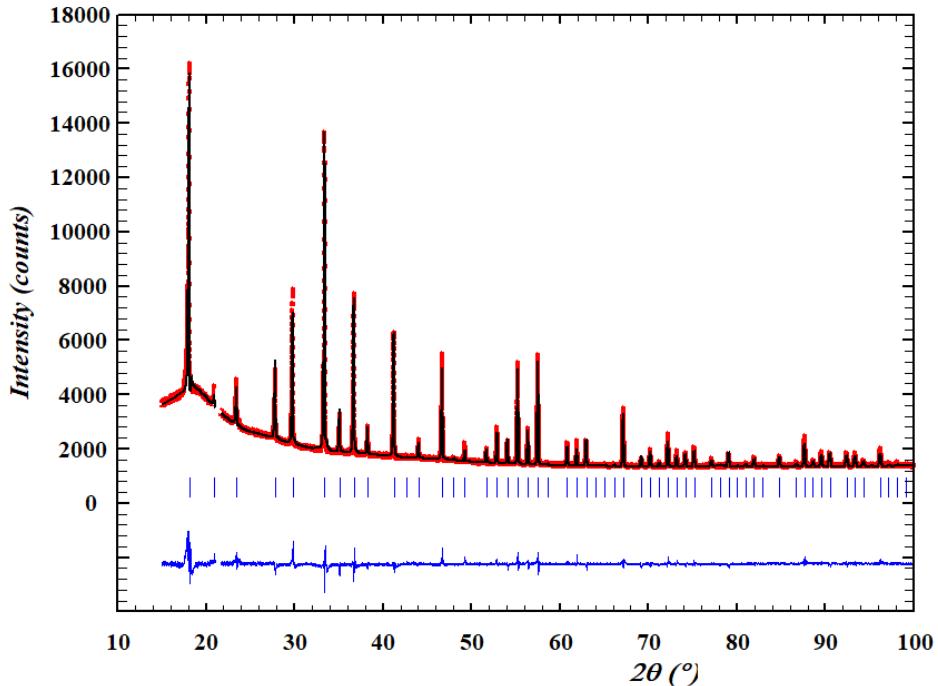


Figure S3. Rietveld refinement of the crystal structure of mayenite electride (vacuum sintering-based C₁₂A₇e⁻ (e) sample) based on X-ray diffraction data (Huber G670, λ : Cu- $K_{\alpha 1}$, $R_{wp} = 2.32\%$, $GoF = 1.37$, $21.1^\circ \leq 2\theta \leq 21.7^\circ$ excluded because of contribution of the sample holder). Bragg markers denote Bragg reflection positions of mayenite electride C₁₂A₇e⁻ (e) sample ($I\bar{4}3d$, $R_{Bragg} = 12.2\%$, $a = 11.9790(2)\text{\AA}$). Red: measurement (*meas*), black: calculated (*calc*), blue: difference *meas-calc*.

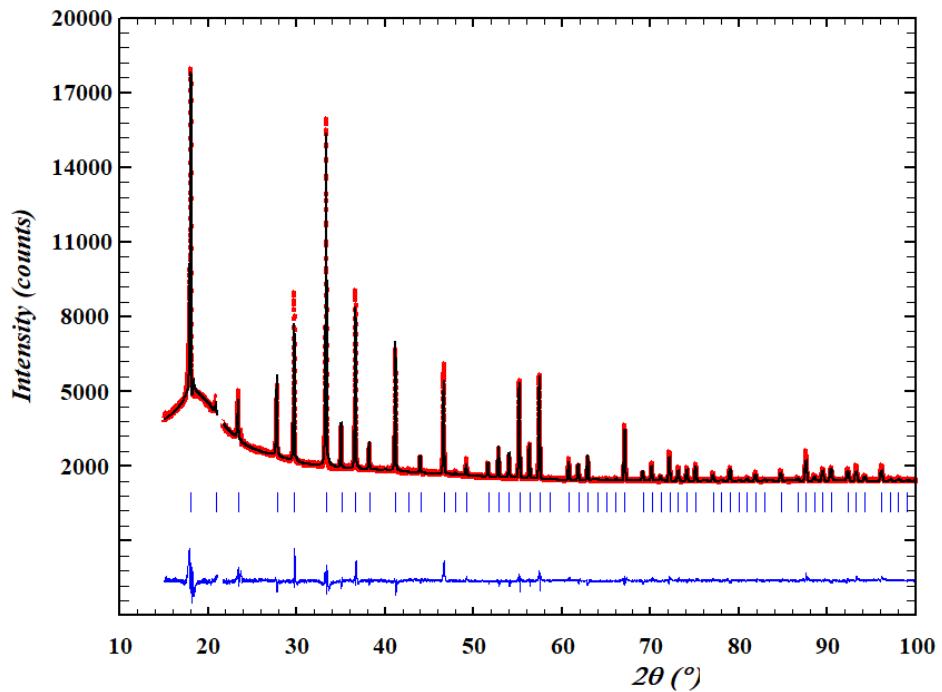


Figure S4. Rietveld refinement of the crystal structure of the deuteride of mayenite electride (C12A7:D (k) sample) based on X-ray diffraction data (Huber G670, λ : Cu- $K_{\alpha 1}$, $R_{wp} = 3.30\%$, $GOF = 1.49$, $21.1^\circ \leq 2\Theta \leq 21.7^\circ$ excluded because of contribution of the sample holder). Bragg markers denote Bragg reflection positions of the deuteride of mayenite electride C12A7:D (k) sample ($I\bar{4}3d$, $R_{Bragg} = 10.9\%$, $a = 11.9874(1)$ Å). Red: measurement (*meas*), black: calculated (*calc*), blue: difference *meas-calc*.

References

- [1] Matsuishi, S., Toda, Y., Miyakawa, M., Hayashi, K., Kamiya, T., Hirano, M., Tanaka, I., Hosono, H. *High-density electron anions in a nanoporous single crystal: $Ca_{24}Al_{28}O_{64}^{4+}(4e^-)$* , *Science* **2003**, *301*, 626-629. 10.1126/science.1083842.
- [2] Matsuishi, S., Nomura, T., Hirano, M., Kodama, K., Shamoto, S., Hosono, H. *Direct Synthesis of Powdery Inorganic Electride $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$ and Determination of Oxygen Stoichiometry*, *Chem. Mater.* **2009**, *21*, 2589-2591. 10.1021/cm9007987.
- [3] Kim, S.W., Shimoyama, T., Hosono, H. *Solvated electrons in high-temperature melts and glasses of the room-temperature stable electride $Ca_{24}Al_{28}O_{64}^{4+}\cdot 4e^-$* , *Science* **2011**, *333*, 71-74. 10.1126/science.1204394.
- [4] Matsuishi, S., Kim, S.W., Kamiya, T., Hirano, M., Hosono, H. *Localized and Delocalized Electrons in Room-Temperature Stable Electride $[Ca_{24}Al_{28}O_{64}]^{4+}(O^{2-})_{2-x}(e^-)_{2x}$ Analysis of Optical Reflectance Spectra*, *J. Phys. Chem. C* **2008**, *112*, 4753-4760. 10.1021/jp711631j.