Supporting Information

$Na_2B_{12}Si_6Se_{18}$: A Novel B_{12}-Cluster-containing Quaternary Selenoborate Framework Material

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During an attempt to synthesize a pentanary compound with the target composition $CaEuUSi_2Se_8$, $Na_2B_{12}Si_6Se_{18}$ was unexpectedly obtained. For this reaction, 30 mg of EuSe, 20 mg of U_3O_8, 20 mg of B, and 90 mg of Se were loaded in a heavily carbon-coated fused silica tube (12 mm outer diameter) along with 75 mg of a NaCl/$CaCl_2$ flux mixture. The tube was then evacuated to a pressure of 10^{-4} torr and flame-sealed using a methane/oxygen torch. The sealed tube was placed in a programmable muffle furnace and subjected to a precise thermal profile: it was heated to 800 °C over 12 hours, held at this temperature for 48 hours, and then gradually cooled to 550 °C over another 48 hours. Afterward, the furnace was turned off, allowing the tube to cool naturally to room temperature. The reaction yielded light yellow, transparent crystals along with black and red impurities (see Fig. S1 and S2). The EDS image of this clear crystal and its EDS plot are shown in Fig.S1 and S2, Table. S1.

We conducted two additional reactions to investigate the role of EuSe and U_3O_8 in crystal formation. In the first reaction, we used EuSe along with other reactants but omitted U_3O_8, while in the second reaction, we used U_3O_8 along with other reactants but excluded EuSe. Both reactions followed an identical heating profile to ensure that any observed differences in crystal formation could be attributed to the presence or absence of these specific compounds. Interestingly, only the reaction containing EuSe yielded transparent crystals with the $Na_2B_{12}Si_6Se_{18}$ composition. This result suggested that the presence of EuSe was necessary for the formation of these crystals, while the absence of U_3O_8 did not impact their formation. To confirm the reproducibility of this result, we repeated the EuSe-based reaction multiple times. Each time, we prepared the reaction mixture

with 50 mg of EuSe, 20 mg of boron (B), and 90 mg of selenium (Se), supplemented with 75 mg of a NaCl/$CaCl_2$ flux mixture. Under these conditions, the transparent $Na_2B_{12}Si_6Se_{18}$ crystals consistently formed.

Subsequent reactions were conducted to optimize the synthesis of $Na_2B_{12}Si_6Se_{18}$. Stoichiometric amounts of Na_2Se, Si, B, and Se were used in a molar ratio of 1:6:12:17, both with and without the NaCl/$CaCl_2$ eutectic flux, following the previously established thermal profile. These experiments produced very small microcrystals or polycrystalline $Na_2B_{12}Si_6Se_{18}$, but the crystal quality was not satisfactory for SCXRD data collection.

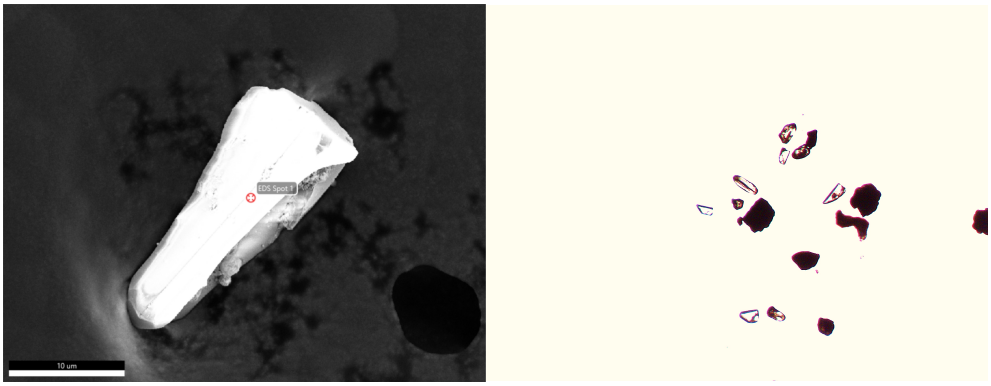

Fig. S1 The (a) SEM image of $Na_2B_{12}Si_6Se_{18}$ single crystal and (b) optical microscopic image of $Na_2B_{12}Si_6Se_{18}$ single crystals (transparent crystals are $Na_2B_{12}Si_6Se_{18}$)

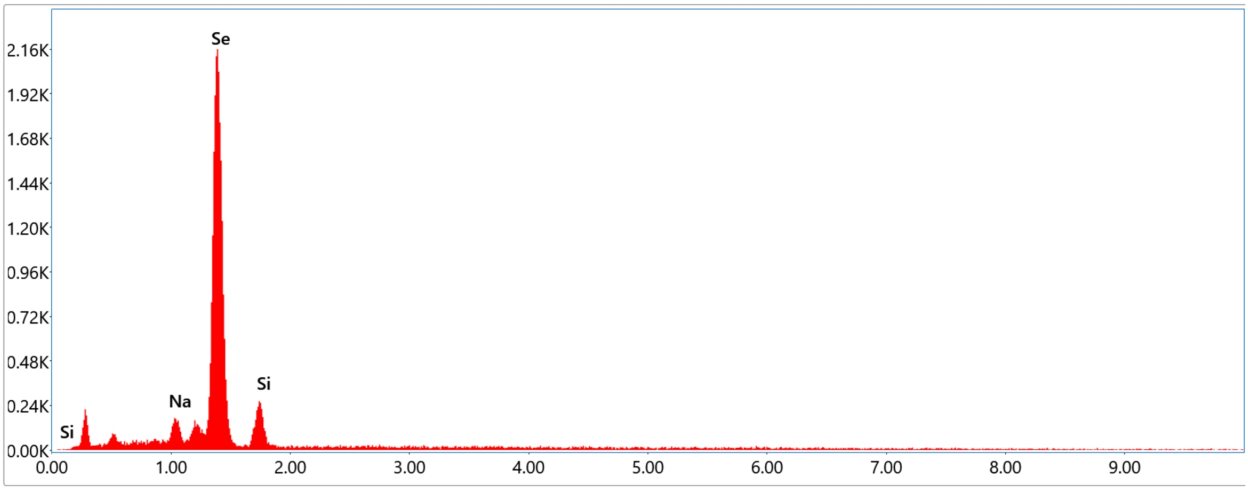

Fig.S2 The EDS plot of $Na_2B_{12}Si_6Se_{18}$ single crystal

Table.S1 Elemental compositions of $Na_2B_{12}Si_6Se_{18}$ single crystal as determined by EDS.

Element	**Weight %**	**Atomic %**
Na	4.1	10.8
Si	11.7	25.1
Se	84.2	64.1

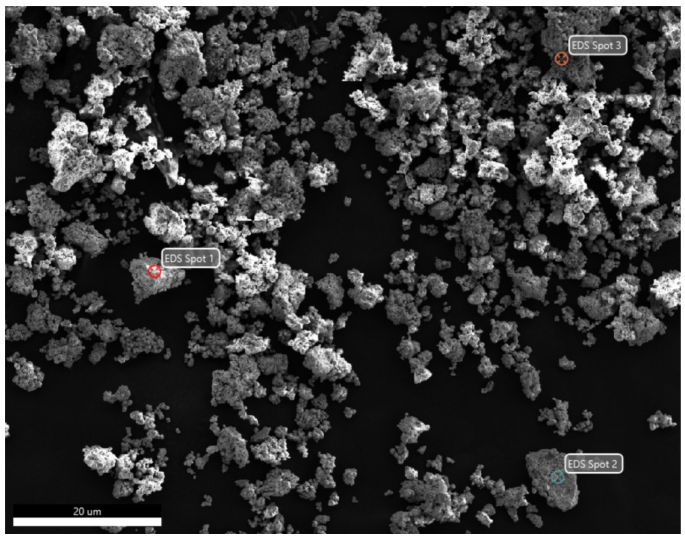

Fig. S3 The SEM image showing where EDS data were collected on polycrystalline $Na_2B_{12}Si_6Se_{18}$.

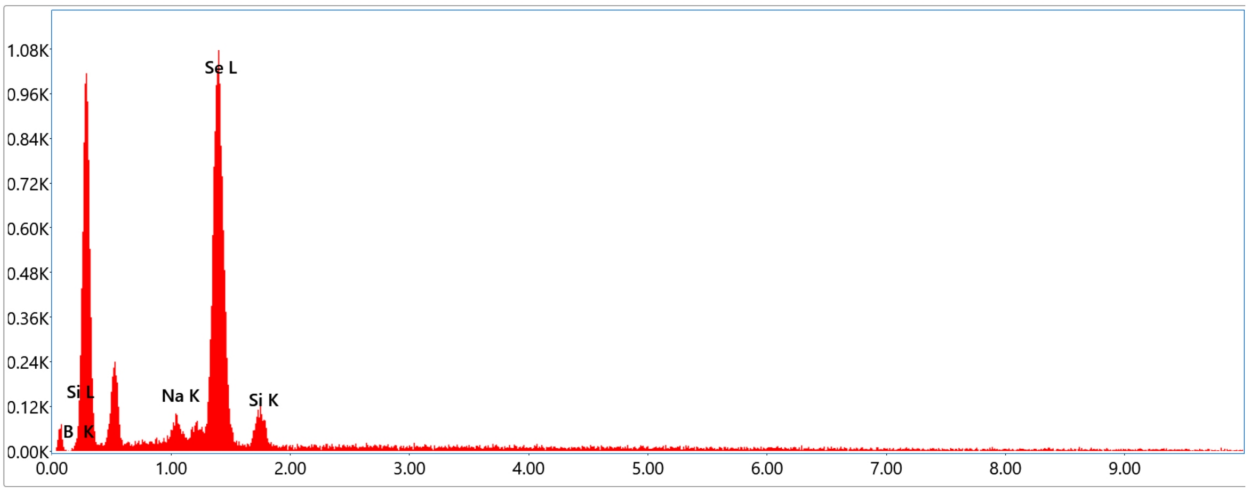

Fig.S4 The EDS plot of polycrystalline $Na_2B_{12}Si_6Se_{18}$ compound.

Table.S2 Average elemental compositions of polycrystalline $Na_2B_{12}Si_6Se_{18}$ compound (spot 1-3) as determined by EDS.

Element	**Weight %**	**Atomic %**
Na	4.45	11.55
Si	12.15	25.75
Se	83.35	62.85

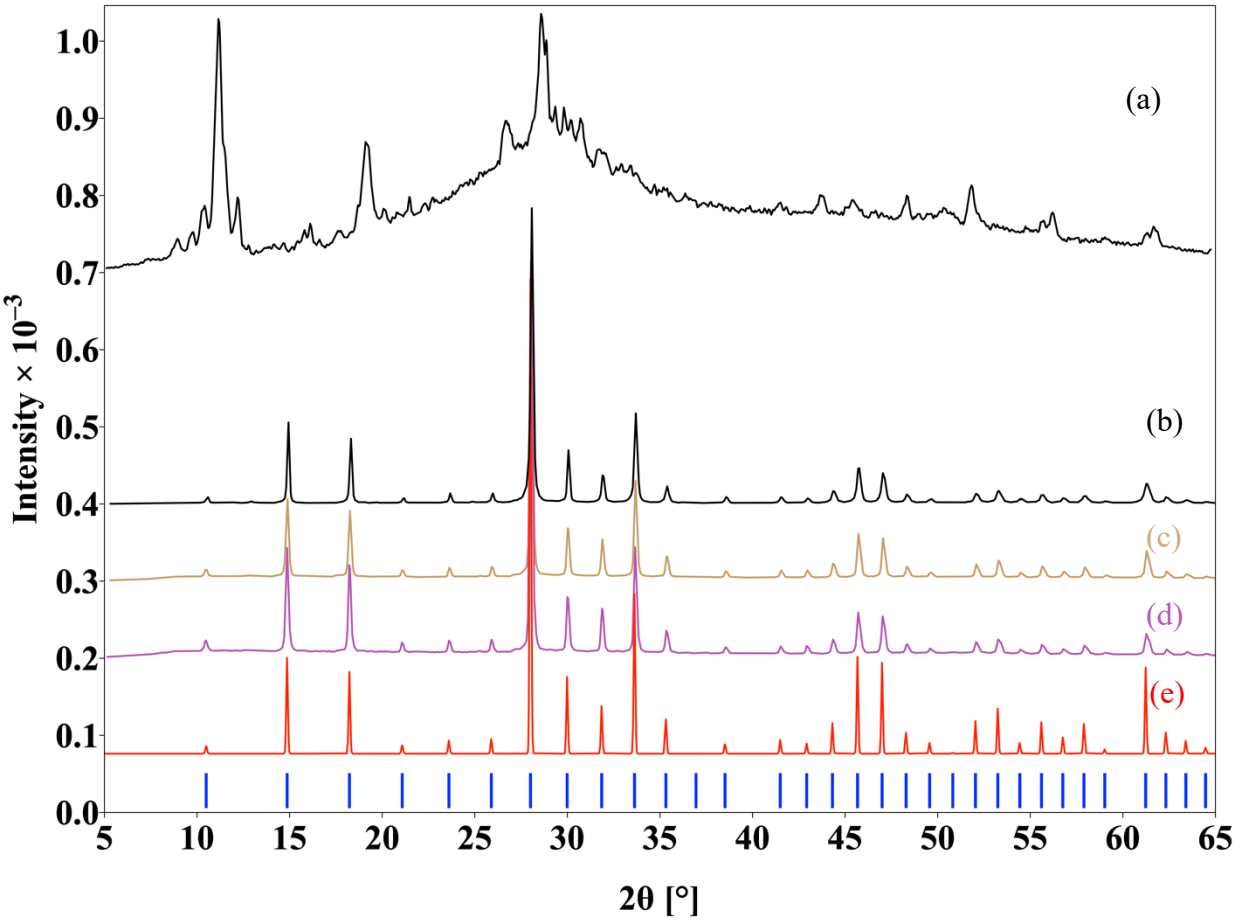

Fig. S5 The PXRD pattern of (a) $Na_2B_{12}Si_6Se_{18}$ compound quench@ 600 °C after dwelling of 36h, (b) $Na_2B_{12}Si_6Se_{18}$ compound quench@ 800 °C after dwelling of 36h, (c) $Na_2B_{12}Si_6Se_{18}$ compound quench@ 800 °C after dwelling of 12h, (d) $Na_2B_{12}Si_6Se_{18}$ compound slow cooling after dwelling of 48h@ 800 °C, (e) Simulated pattern of $Na_2B_{12}Si_6Se_{18}$, and Bragg position of $Na_2B_{12}Si_6Se_{18}$ (blue lines).

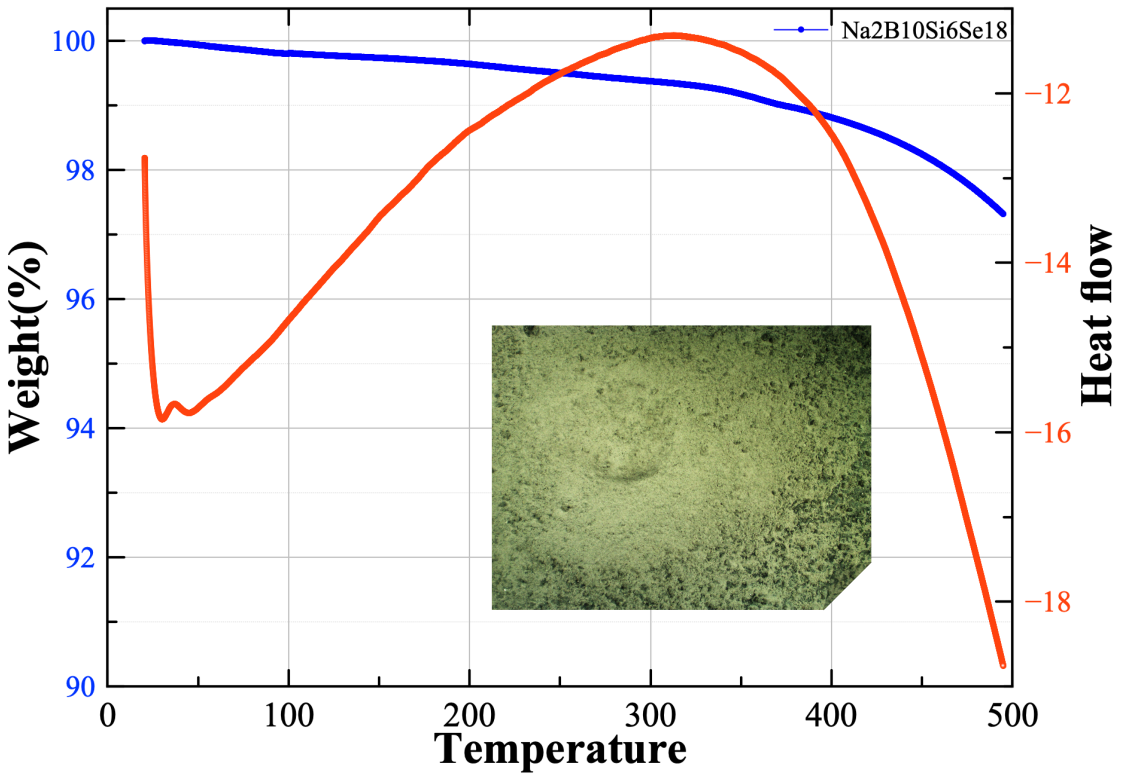

Fig.S6 The TGA/DSC plot of polycrystalline $Na_2B_{12}Si_6Se_{18}$ compound in N_2-atmopshere (inset shows the color of polycrystalline compound).

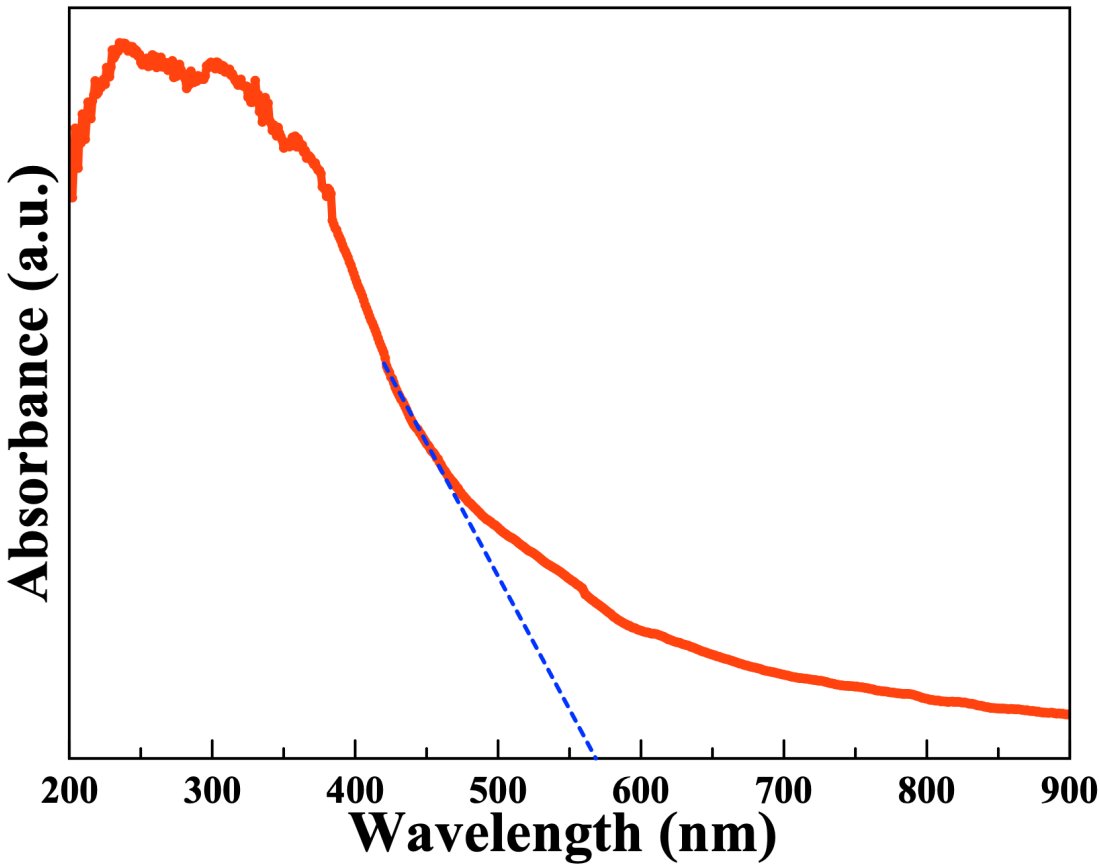

Fig. S7 The optical absorption plot of polycrystalline $Na_2B_{12}Si_6Se_{18}$ compound.