# Supporting information

## Growth of Submillimeter $SrTaO_2N$ Single Crystals by an $NH_3$-Assisted $SrCl_2$ Flux Method

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**Table S1. Synthesis conditions and crystal sizes of $SrTaO_2N$ crystals reported in various literatures.**

| Synthesis method | Raw Material | Temp. Atmosphere | Crystal size | Remark | Ref. |
|---|---|---|---|---|---|
| Reactive inorganic vapor deposition method | $SrCO_3$ $SrCl_2 \cdot 6H_2O$ | 950°C $NH_3$ | 25 μm × 0.5 cm × 1 cm | Epitaxial layer on $LiTaO_3$ single crystals | [1] |
| Nitridation | $SrCl_2$-flux-grown $Sr_2Ta_2O_7$ | 950°C $NH_3$ | 25 μm (Max.) | Porous polycrystal | [2] |
| Topotactic nitridation | $SrCl_2$-flux-grown $Sr_2Ta_2O_7$ | 950°C $NH_3$ | 300 nm ×198 nm × 30 nm (Avg.) | Single crystal | [3] |
| $BaCN_2$ flux method | $BaCN_2$ $SrTaO_2N$ | 900°C $N_2$ | 3.7 μm (Max.) | Single crystal $Sr_{1-x}Ba_xTaO_2N$ ($0.04 \leq x \leq 0.23$) | [4] |
| One pot flux assisted nitridation | $Ta_2O_5$, $SrCl_2$, NaOH | 950°C $NH_3$ | 124 nm (Avg.) | Single crystal | [5] |
| $NH_3$-assisted $SrCl_2$ flux method | $Ta_2O_5$, $SrCl_2$ | 1200°C $NH_3$ | 300 μm (Max.) | Single crystal | This work |

**Table S2. Experimental conditions for $SrCl_2$ flux growth of $SrTaO_2N$ crystals.**

| Run No. | Holding temp. /ºC | Holding time /h | Cooling rate /ºC·h$^{-1}$ | Solute $Ta_2O_5$ /g | Flux & Solute $SrCl_2$ /g | Solute conc. (mol%) |
|---|---|---|---|---|---|---|
| 1 | 1200 | 10 | 150 | 0.2443 | 5.7557 | 1.5 |
| 2 | 1150 | 10 | 150 | 0.2443 | 5.7557 | 1.5 |
| 3 | 1050 | 10 | 150 | 0.2443 | 5.7557 | 1.5 |
| 4 | 950 | 10 | 150 | 0.2443 | 5.7557 | 1.5 |
| 5 | 850 | 10 | 150 | 0.2443 | 5.7557 | 1.5 |
| 6 | 750 | 10 | 150 | 0.2443 | 5.7557 | 1.5 |
| 7 | 650 | 10 | 150 | 0.2443 | 5.7557 | 1.5 |
| 8 | 1200 | 1 | 150 | 0.2443 | 5.7557 | 1.5 |
| 9 | 1200 | 0 | 150 | 0.2443 | 5.7557 | 1.5 |
| 10 | 1200 | 10 | 15 | 0.2443 | 5.7557 | 1.5 |
| 11 | 1200 | 10 | 150 | 0.1643 | 5.8357 | 1 |
| 12 | 1200 | 10 | 150 | 0.4762 | 5.5238 | 3 |
| 13 | 1200 | 10 | 150 | 0.9063 | 5.0937 | 6 |
| 14 | 1200 | 10 | 150 | 2.4642 | 3.5358 | 20 |
| 15 | 950 | 0 | 150 | 0.2443 | 5.7557 | 1.5 |
| 16 | 850 | 0 | 150 | 0.2443 | 5.7557 | 1.5 |
| 17 | 750 | 0 | 150 | 0.2443 | 5.7557 | 1.5 |

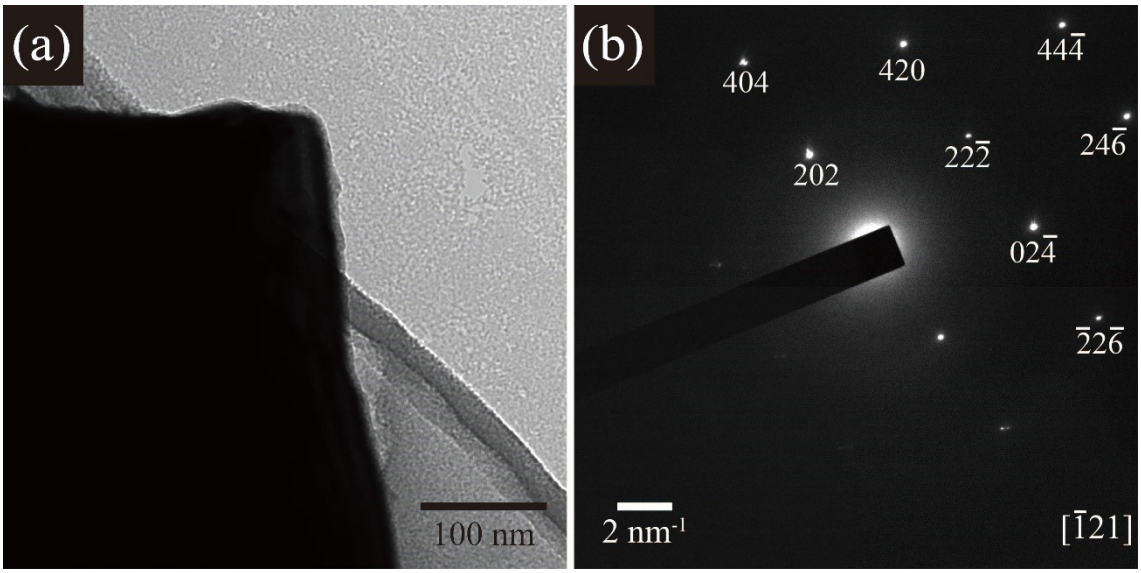


**Figure S1. (a) Bright field TEM image and (b) SAED patterns of pulverized $SrTaO_2N$ crystals grown by the $NH_3$-assisted $SrCl_2$ flux method (Run No.1).**

EDX was performed in order to investigate the chemical compositions of the flux-grown $SrTaO_2N$ crystals (Figure S1). Peaks of nitrogen (N), oxygen (O), tantalum (Ta), and strontium (Sr) were attributed to $SrTaO_2N$, peaks of carbon (C) and gold (Au) were attributed to carbon tape and gold sputtering for measurements, and an unidentified peak was caused by a sample chamber or a sample holder because it appeared at any cases.

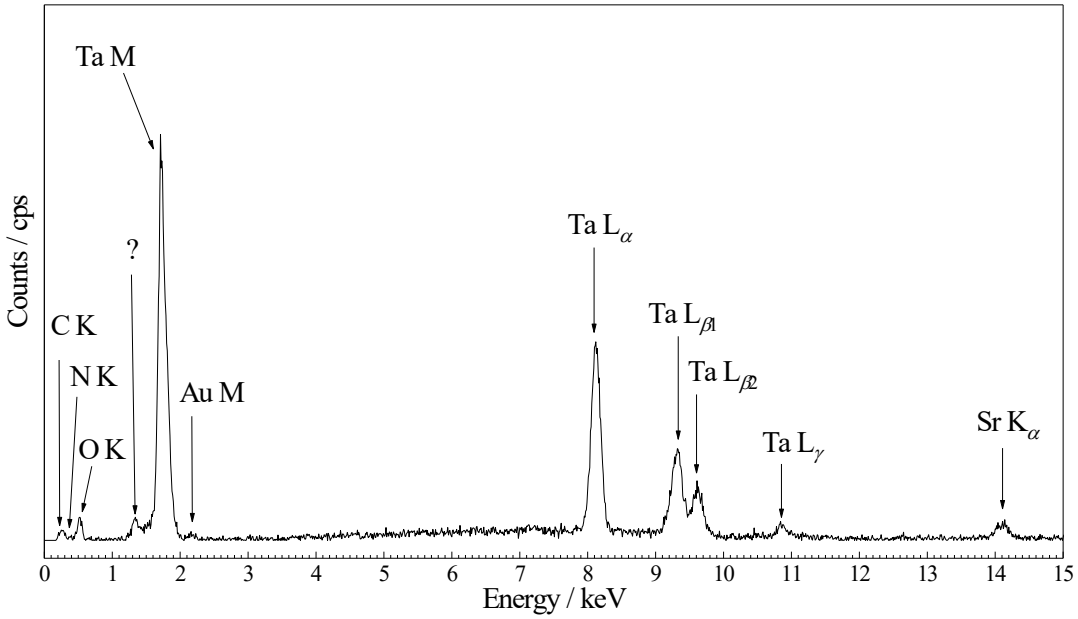


**Figure S2. EDX spectrum of crystals grown by an $NH_3$-assisted $SrCl_2$ flux method (Run No. 1).**

The atomic ratio of Sr and Ta in the flux-grown $SrTaO_2N$ crystals (Run No. 1) is given as Sr:Ta = 1.0:1.0 from the EDX spectrum (Figure S1). If we assume that oxidation states of all tantalum cations are five ($Ta^{5+}$) in the $SrTaO_2N$ crystal, its chemical formula is expressed as $SrTaO_{3.5-1.5y}N_y$, where $y$ is nitrogen content in oxynitride and 3.5-1.5$y$ is oxygen content, considering electrical neutrality. A chemical reaction formula during TG-DTA measurement is expressed as below because the sample after TG-DTA analysis was identified as $Sr_2Ta_2O_7$ without any impurities.

$$2\,SrTaO_{3.5-1.5y}N_y + \frac{3y}{2}O_2 \rightarrow Sr_2Ta_2O_7 + y\,N_2$$

Since increment of the mass of the sample after TG-DTA is relevant to the mass of nitrogen released from the sample, nitrogen content $y$ in $SrTaO_{3.5-1.5y}N_y$ can be calculated from following formula (1):

$$y = \left(\frac{\Delta m}{3/2\,M(O_2) - M(N_2)}\right) \times \frac{M(Sr_2Ta_2O_7)}{m(Sr_2Ta_2O_7)} \quad (1)$$

where $\Delta m$ is total mass change, $M(O_2)$ and $M(N_2)$ are molecular weights of oxygen ($O_2$) and nitrogen ($N_2$), $m(Sr_2Ta_2O_7)$ is mass of the sample after TG-DTA, $M(Sr_2Ta_2O_7)$ is formula weight of $Sr_2Ta_2O_7$. The total mass change $\Delta m$ was calculated from the difference between mass at 400°C in the TG-DTA curve and that after the TG-DTA measurement, which is caused by transformation of $SrTaO_2N$ to $Sr_2Ta_2O_7$ as the above chemical formula. Since $\Delta m$ is 1.83 mg and $m(Sr_2Ta_2O_7)$ is 51.31 mg, $y$ is calculated to be 1.16. Therefore, chemical formula of the flux-grown $SrTaO_2N$ crystal is "$SrTaO_{1.76}N_{1.16}$".

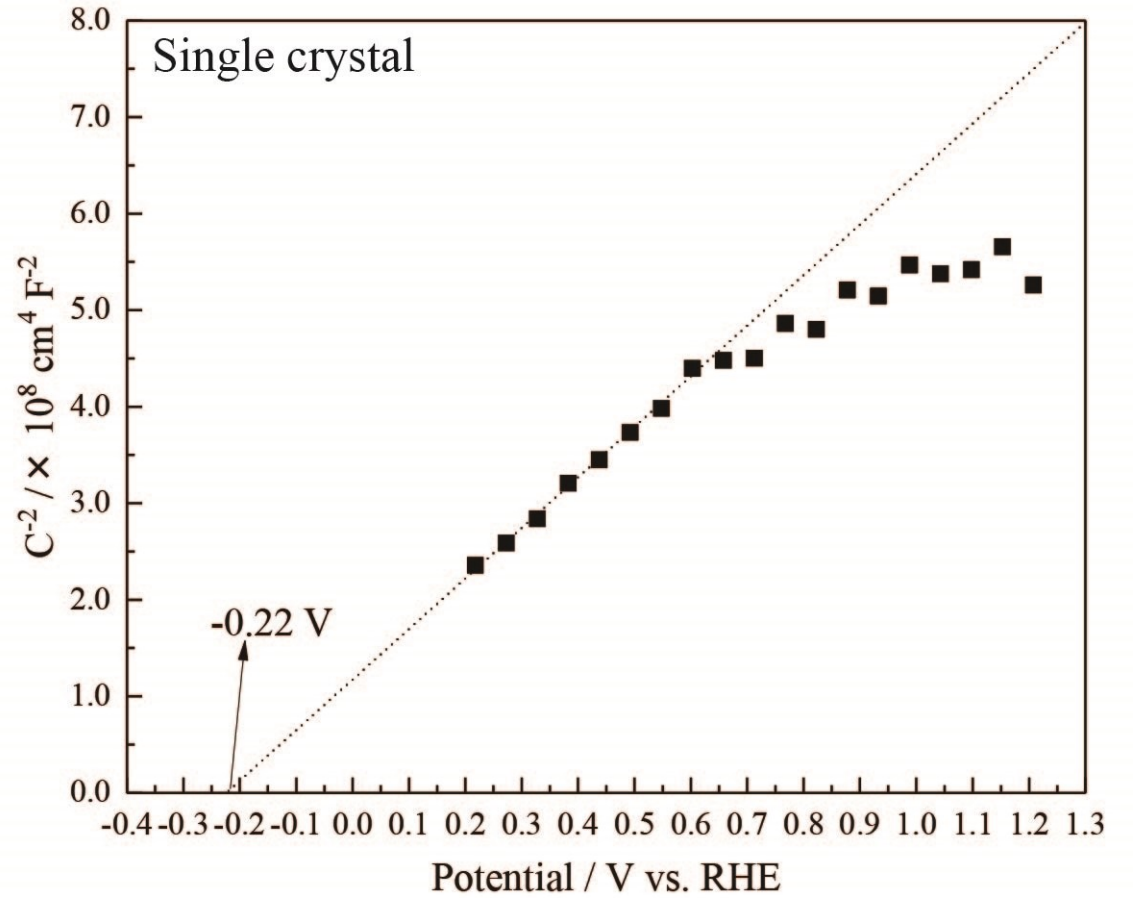


**Figure S3. Mott-Schottky measurements of a $SrTaO_2N$ single crystal grown by the $NH_3$-assisted $SrCl_2$ flux method (Run No.1).**

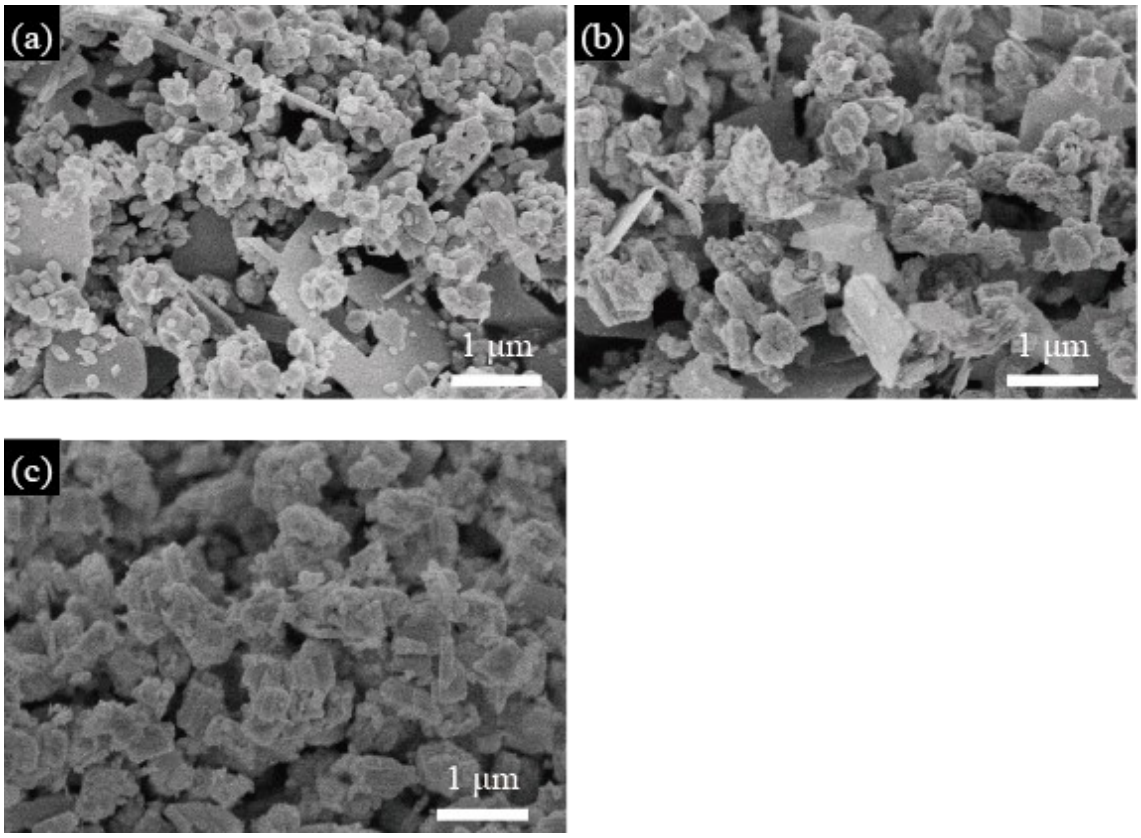


**Figure S4. SEM images of samples prepared by the $NH_3$-assisted $SrCl_2$ flux method at holding temperatures of (a) 850°C, (b) 750°C, and (c) 650°C for 10 h with a solute concentration of 1.5 mol% and a cooling rate of 150°C $h^{-1}$ (Run Nos. 5–7).**

Flux evaporation ratio (evap %) was calculated using the following formula:

$$
\begin{aligned}
&evap\ (\%) \\
&= \frac{m_{SrCl2,\ Evap}}{m_{SrCl2,\ B}} \times 100 \\
&= \frac{m_{SrCl2,B} - m_{SrCl2,\ A}}{m_{SrCl2,\ B}} \times 100 \\
&= \frac{m_{SrCl2,B} - (m_{all,\ A} - m_{SrTaO2N})}{m_{SrCl2,\ B}} \times 100
\end{aligned} \qquad (S1)
$$

where $m_{\mathrm{SrCl2,Evap}}$ is mass of $SrCl_2$ flux evaporated during the reaction, $m_{\mathrm{SrCl2,B}}$ is mass of $SrCl_2$ flux before the reaction, $m_{\mathrm{SrCl2,A}}$ is mass of $SrCl_2$ flux after the reaction, $m_{\mathrm{all,A}}$ is mass of all samples including $SrCl_2$ flux and product ($SrTaO_2N$) after the reaction, $m_{\mathrm{SrTaO2N}}$ is mass of resulting product ($SrTaO_2N$) after the reaction.

All the masses were measured by a precision valance (XS205, METTLER TOLEDO) with an accuracy of 0.01 mg. $m_{\mathrm{SrCl2,B}}$ is measured from amount of $SrCl_2$ before mixing. $m_{\mathrm{all,A}}$ is calculated by subtracting the mass of the platinum boat from the total mass of the sample and the platinum boat after the reaction. $m_{\mathrm{SrTaO2N}}$ is measured from amount of the obtained crystals.

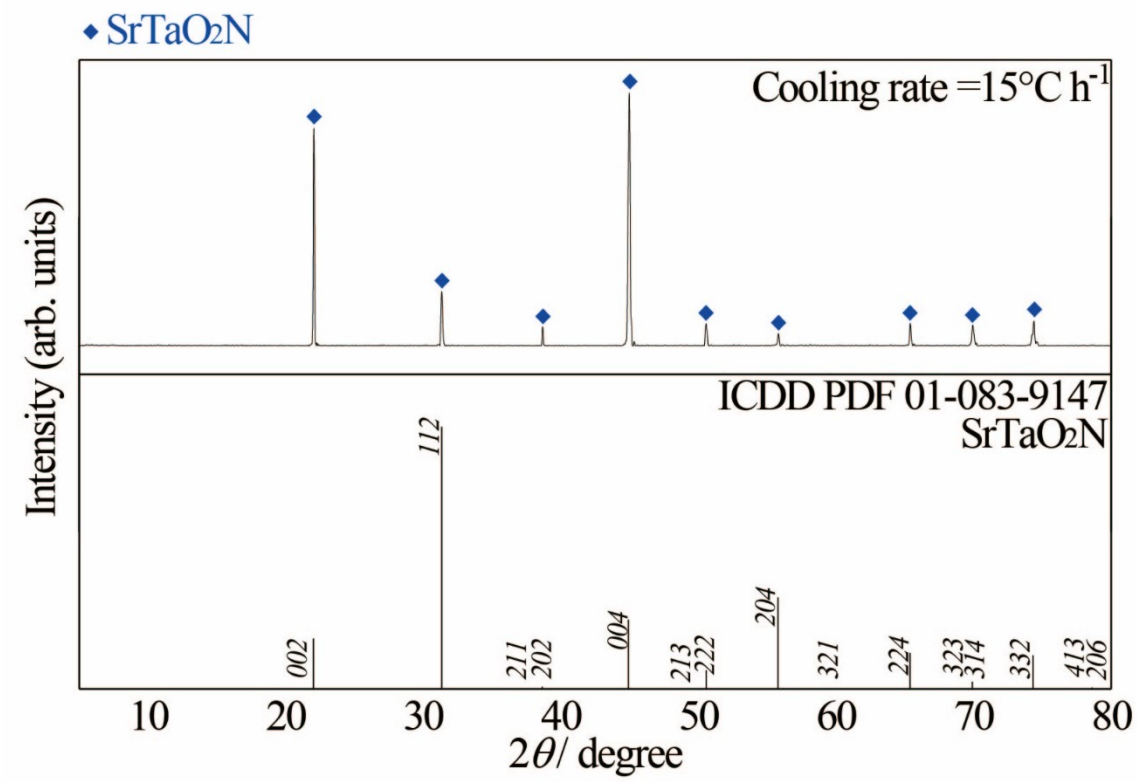


**Figure S5. XRD patterns of pulverized crystals grown by the $NH_3$-assisted $SrCl_2$ flux method at a holding temperature of 1200°C for 10 h with a solute concentration of 1.5 mol% and a cooling rate of 15°C $h^{-1}$ (Run No.10). The XRD pattern of tetragonal $SrTaO_2N$ (ICDD PDF 01-083-9147) is shown for reference.**

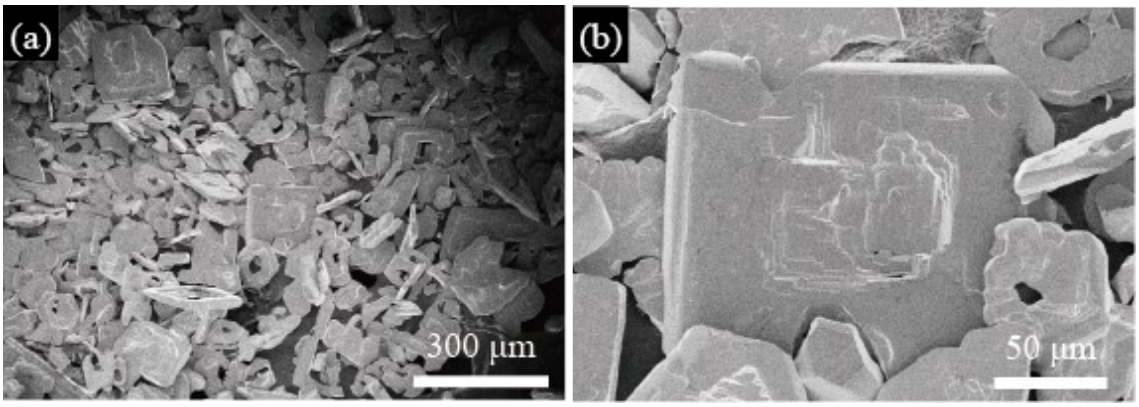


**Figure S6. Low- and high-magnification SEM images of samples prepared by the $NH_3$-assisted $SrCl_2$ flux method at a holding temperature of 1200°C for 10 h with a solute concentration of 1.5 mol% at a cooling rate of 15°C $h^{-1}$ (Run No.10).**

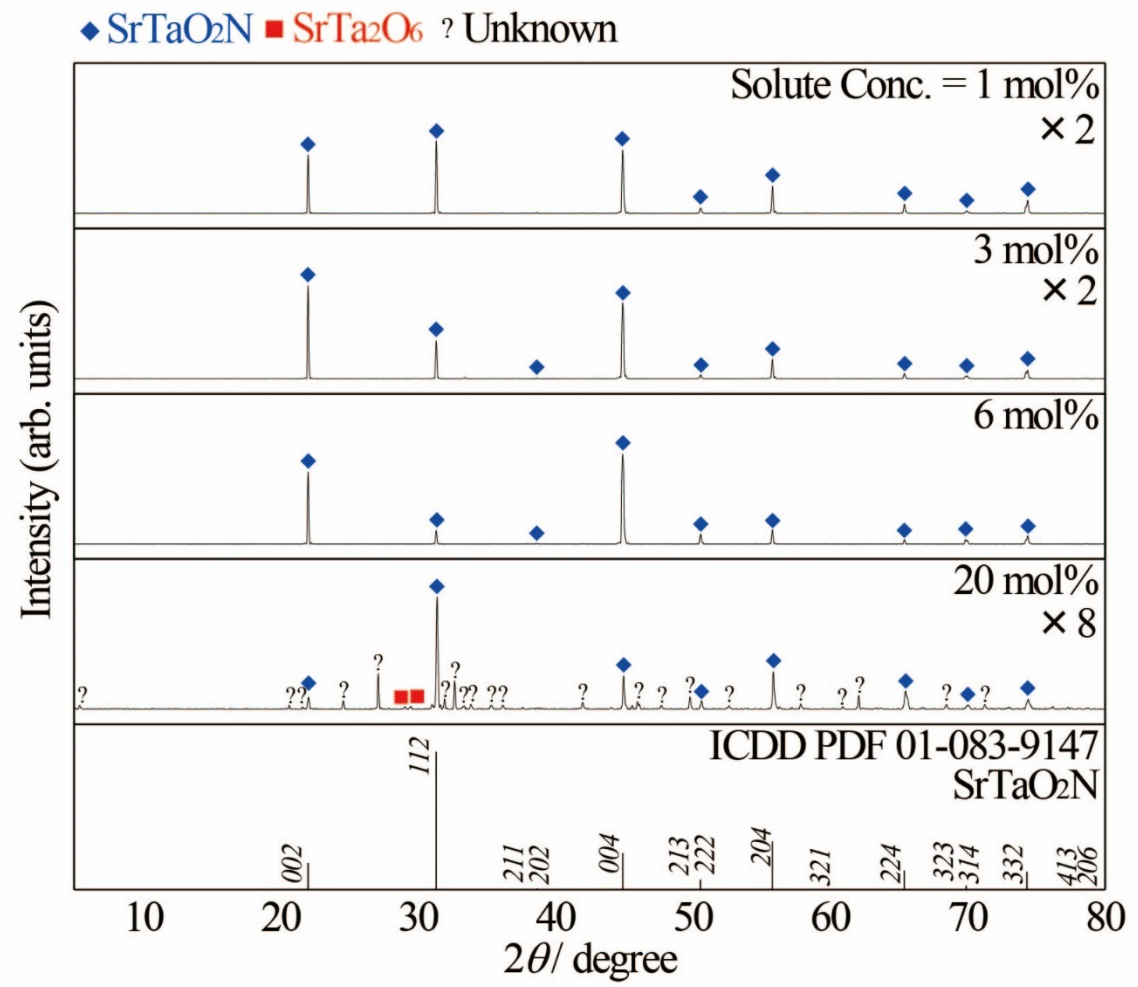


**Figure S7. XRD patterns of pulverized crystals grown by the $NH_3$-assisted $SrCl_2$ flux method at a holding temperature of 1200°C for 10 h with various solute concentrations at a cooling rate of 150°C $h^{-1}$ (Run Nos. 11–14). The XRD pattern of tetragonal $SrTaO_2N$ (ICDD PDF 01-083-9147) is shown for reference.**

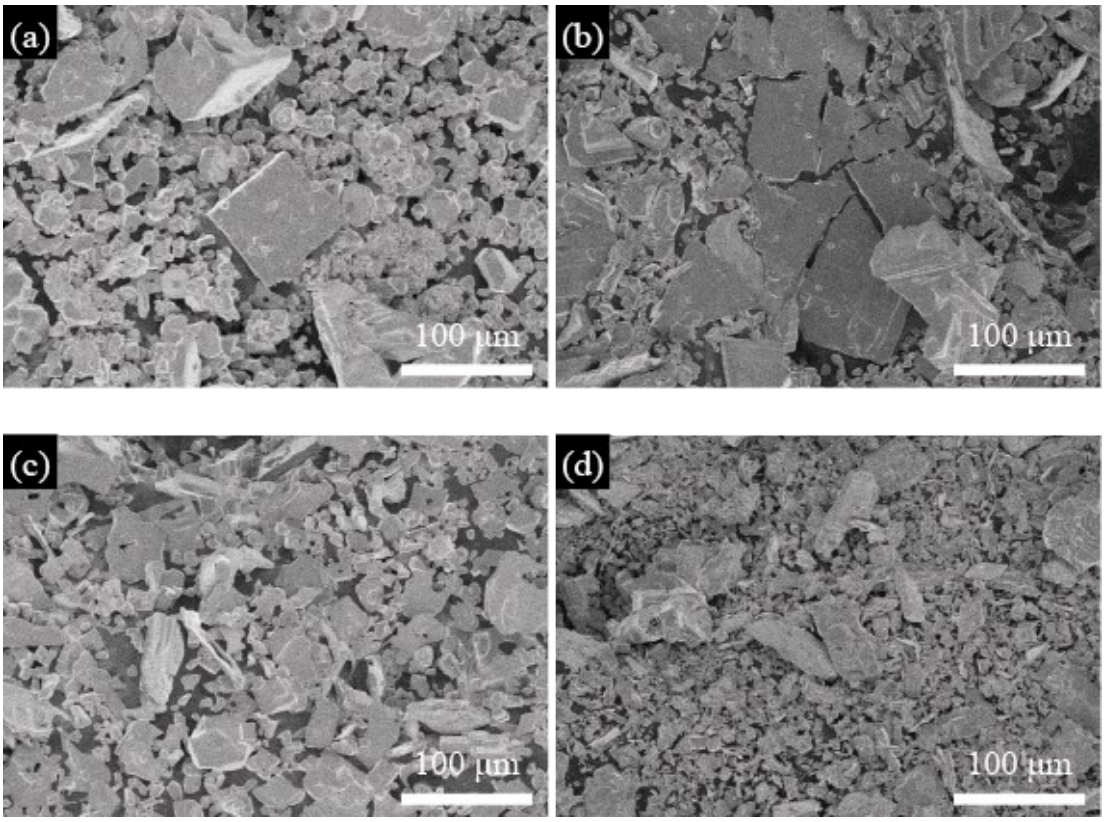


**Figure S8. SEM images of samples prepared by the $NH_3$-assisted $SrCl_2$ flux method at holding temperature of 1200°C for 10 h with solute concentrations of (a) 1 mol%, (b) 3 mol%, (c) 6 mol%, and (d) 20 mol% and a cooling rate of 150°C $h^{-1}$ (Run Nos. 11–14).**

## REFERENCES


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