



**Figure S1.** Schematic illustration of a stainless steel (SUS) container and a tubular electric furnace.

**Table S1** Atomic coordinates and isotropic and equivalent isotropic displacement parameter ( $U_{\text{eq}} / \text{\AA}^2$ ) for **Crystals 1–5**.

atom	site	occupancy	$x$	$y$	$z$	$U_{\text{eq}}$
<b>Crystal 1</b> ( $\text{Na}_8\text{Ga}_{5.70(7)}\text{Si}_{40.30}$ )						
Na1	$6d$	1	1/4	1/2	0	0.0678(7)
Na2	$2a$	1	0	0	0	0.0235(6)
Si/Ga1	$24k$	0.945 / 0.055(2)	0	0.30544(4)	0.11644(4)	0.00831(16)
Si2	$16i$	1	0.18400(3)	$x$	$x$	0.0075(2)
Si/Ga3	$6c$	0.270 / 0.730(4)	1/4	0	1/2	0.00801(17)
<b>Crystal 2</b> ( $\text{Na}_8\text{Ga}_{5.52(7)}\text{Si}_{40.48}$ )						
Na1	$6d$	1	1/4	1/2	0	0.0664(7)
Na2	$2a$	1	0	0	0	0.0238(6)
Si/Ga1	$24k$	0.947 / 0.053(2)	0	0.30552(4)	0.11645(4)	0.00861(16)
Si2	$16i$	1	0.18405(3)	$x$	$x$	0.0081(2)
Si/Ga3	$6c$	0.292 / 0.708(4)	1/4	0	1/2	0.00852(17)
<b>Crystal 3</b> ( $\text{Na}_8\text{Ga}_{5.39(11)}\text{Si}_{40.61}$ )						
Na1	$6d$	1	1/4	1/2	0	0.0662(10)
Na2	$2a$	1	0	0	0	0.0238(9)
Si/Ga1	$24k$	0.947 / 0.053(3)	0	0.30560(5)	0.11650(5)	0.0092(2)
Si2	$16i$	1	0.18407(4)	$x$	$x$	0.0086(3)
Si/Ga3	$6c$	0.315 / 0.685(6)	1/4	0	1/2	0.0090(2)
<b>Crystal 4</b> ( $\text{Na}_8\text{Ga}_{5.06(7)}\text{Si}_{40.94}$ )						
Na1	$6d$	1	1/4	1/2	0	0.0636(6)
Na2	$2a$	1	0	0	0	0.0236(5)
Si/Ga1	$24k$	0.955 / 0.045(2)	0	0.30566(3)	0.11651(3)	0.00825(15)
Si2	$16i$	1	0.18407(2)	$x$	$x$	0.00793(18)
Si/Ga3	$6c$	0.336 / 0.664(4)	1/4	0	1/2	0.00809(16)
<b>Crystal 5</b> ( $\text{Na}_8\text{Ga}_{4.94(6)}\text{Si}_{41.06}$ )						
Na1	$6d$	1	1/4	1/2	0	0.0619(6)
Na2	$2a$	1	0	0	0	0.0229(5)
Si/Ga1	$24k$	0.9561 / 0.0439(18)	0	0.30573(3)	0.11652(3)	0.00825(14)
Si2	$16i$	1	0.18408(2)	$x$	$x$	0.00778(17)
Si/Ga3	$6c$	0.352 / 0.648(3)	1/4	0	1/2	0.00807(15)

**Table S2** Atomic coordinates and isotropic and equivalent isotropic displacement parameter ( $U_{ij} / \text{\AA}^2$ ) for **Crystals 1–5**.

atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
<b>Crystal 1</b> ( $\text{Na}_8\text{Ga}_{5.70(7)}\text{Si}_{40.30}$ )						
Na1	0.0459(13)	0.0787(11)	$= U_{22}$	0	0	0
Na2	0.0235(6)	$= U_{11}$	$= U_{11}$	0	0	0
Si / Ga1	0.0083(2)	0.0090(2)	0.0077(2)	-0.00011(14)	0	0
Si2	0.0075(2)	$= U_{11}$	$= U_{11}$	-0.00038(10)	$= U_{23}$	$= U_{23}$
Si / Ga3	0.0089(2)	0.00757(18)	$= U_{22}$	0	0	0
<b>Crystal 2</b> ( $\text{Na}_8\text{Ga}_{5.52(7)}\text{Si}_{40.48}$ )						
Na1	0.0462(14)	0.0765(11)	$= U_{22}$	0	0	0
Na2	0.0238(6)	$= U_{11}$	$= U_{11}$	0	0	0
Si1 / Ga1	0.0086(2)	0.0091(2)	0.0082(2)	-0.00014(12)	0	0
Si2	0.0081(2)	$= U_{11}$	$= U_{11}$	-0.00031(9)	$= U_{23}$	$= U_{23}$
Si3 / Ga3	0.0096(2)	0.00799(19)	$= U_{22}$	0	0	0
<b>Crystal 3</b> ( $\text{Na}_8\text{Ga}_{5.39(11)}\text{Si}_{40.61}$ )						
Na1	0.046(2)	0.0765(16)	$= U_{22}$	0	0	0
Na2	0.0238(9)	$= U_{11}$	$= U_{11}$	0	0	0
Si1 / Ga1	0.0091(3)	0.0098(3)	0.0087(3)	0.0000(2)	0	0
Si2	0.0086(3)	$= U_{11}$	$= U_{11}$	-0.00044(15)	$= U_{23}$	$= U_{23}$
Si3 / Ga3	0.0097(4)	0.0087(3)	$= U_{22}$	0	0	0
<b>Crystal 4</b> ( $\text{Na}_8\text{Ga}_{5.06(7)}\text{Si}_{40.94}$ )						
Na1	0.0451(12)	0.0728(9)	$= U_{22}$	0	0	0
Na2	0.0236(5)	$= U_{11}$	$= U_{11}$	0	0	0
Si1 / Ga1	0.0081(2)	0.0087(2)	0.0079(2)	-0.00022(12)	0	0
Si2	0.00793(18)	$= U_{11}$	$= U_{11}$	-0.00041(9)	$= U_{23}$	$= U_{23}$
Si3 / Ga3	0.0091(2)	0.00757(17)	$= U_{22}$	0	0	0
<b>Crystal 5</b> ( $\text{Na}_8\text{Ga}_{4.94(6)}\text{Si}_{41.06}$ )						
Na1	0.0428(11)	0.0715(9)	$= U_{22}$	0	0	0
Na2	0.0229(5)	$= U_{11}$	$= U_{11}$	0	0	0
Si / Ga1	0.00813(19)	0.00885(19)	0.00776(19)	-0.00024(12)	0	0
Si2	0.00778(17)	$= U_{11}$	$= U_{11}$	-0.00035(9)	$= U_{23}$	$= U_{23}$
Si / Ga3	0.0089(2)	0.00768(16)	$= U_{22}$	0	0	0

**Table S3** Atomic distances (Å) for **Crystals 1–5**.

crystal	1	2	3	4	5
composition	Na <sub>8</sub> Ga <sub>5.70(7)</sub> Si <sub>40.30</sub>	Na <sub>8</sub> Ga <sub>5.52(7)</sub> Si <sub>40.48</sub>	Na <sub>8</sub> Ga <sub>5.39(11)</sub> Si <sub>40.61</sub>	Na <sub>8</sub> Ga <sub>5.06(7)</sub> Si <sub>40.94</sub>	Na <sub>8</sub> Ga <sub>4.94(6)</sub> Si <sub>41.06</sub>
[Si/Ga] <sub>24</sub> cage					
Na1-Si/Ga1	3.4853(3)	3.4830(3)	3.4827(4)	3.4783(2)	3.4755(2)
Na1-Si2	3.8371(4)	3.8348(4)	3.8347(5)	3.8302(3)	3.8275(3)
Na1-Si/Ga3	3.6510(1)	3.6490(1)	3.6490(1)	3.6448(1)	3.6423(1)
Si/Ga1-Si/Ga1	2.4049(7)	2.4037(8)	2.4048(11)	2.4022(7)	2.4007(6)
Si/Ga1-Si2	2.3811(3)	2.3805(3)	2.3809(4)	2.3785(2)	2.3772(2)
Si/Ga1-Si/Ga3	2.4370(4)	2.4350(4)	2.4339(6)	2.4306(3)	2.4283(3)
Si2-Si2	2.3610(10)	2.3580(10)	2.3575(15)	2.3544(9)	2.3526(8)
Si-Si ave.	2.4001(5)	2.3987(5)	2.3986(7)	2.3958(4)	2.3941(3)
[Si/Ga] <sub>20</sub> cage					
Na2-Si/Ga1	3.3756(4)	3.3745(4)	3.3756(6)	3.3722(3)	3.3706(3)
Na2-Si2	3.2910(5)	3.2901(5)	3.2904(7)	3.2867(4)	3.2846(4)
Si/Ga1-Si/Ga1	2.4049(7)	2.4037(8)	2.4048(11)	2.4022(7)	2.4007(6)
Si/Ga1-Si2	2.3811(3)	2.3805(3)	2.3809(4)	2.3785(2)	2.3772(2)
Si-Si ave.	2.3859(4)	2.3851(4)	2.3857(5)	2.3832(3)	2.3819(3)