S1. Rietveld refinement profiles from combined refinement using 295 K a) XRPD data, b) backscattered NPD data, c) 90° NPD data and d) 30° NPD data for Ce$_2$O$_2$FeSe$_2$ with observed and calculated patterns shown in grey and black, respectively; difference profile shown below in grey, peak positions shown with vertical tick marks for Ce$_2$O$_2$FeSe$_2$ (directly below profile), Ce$_2$O$_2$Se (second from top) and vanadium (bottom, NPD refinements only).
S2. Plots of unit cell parameters as a function of temperature determined from sequential Rietveld refinements using XRPD data. a) $a$ and $b$ lattice parameters shown with closed and open points, respectively, and b) $c$ lattice parameter. Thermal expansion was modeled using the expression:

$$\ln \left( \frac{a_T}{a_0} \right) = \frac{C_i \theta_i}{\exp \left( \frac{\theta_i}{T} \right) - 1}$$

where $a_T$ is the $a$ lattice parameter at temperature $T$, $a_0$ is the $a$ lattice parameter at 0 K, $C_i$ a constant, and $\theta_i$ the Einstein temperature. Einstein temperatures are 110(4) K, 89(6) K, and 280(15) K for $a$, $b$, and $c$, respectively, corresponding to increases of 0.36%, 0.26%, 0.17%, and 0.79% in $a$, $b$, $c$ and volume, respectively.
S3. Rietveld refinement profiles from combined refinement using 12 K a) XRPD data, b) backscattered NPD data, c) 90° NPD data and d) 30° NPD data for Ce$_2$O$_2$FeSe$_2$ with observed and calculated patterns shown in grey and black, respectively; difference profile shown below in grey, peak positions shown with vertical tick marks for Ce$_2$O$_2$FeSe$_2$ (directly below profile), Ce$_2$O$_2$Se (second from top) and vanadium (bottom, NPD refinements only).
S4. Plots of magnetization versus field for Ce$_2$O$_2$SeFe$_2$ at 295 K (red) and 12 K (blue).

S5. a) Electrical resistivity of Ce$_2$O$_2$FeSe$_2$ as a function of temperature and inset, Arrhenius plot of log(conductivity) versus reciprocal temperature, with data collected on cooling (blue, closed points) and on warming (red, open points).