Supplementary information

New layered chromium chalcogenides $CsLiCrSe_2$, $RbLiCrS_2$ and $CsLiCrS_2$: structure and properties

Xiaoning Sun,[a,b] Yanpeng Song,[a,b] Jun Deng,[a,b] Shifeng Jin,*[a,c] and Xiaolong Chen *[a,b,c,d]

[a]*Research and Development Center for Functional Crystals, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.*
[b]*University of Chinese Academy of Sciences, Beijing 100049, China.*
[c]*School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 101408, China*
[d]*Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China.*

Table S1 Summary of Rietveld refinement parameters for $CsLiCrSe_2$, $CsLiCrS_2$ and $RbLiCrS_2$.

	CsLiCrSe2	CsLiCrS2	RbLiCrS2
Space group		I4/mmm (No. 139)	
a (Å)	4.4185(2)	4.2678(1)	4.1799(2)
c (Å)	13.8002(7)	13.2824(3)	12.9501(8)
V (Å^3)	269.42(2)	241.93(1)	226.26(2)
R_p (%)	5.84	6.24	4.36
R_{wp} (%)	7.38	8.32	5.59
R_{exp} (%)	4.52	4.93	3.73
χ^2	2.67	2.85	2.25
Ch-Cr/Li-*Ch* (°)	120.2(1) × 2 104.35(5) × 4	125.0(1) × 2 102.30(5) × 4	121.1(1) × 2 103.96(6) × 4
d(Cr/Li-*Ch*) (Å)	2.547(1) × 4	2.414(2) × 4	2.397(2) × 4
A= Cs, Rb (x, y ,z)		2a (0, 0, 0)	
A= Cs, Rb occupancy		1	
A= Cs, Rb U_{iso} (Å^2)	0.025(1)	0.0263(6)	0.0252(8)
Cr/Li (x, y ,z)		4d (0, 0.5, 0.25)	
Cr/Li occupancy		1	
Cr/Li U_{iso} (Å^2)	0.055(2)	0.028(1)	0.044(1)
Ch= Se, S (x, y ,z)	4d (0, 0, 0.3419(2))	4d (0, 0, 0.3350(2))	4d (0, 0, 0.3407(3))
Ch= Se, S occupancy		1	
Ch=Se, S U_{iso} (Å^2)	0.021(1)	0.023(1)	0.029(1)

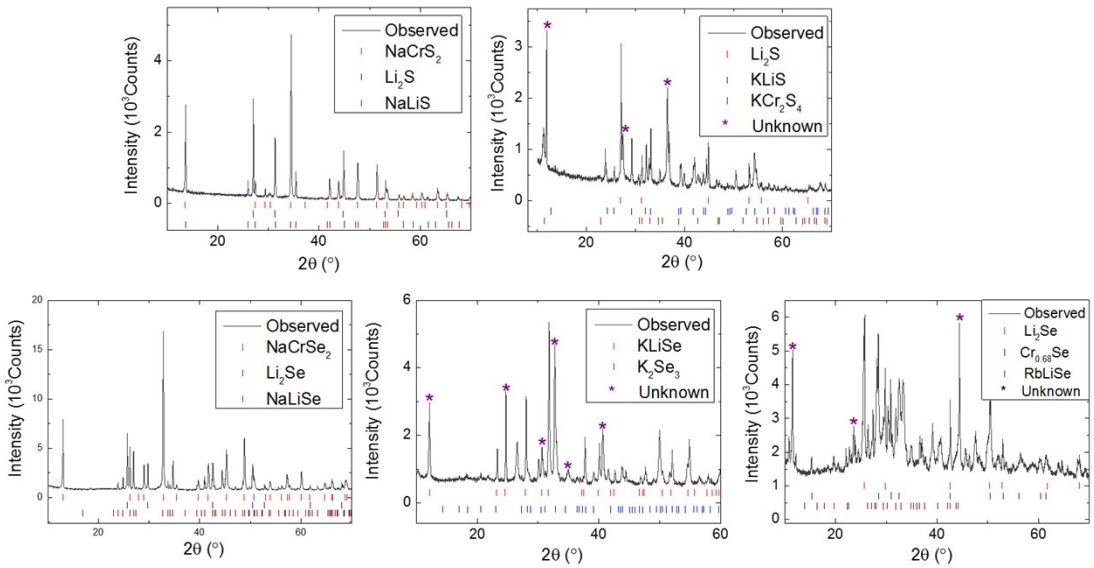

Fig S1 XRD patterns and the identified products for the failed reactions list in Table 1.

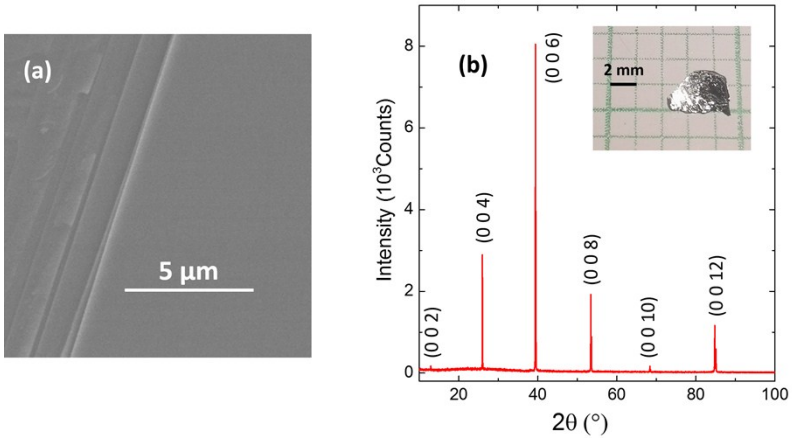

Fig S2 (a) Electron microscope image, (b) the XRD pattern and photograph of $CsLiCrSe_2$ single crystal (nominal).

Table S2 Chemical compositions, lattice parameters and spin-glass transiton temperature in $Cs(Li_{1-x}Cr_x)_2Se_2$.

Nominal formula	Formula from refinements	Formula from EDS & ICP-AES	*a* (Å)	c (Å)	T_S (K)
$Cs(Li_{0.55}Cr_{0.45})_2Se_2$	$Cs(Li_{0.552}Cr_{0.448})_2Se_2$	$Cs_{1.10(5)}(Li_{0.62(3)}Cr_{0.42(2)})_2Se_2$	4.41603(18)	13.82173(65)	8
$Cs(Li_{0.5}Cr_{0.5})_2Se_2$	$Cs(Li_{0.496}Cr_{0.504})_2Se_2$	$Cs_{1.08(5)}(Li_{0.55(3)}Cr_{0.50(3)})_2Se_2$	4.41855(21)	13.80022(69)	15
$Cs(Li_{0.45}Cr_{0.55})_2Se_2$	$Cs(Li_{0.424}Cr_{0.576})_2Se_2$	$Cs_{0.97(5)}(Li_{0.46(2)}Cr_{0.59(3)})_2Se_2$	4.43787(20)	13.72584(71)	18

Table S3 Comparison of lattice parameters, bond length d(*M'*/*M*-*Ch*) and bond angle β in *AM'MCh*$_2$.

	***a* (Å)**	***c* (Å)**	**d(*M'*/*M*-*Ch*) (Å)**	**β(°)**
$KLiFeSe_2$[1]	4.1044(2)	13.7194(9)	2.5050 (1)	110.020(2)
$RbLiFeSe_2$[1]	4.1609(1)	14.0420(5)	2.5218 (2)	111.172(1)
$KCoCuS_2$[2]	3.8831(9)	13.058(1)	2.5198(4)	100.8019
$RbCoCuS_2$[2]	3.9314(5)	13.448(2)	2.5691(3)	99.8399
$CsCoCuS_2$[2]	3.9667(9)	13.833(4)	2.6313(5)	97.8348
$KLiMnS_2$[3]	4.070(3)	13.227(7)	2.439(4)	113.0(2)
$RbLiMnS_2$[3]	4.106(2)	13.579(6)	2.4765(9)	111.9888
$CsLiMnS_2$[3]	4.168(5)	14.006(9)	2.592(3)	107.0504
$KLiZnS_2$[3]	3.998(2)	13.262(6)	2.411(4)	111.9(2)
$RbLiZnS_2$[3]	4.046(2)	13.537(5)	2.4493(9)	111.37

1. D. D. Yuan, N. Liu, K. K. Li, S. F. Jin, J. G. Guo and X. L. Chen, *Inorg Chem*, 2017, **56**, 13187 13193.
2. M. Oledzka, J. G. Lee, K. V. Ramanujachary and M. Greenblatt, *J Solid State Chem*, 1996, **127**, 151-160.
3. D. Schmitz and W. Bronger, *Z Anorg Allg Chem*, 1987, **553**, 248-260.

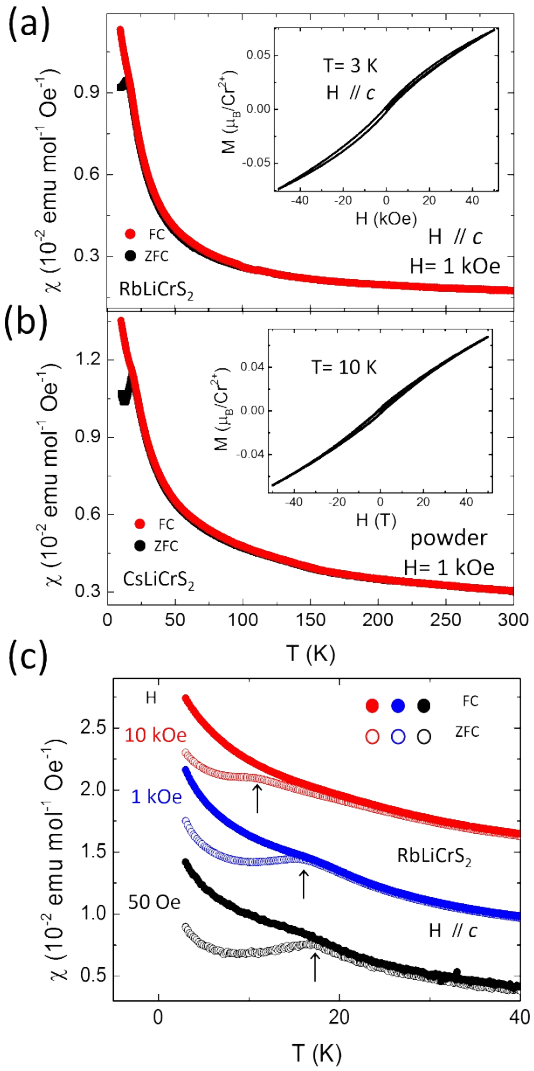

Fig S3 Zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities of (a) $RbLiCrS_2$ single crystal for H // *c* axis and (b) $CsLiCrS_2$ powder sample at H= 1 kOe. Insets show their M-H curves, respectively. (c) ZFC and FC curves of $RbLiCrS_2$ single crystal under different magnetic fields.

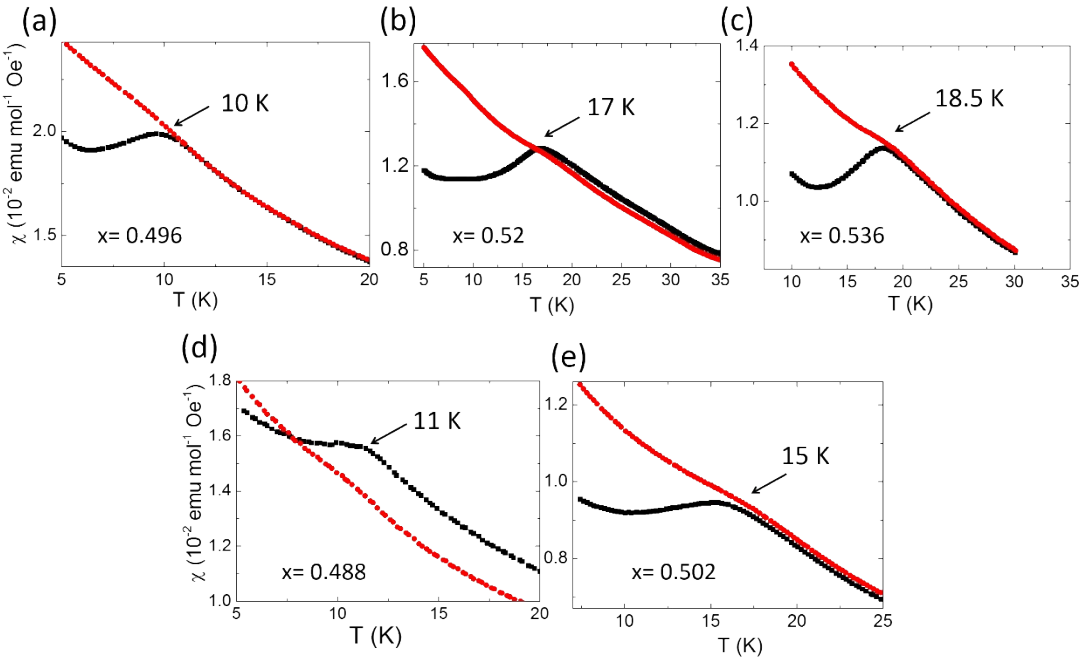

Fig S4 ZFC and FC curves of (a-c) $Cs(Li_{1-x}Cr_x)_2S_2$ and (d-e) $Rb(Li_{1-x}Cr_x)_2S_2$ with different x. x is obtained from Rietveld refinements.

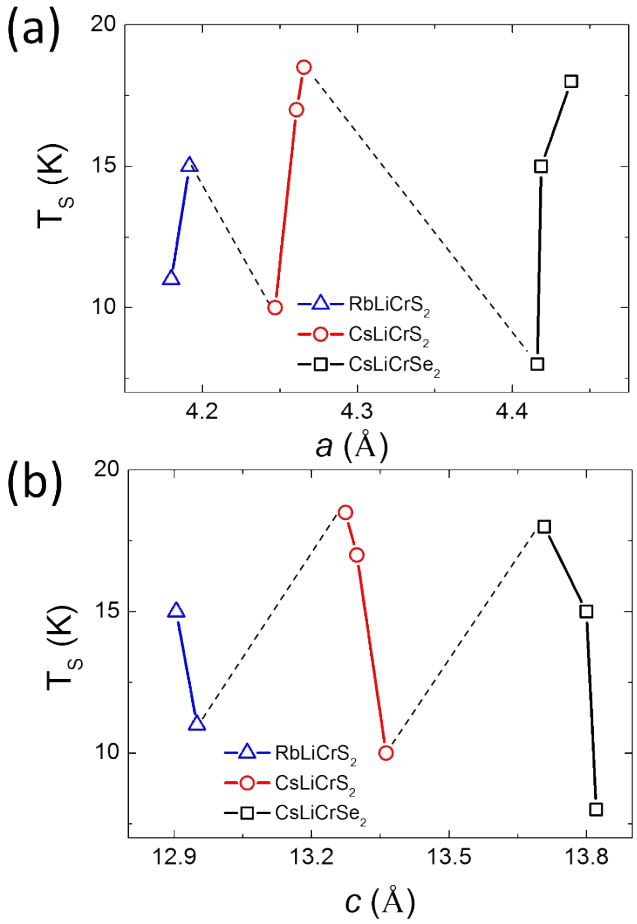

Fig S5 T_S in $A(Li_{1-x}Cr_x)_2Ch_2$ (A= Cs, Rb, Ch= S,Se)drawn against lattice parameter (a) a and (b) c.

Since the Cr concentration x affects both lattice parameters and the spin-glass temperature T_S, the relationship between lattice parameters and T_S can be established via x in $Cs(Li_{1-x}Cr_x)_2Se_2$, $Cs(Li_{1-x}Cr_x)_2S_2$ and $Rb(Li_{1-x}Cr_x)_2S_2$. As shown in Fig S6, higher T_S corresponds to larger a and smaller c. However, when the $A(Li_{1-x}Cr_x)_2Ch_2$ system is considered as a whole, T_S shows no clear dependence on a or c.