Figure S1. Schematic illustration of a stainless steel (SUS) container and a tubular electric furnace.
| Crystal  | Na | Ga | Si  |
|----------|----|----|-----|
| 1        | 8  | 5.70(7) | 40.30 |
| 2        | 8  | 5.52(7) | 40.48 |
| 3        | 8  | 5.39(11)| 40.61 |
| 4        | 8  | 5.06(7) | 40.94 |
| 5        | 8  | 4.94(6) | 41.06 |

| Atom | x  | y  | z  | Ueq/Å² |
|------|----|----|----|--------|
| Na1  | 1/4| 1/2| 0  | 0.0678(7) |
| Na2  | 1  | 0  | 0  | 0.0235(6) |
| Si/Ga1 | 24 | k  | 0  | 0.00831(16) |
| Si2  | 16 | i  | 0  | 0.0081(2) |
| Si/Ga3 | 6  | c  | 0  | 0.00852(17) |
| Na3  | 1  | 0  | 0  | 0.0238(9) |
| Si/Ga4 | 24 | k  | 0  | 0.00825(15) |
| Si5  | 16 | i  | 0  | 0.00793(18) |
| Si/Ga6 | 6  | c  | 0  | 0.00809(16) |

**Table S1**
Atomic coordinates and isotropic and equivalent isotropic displacement parameter ($U_{eq}$/Å²) for Crystals 1−5.
Table S2: Atomic coordinates and isotropic and equivalent isotropic displacement parameter ($U_{ij}/\text{Å}^2$) for Crystals 1–5.
| Crystal | Composition   | \[\text{Si/Ga}\]_{24} \text{cage} | \text{Na}_1-\text{Si/Ga}_1 | \text{Na}_1-\text{Si}_2 | \text{Na}_1-\text{Si/Ga}_3 | \text{Si/Ga}_1-\text{Si/Ga}_1 | \text{Si/Ga}_1-\text{Si}_2 | \text{Si/Ga}_1-\text{Si/Ga}_3 | \text{Si}_2-\text{Si}_2 | \text{Si}-\text{Si ave.} |
|---------|---------------|-----------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 1       | Na$_8$Ga$_{5.70(7)}$Si$_{40.30}$ | 3.4853(3)                         | 3.4830(3)                   | 3.4827(4)                   | 3.4830(4)                   | 3.4827(4)                   | 2.4049(7)                   | 2.4037(8)                   | 2.4048(11)                  | 2.4030(10)                  | 2.4001(5)                   |
| 2       | Na$_8$Ga$_{5.52(7)}$Si$_{40.48}$ | 3.4783(2)                         | 3.4755(2)                   | 3.4783(2)                   | 3.4755(2)                   | 3.4783(2)                   | 2.4022(7)                   | 2.4007(6)                   | 2.4022(7)                  | 2.4007(6)                  | 2.3987(5)                   |
| 3       | Na$_8$Ga$_{5.39(11)}$Si$_{40.61}$| 3.4755(2)                         | 3.4727(2)                   | 3.4755(2)                   | 3.4727(2)                   | 3.4755(2)                   | 2.4007(6)                   | 2.3982(5)                   | 2.4007(6)                  | 2.3982(5)                  | 2.3986(7)                   |
| 4       | Na$_8$Ga$_{5.06(7)}$Si$_{40.94}$ | 3.4727(2)                         | 3.4699(2)                   | 3.4727(2)                   | 3.4699(2)                   | 3.4727(2)                   | 2.4007(6)                   | 2.3982(5)                   | 2.4007(6)                  | 2.3982(5)                  | 2.3986(7)                   |
| 5       | Na$_8$Ga$_{4.94(6)}$Si$_{41.06}$ | 3.4699(2)                         | 3.4671(2)                   | 3.4699(2)                   | 3.4671(2)                   | 3.4699(2)                   | 2.4007(6)                   | 2.3982(5)                   | 2.4007(6)                  | 2.3982(5)                  | 2.3986(7)                   |