

Supplementary information

The supplementary information addresses five different references of Raman spectra of groups: SO_4^{2-} , Cl^- , NO_3^- , CO_3^{2-} , and CH_3SO_3^- . Raman spectra are taken from reference specimens of simple salts such as reagent-grade chemicals, 99.5wt% Na_2SO_4 (Kishida Chemical), 98.0wt% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Kishida Chemical), 98.0wt% $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (Kishida Chemical), 99.5wt% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Kishida Chemical), 98.0wt% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Kishida Chemical), $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (Kanto Chemical), 99.5wt% $(\text{NH}_4)_2\text{SO}_4$ (Kishida Chemical), 99.5wt% NaCl (Kishida Chemical), 98.0wt% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Kishida Chemical), 99.0wt% NaNO_3 (Kishida Chemical), 99.0wt% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Kishida Chemical), 98.5wt% $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Kishida Chemical), 99.0wt% NH_4NO_3 (Kishida Chemical), 99.5wt% Na_2CO_3 (Kishida Chemical), 99.0wt% $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (Kishida Chemical), 99.5wt% CaCO_3 (Kishida Chemical), 98wt% $\text{CH}_3\text{SO}_3\text{Na}$ (Alfa Aesar), 99wt% $(\text{CH}_3\text{SO}_3)_2\text{Mg}$ (Daniels Fine Chemicals), 98wt% $\text{CH}_3\text{SO}_3\text{K}$ (Tokyo Kasei Kogyo), and 98wt% $(\text{CH}_3\text{SO}_3)_2\text{Ca}$ (Tokyo Kasei Kogyo).

Raman spectra of $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ are synthesized using previous methods [S1, S2], respectively. $\text{NaCl} \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, $\text{CH}_3\text{SO}_3\text{Na} \cdot n\text{H}_2\text{O}$, $(\text{CH}_3\text{SO}_3)_2\text{Mg} \cdot n\text{H}_2\text{O}$, $\text{CH}_3\text{SO}_3\text{K} \cdot n\text{H}_2\text{O}$, $(\text{CH}_3\text{SO}_3)_2\text{Ca} \cdot n\text{H}_2\text{O}$ are synthesized at eutectic concentration and measured below the eutectic temperature.

Reference

- [S1] Hamilton, A., Hall, C., Sodium sulfate heptahydrate: a synchrotron energy-dispersive diffraction study of an elusive metastable hydrated salt, *J. Anal. At. Spectrom.*, 2008, 23, 840-844.
- [S2] Genceli, F.E., Lutz, M., Spek, A.L., Witkamp, G-J., Crystallization and Characterization of a New Magnesium Sulfate Hydrate $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$, *Cryst. Growth. Des.*, 2007, 7(12), 2460-2466.

Figure A. Reference Raman spectra of SO_4^{2-} salts. a. Na_2SO_4 ; b. $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ [S1]; c. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; d. $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$; e. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; f. $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ [S2]; g. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; h. $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$; i. $(\text{NH}_4)_2\text{SO}_4$.

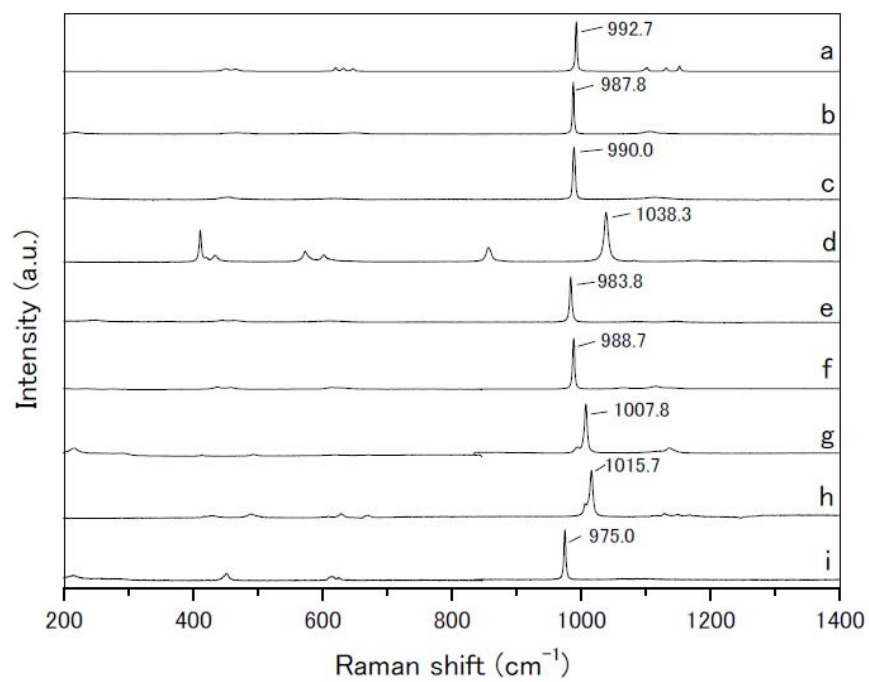


Figure B. Reference Raman spectra of Cl⁻ salts. a. NaCl·2H₂O; b. MgCl₂·6H₂O; c. MgCl₂·12H₂O.

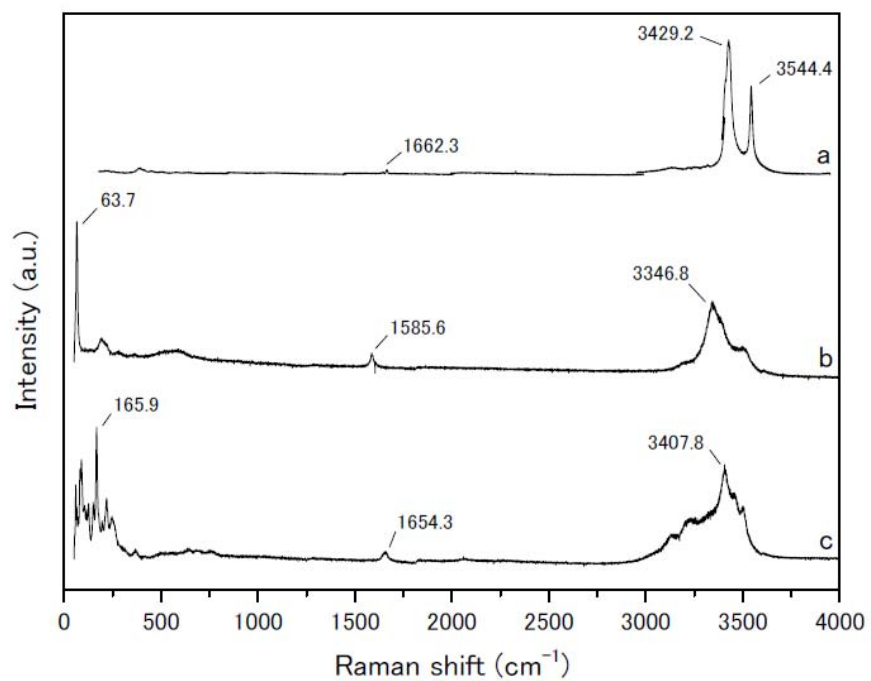


Figure C. Reference Raman spectra of NO_3^- salts. a. NaNO_3 ; b. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, c. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; d. NH_4NO_3 .

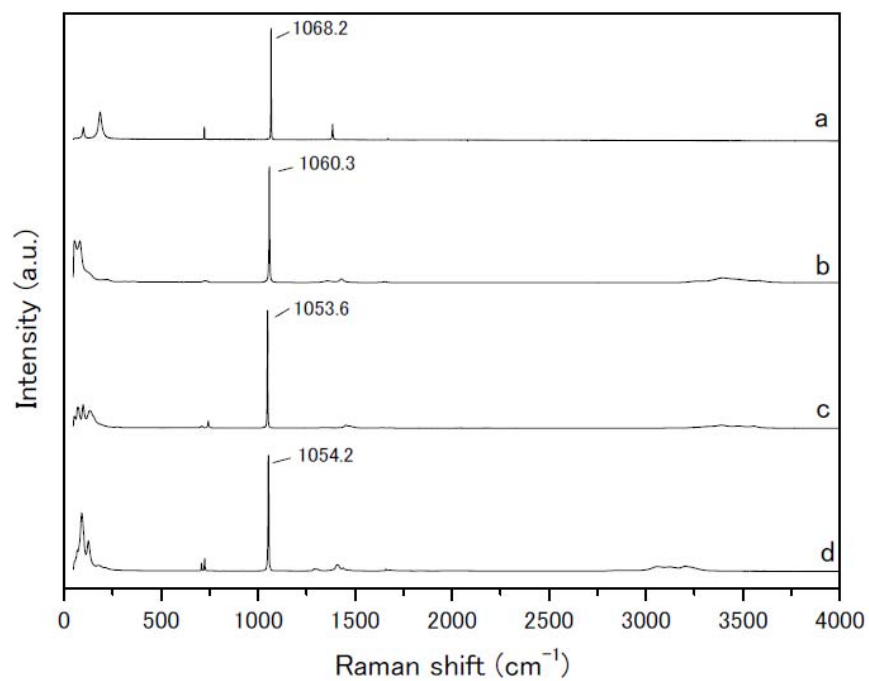


Figure D. Reference Raman spectra of CO_3^{2-} salts. a. Na_2CO_3 ; b. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; c. CaCO_3 .

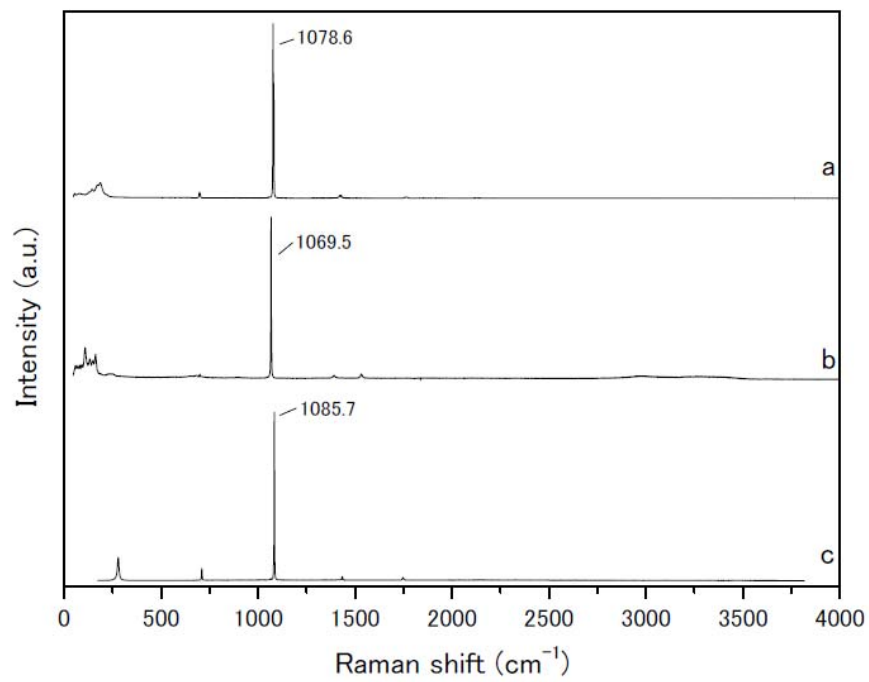


Figure E. Reference Raman spectra of CH_3SO_3^- salts. a. $\text{CH}_3\text{SO}_3\text{Na} \cdot n\text{H}_2\text{O}$; b. $(\text{CH}_3\text{SO}_3)_2\text{Mg} \cdot n\text{H}_2\text{O}$; c. $\text{CH}_3\text{SO}_3\text{K} \cdot n\text{H}_2\text{O}$; d. $(\text{CH}_3\text{SO}_3)_2\text{Ca} \cdot n\text{H}_2\text{O}$.

