## Supporting information for: Superconductivity in an inorganic electride 12CaO·7Al<sub>2</sub>O<sub>3</sub>:e<sup>-</sup>.

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## **Experimental section**

The single-crystal electride was prepared by a reduction treatment of  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  (C12A7) single-crystal using Ti metal. The single-crystal ingot, grown by a floating zone method, was cut into  $\sim 4 \times 15 \times 2 \text{ mm}^3$  (sample A) and  $\sim 2 \times 6 \times 1 \text{ mm}^3$  (sample B) blocks. Each block was sealed in a silica glass tube with a Ti metal shot under a vacuum of  $\sim 10^{-1}$  Pa and then the sealed tube was heated at  $1100^{\circ}\text{C}$  for 24 h. During the heating the extra-framework oxygen ions were almost exclusively replaced with electrons as a result of reactions: Ti (surface) +  $xO^{2-}$  (cage)  $\rightarrow$  TiO<sub>x</sub> (surface) + 2xe<sup>-</sup> (cage). The TiO<sub>x</sub> layer on the surface was mechanically removed before subsequent measurements.

The electride thin films were fabricated by a reduction of a C12A7 film on  $Y_3Al_5O_{12}$  (YAG) substrate through a two-step C12A7 film deposition process. First, an a-C12A7 film was deposited on a YAG(100) single-crystal substrate by a pulsed laser deposition (PLD) method at room-temperature (RT) in  $O_2$  pressure of ~1×10<sup>-4</sup> Pa, followed by a post-annealing at 1000°C in dry  $O_2$  atmosphere for crystallization. Then, a-C12A7 film with a thickness of ~30 nm was deposited again on the crystallized C12A7 film by the PLD. Since the deposition was performed in the reducing atmosphere, the deposited amorphous thin films are oxygen-deficient. Thus, almost all of the extra-framework oxygen ions in the crystallized film were transferred to the amorphous film during the deposition and cooling processes.

Cross-sectional structure of the films was characterized by a high-resolution transmission electron microscopy operating at 400 kV using JEM-4000EX (JEOL). Hall voltage measurements of thin film electrides were performed by a van der Pauw method at RT using an ac magnetic field Hall measurement equipment (Toyo Technica). Optical absorption spectra in a visible region were measured using a spectrophotometer (Hitachi U4000). Electrical resistivity measurements were carried out by a four-probe method in the range 2-300 K using a Physical Properties Measurement System (Quantum Design). They were extended down to 85 mK in a dilution refrigerator. An ac magnetic susceptibility was taken by recording the change in the mutual inductance between two small coils at 120 Hz with a conventional lock-in amplifier. The coil response was calibrated by measuring aluminum and titanium bulk metals with similar size and shape.

## Additional data of the C12A7 electride thin films by TEM and optical measurements.

The figure S1 below shows TEM images and optical properties of (100)-oriented C12A7 electride films on YAG(100) substrate.



Figure S1. (A) Cross-sectional images of a transmission electron microscopy and electron diffraction patterns of the C12A7 electride thin film on YAG(100) substrate. (Top) high-resolution image of near the interface, and (bottom) a whole image. (B) Internal optical transmission and absorption coefficient spectra of C12A7 electride thin film (245-nm thickness) on YAG(100) in the visible region (400~800 nm) at room-temperature. The average internal-transmission is ~60 %. Inset shows a photo of the thin film.