## **Supporting Information**

## SU-75: A Disordered Ge<sub>10</sub> Germanate with the pcu Topology

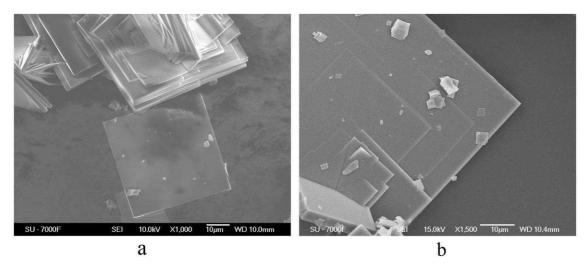
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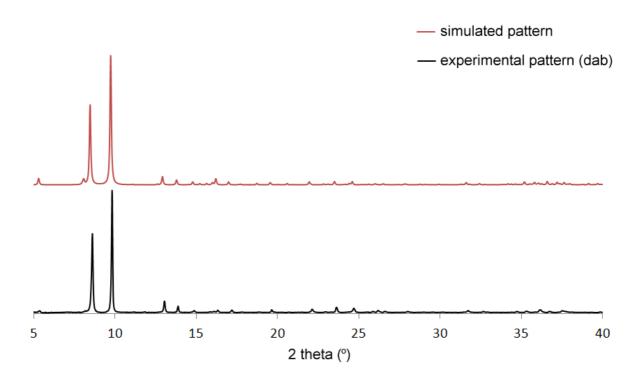
<sup>c</sup> Diamond Light Source Ltd, Diamond House, Harwell Science and Innovation Campus, Dicot, Oxfordshire, OX11 0DE, United Kingdom

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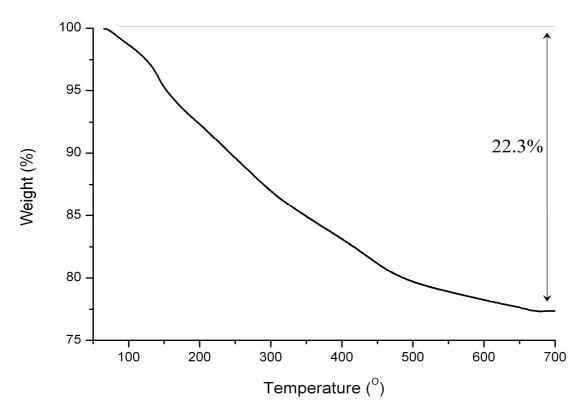
- Figure S1 SEM images of SU-75.
- Figure S2 Experimental powder X-ray diffraction (XRD) pattern of SU-75(dab).
- Figure S3 Thermogravimetric analysis of SU-75(dien).
- Figure S4 Powder XRD patterns of SU-75(dien) before and after ion-exchanging.
- Figure S5 Different choices of SBU in Ge<sub>10</sub> germanate.
- Figure S6 In-situ powder XRD patterns of SU-75(dien).
- Figure S7 In-situ powder XRD patterns of LNM-1 (Ge-pharmacosiderite).



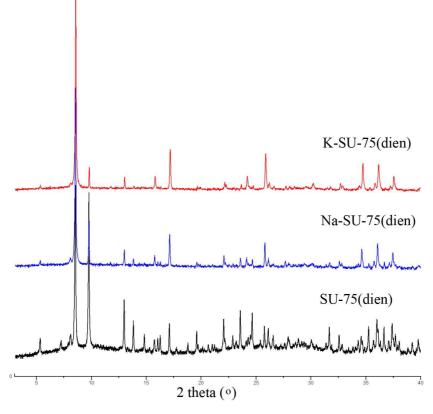
*Figure S1* SEM images of SU-75. (a) The crystals synthesized with diethylenetriamine (dien) as the structure directing agent; (b) The crystals synthesized with diaminebutane (dab) as the structure directing agent.



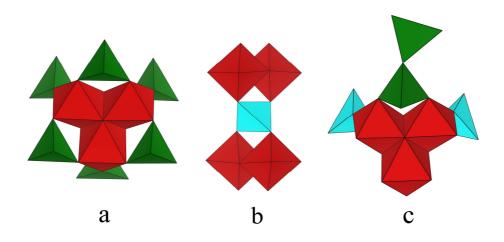
*Figure S2* The experimental powder XRD pattern of SU-75(dab) compared to the simulated powder XRD pattern.



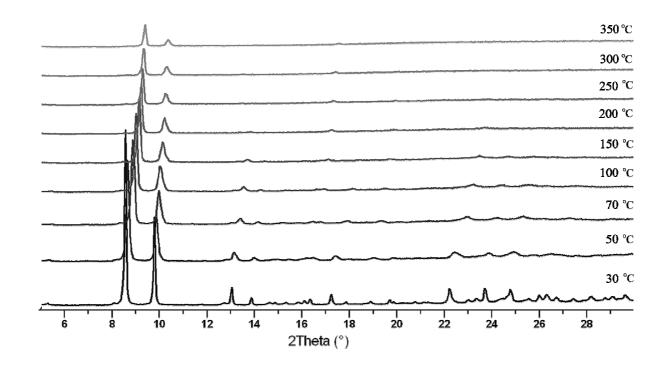
*Figure S3* Thermogravimetric curve of SU-75(dien) performed in N<sub>2</sub> flow from 50 to 700 °C at a heating rate of 5 °C/min. The total weight loss of 22.3% between 50°C and 700°C was attributed to the loss of water and the dien molecules. The content of water and dien molecules calculated from the chemical formula 21.6 w.t% (n=5) or 22.8 w.t% (n=6), which is consistent with the TGA result.



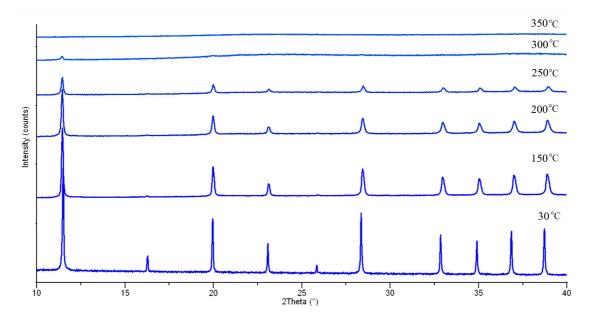
*Figure S4* Powder XRD patterns of SU-75(dien) before and after ion-exchanging. The framework was kept after 50% of SDAs were exchanged by  $Na^+$  or  $K^+$ .



*Figure S5* Different secondary building units (SBUs) used for describing the  $Ge_{10}$  germanates. (a) The  $Ge_{10}$  cluster in SU-75, (b) a  $Ge_5$  building unit in LNM-1 and (c) a  $Ge_8$  building unit in IM-14.



*Figure S6 In-situ* powder XRD patterns for SU-75. SU-75 was stable up to 50 °C before the crystallinity started to degrade.



*Figure S7 In-situ* powder XRD patterns for LNM-1 (Ge-pharmacosiderite). LNM-1 was stable up to 250 °C.