Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information: Selective metathesis synthesis of $MgCr_2S_4$ by control of thermodynamic driving forces

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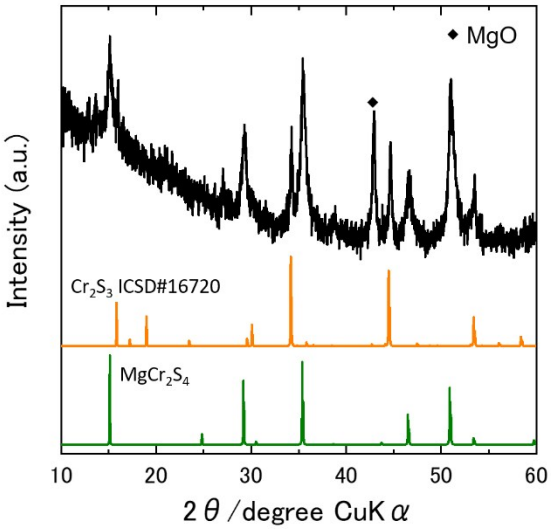

Figure S1. XRD patterns of $MgCr_2S_4$ synthesized from $NaCrS_2$ and $MgBr_2$-KBr flux with excess Na_2S and subsequent washing with methanol.

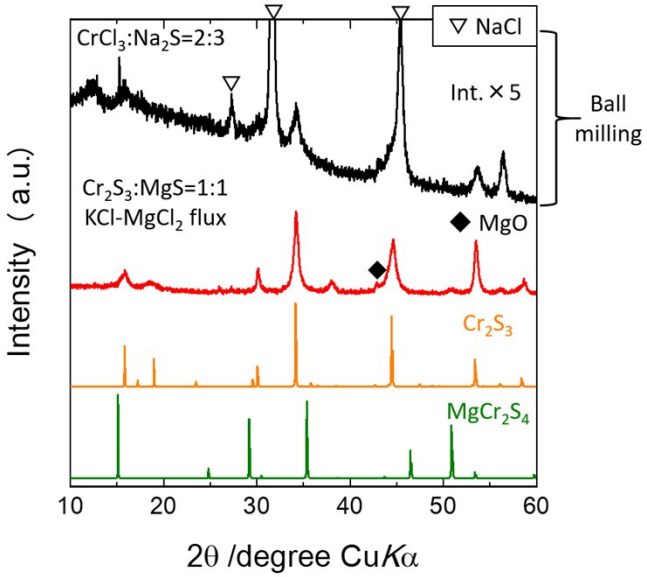

Figure S2. XRD patterns of (black) the mixture of Cr_2S_3 and NaCl ball-milling of $CrCl_3$ and Na_2S in the molar ratio of 2:3 according to 2 $CrCl_3$ + 3 Na_2S → Cr_2S_3 + 6 NaCl, and (red) the product of the subsequent reaction between Cr_2S_3 and MgS with KCl-$MgCl_2$ flux at 500 °C for 30 min and wash with water. The product phase primarily shows Cr_2S_3, and no $MgCr_2S_4$ is seen.

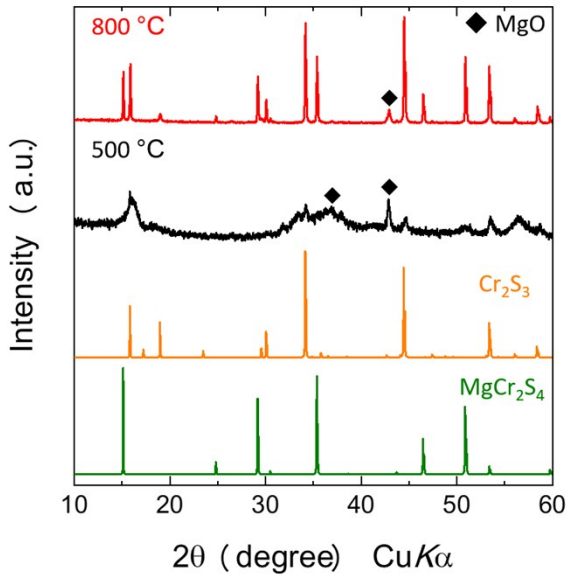

Figure S3. XRD pattern of the product of the reaction between $NaCrS_2$ and $MgCl_2$ without KCl at (black) 500 °C and (red) 800 °C for 30 min. No Na_2S excess was added. The reaction at 500 °C does not yield $MgCr_2S_4$ peaks. The 800 °C sample does show $MgCr_2S_4$ peaks, whose formation is likely facilitated by $MgCl_2$ melting at 714°C.

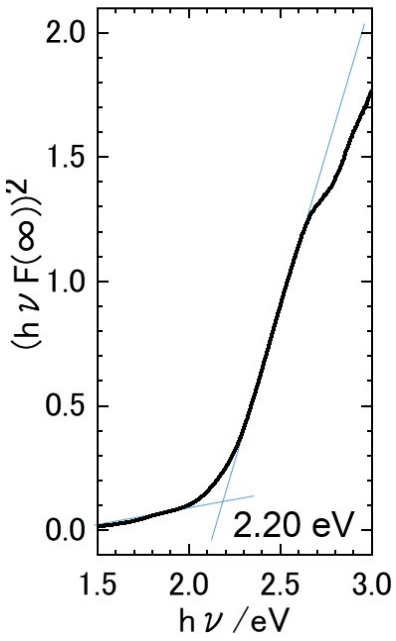

Figure S4. Tauc plot of $MgCr_2S_4$ powders synthesized under Na_2S excess condition.

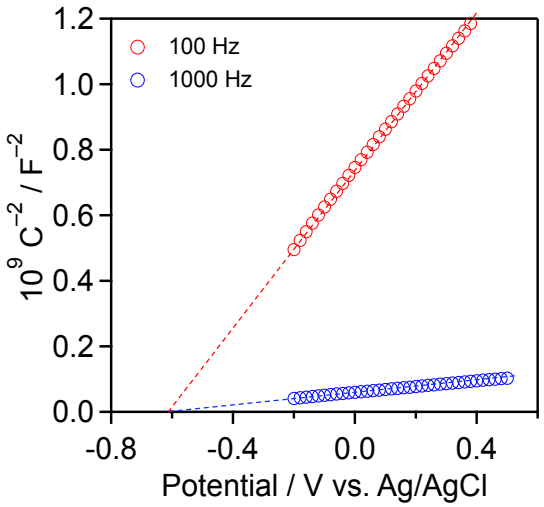

Figure S5. Mott–Schottky plot of the $MgCr_2S_4$/FTO electrode measured in aqueous NaH_2PO_4–Na_2HPO_4 solution (PO_4^{3-} = 0.1 M) at pH 7.0. The electrode was prepared by electrophoretic deposition in a 50 mL acetone solution (>99.5%, Kanto Chemical) containing 0.05 g $MgCr_2S_4$ powder (synthesized under Na_2S excess condition) and 10 mg iodine (>99.8%, Wako Pure Chemicals). Two parallel FTO electrodes were immersed in the solution with ca. 15 mm separation, and a 20 V bias was applied between them for 30 s using a potentiostat (PSW 80-13.5, GW Instek). The $MgCr_2S_4$-coated area was fixed ca. 1.5 cm × 3.5 cm.

Table S1. Comparing reaction enthalpies, ΔH_r, with Gibbs energies of reaction at 1000 K, ΔG_r(1000 K), for each reaction shown in the main text.

Eq	ΔH_r (kJ/mol)	ΔG_r(1000 K) (kJ/mol)	Reaction
1	-2	-9	$MgS + Cr_2S_3 \rightarrow MgCr_2S_4$
2	-47	-50	$2\ NaCrS_2 + MgCl_2 \rightarrow MgCr_2S_4 + 2\ NaCl$
3	-359	-326	$CrCl_3 + 2\ Na_2S \rightarrow NaCrS_2 + 3\ NaCl$
4	-16	-5	$NaCrS_2 + LiCl \rightarrow LiCrS_2 + NaCl$
5	33	36	$NaCrS_2 + KCl \rightarrow KCrS_2 + NaCl$