

Perovzalates: a Family of Perovskite-Related Oxalates

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Supplementary Information

1. Synthesis

Compounds were synthesised *via* a hydrothermal method using different temperatures, reactions times and ratios of reactants. The optimal conditions are given in Table S1 and the ratios are shown in the order of alkali metal carbonate : lithium carbonate : transition metal chloride : oxalic acid dihydrate.

Table S1 Synthesis conditions of the eight perovskite-related oxalates

Compound	Temperature	Ratio of Reactants	Reaction Time
$\text{KLi}_3\text{Co}(\text{C}_2\text{O}_4)_3$	190 °C	1:2:1.5:4	4 Days
$\text{KLi}_3\text{Ni}(\text{C}_2\text{O}_4)_3$	190 °C	1:2:1.5:4	4 Days
$\text{RbLi}_3\text{Fe}(\text{C}_2\text{O}_4)_3$	160 °C	1:2:1.5:4	4 Days
$\text{RbLi}_3\text{Co}(\text{C}_2\text{O}_4)_3$	160 °C	1:2:1.5:4	4 Days
$\text{RbLi}_3\text{Ni}(\text{C}_2\text{O}_4)_3$	160 °C	1:2:2:4	4 Days
$\text{CsLi}_3\text{Fe}(\text{C}_2\text{O}_4)_3$	160 °C	1:2:1:4	5 Days
$\text{CsLi}_3\text{Co}(\text{C}_2\text{O}_4)_3$	160 °C	1:2:1.5:4	4 Days
$\text{CsLi}_3\text{Ni}(\text{C}_2\text{O}_4)_3$	160 °C	1:2:2:4	4 Days

2. Powder X-ray Diffraction

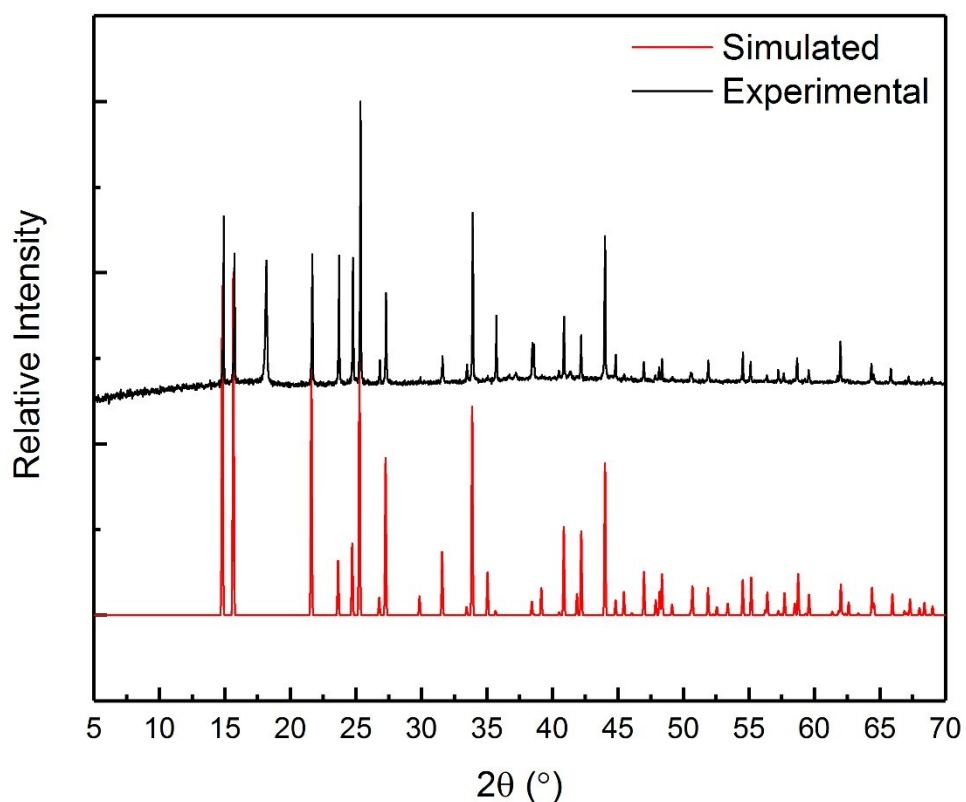


Figure S1 Powder X-ray diffraction pattern of $\text{KLi}_3\text{Co}(\text{C}_2\text{O}_4)_3$ and comparison with that simulated from single crystal X-ray diffraction data. The peak near 18° is from the sample holder.

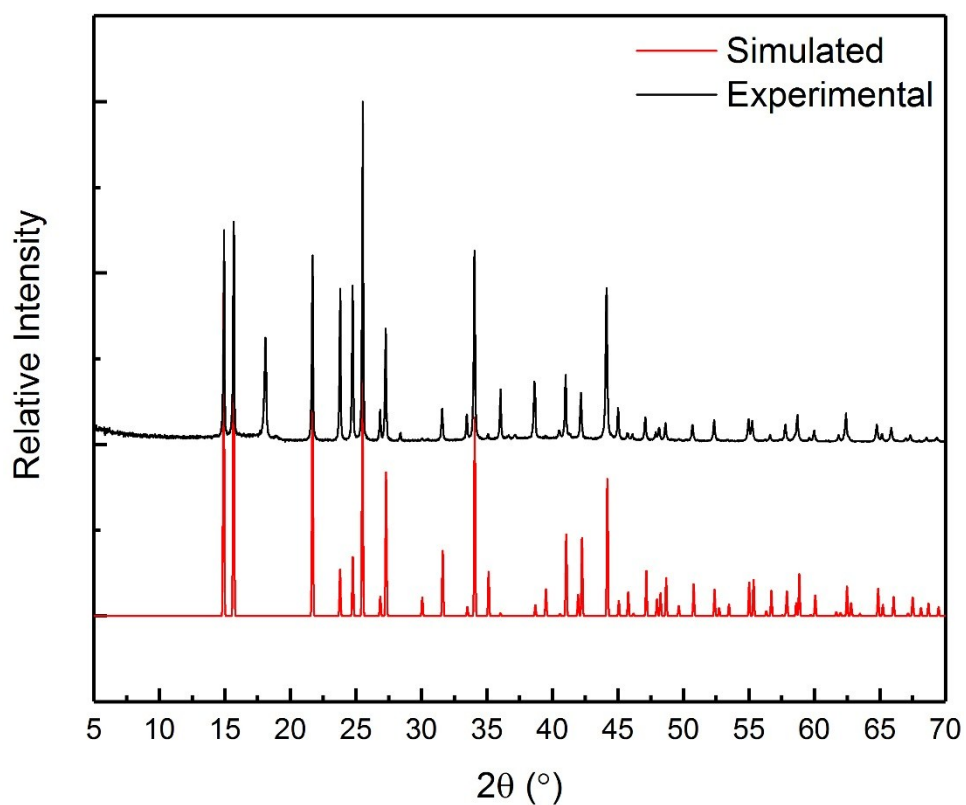


Figure S2 Powder X-ray diffraction pattern of $\text{KLi}_3\text{Ni}(\text{C}_2\text{O}_4)_3$ and comparison that simulated from single crystal X-ray diffraction data. The peak near 18° is from the sample holder.

3. Cs-O Bond Valence Sum Calculations

BVS values were calculated using Equation S1 and the R_o and b parameters shown in Table S2.¹⁻³

Equation S1

$$V_i = \exp\left(\frac{R_o - R_i}{b}\right)$$

Table S2 Bond valence parameters used in BVS calculations

	Breese	Gagne 2015	Gagne 2016
R_o	2.42	2.296	1.966
b	0.37	0.411	0.561

Table S3 Cs-O bond valence sum calculations for the 10 compounds with highest values

ICSD No.	Formula	Breese	Gagne 2015	Gagne 2016
79098	CsNa ₃ Li ₁₂ (GeO ₄) ₄	1.618	1.433	1.350
56252	Cs ₂ PbCu(NO ₂) ₆	1.434	1.311	1.315
74863	CsKNaLi ₉ (Li(SiO ₄)) ₄	1.3964	1.255	1.226
2381	Cs ₂ PbCu(NO ₂) ₆	1.385	1.270	1.286
89508	CsMnO ₄	1.384	1.264	1.270
90111	Cs ₂ (TeMo ₂ O ₆ (PO ₄) ₂)	1.378	1.241	1.219
280831	Cs ₅ (P(Mo ₄ O ₁₄ (OH)) ₂)(H ₂ O) ₂	1.375	1.243	1.228
74864	CsKNa ₂ Li ₈ (Li(SiO ₄)) ₄	1.372	1.237	1.215
170083	(Cs ₂ (Cr ₄ O ₁₃))	1.337	1.218	1.223
63259	Cs ₄ (Mo ₈ P ₁₂ O ₅₂)	1.325	1.196	1.183

Table S4 Cs-O bond valence sum calculations for other Cs containing oxalate compounds

ICSD No.	Formula	Breese	Gagne 2015	Gagne 2016
39364	CsHC ₂ O ₄	1.195	1.100	1.132
109663	Cs(V(H ₂ O) ₂ (C ₂ O ₄) ₂)(H ₂ O) ₄	0.863	0.823	0.920
109838	Cs ₈ (TiO(C ₂ O ₄) ₂) ₄ (H ₂ O) ₆	1.060	0.991	1.059
109908	Cs ₂ (Mo ₃ O ₄ (C ₂ O ₄) ₃ (H ₂ O) ₃)(H ₂ O) ₄)(C ₂ H ₂ O ₄) _{0.5}	0.955	0.893	0.962
249033	Cs((UO ₂) ₂ (C ₂ O ₄) ₂ (OH))(H ₂ O)	1.006	0.981	1.036

Table S5 Cs-O bond valence sum calculations for the Cs-containing perovskite-related oxalates (present work)

Compound	Breese	Gagne 2015	Gagne 2016
CsLi ₃ Fe(C ₂ O ₄) ₃	1.56	1.41	1.39
CsLi ₃ Co(C ₂ O ₄) ₃	1.62	1.46	1.42

References

- 1 N. E. Brese and M. O’Keeffe, *Acta Crystallogr. Sect. B*, 1991, **47**, 192–197.
- 2 O. C. Gagné and F. C. Hawthorne, *Acta Crystallogr. Sect. B*, 2015, **71**, 562–578.
- 3 O. C. Gagné and F. C. Hawthorne, *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.*, 2016, **72**, 602–625.