Electronic Supplementary Material (ESI) for Materials Horizons.

How to quantify isotropic negative thermal expansion: magnitude, range, or both?

Supplementary Information

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31st August 2018

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The following tables enumerate the data used in Fig. 5 of the main text, separated by compound class. The coefficients of thermal expansion, α_V are listed, alongside the temperature window of NTE, ΔT and the experimental method used to collect lattice expansion data. PXRD = powder X-ray diffraction, NPD = neutron powder diffraction, SCXRD = single-crystal X-ray diffraction, D = dilatometry, SG = strain gauge measurements. In some cases either α_V or ΔT values were not reported, in which case: either (i) α_V was calculated from values given in Supporting Information or (ii) the experimental data were digistised and α_V subsequently calculated[S1]. In both cases α_V was calculated from variable temperature data using PASCal[S2].

Table S1: Oxide and fluoride frameworks

Compound	α_V (MK^{-1})	T_1 (K)	T_2 (K)	ΔT (K)	χ_α (%)	Exp.	Ref.
ReO_3	$-3.0(3)$	15	294	279	-0.08	NPD	[S3]
Ag_2O*	$-21.0(6)$	40	470	430	-0.90	PXRD/NPD	[S4]
Cu_2O	-7.2	9	240	231	-0.17	PXRD	[S5]
ZrW_2O_8	-26.1	0.3	1050	1049.7	-2.74	PXRD/NPD	[S6, S7]
$Zr_{0.7}V_{1.33}Mo_{0.67}O_{6.73}$	-12.03	103	673	570	-0.69	PXRD/D	[S8]
SiO_2 (cristobalite)	$-6.9(6)$	1429	1977	548	-0.38	PXRD	[S9]
HfW_2O_8	-26.4	90	300	210	-0.55	PXRD	[S10]
$ZrMo_2O_8$	-15.0	11	573	562	-0.84	PXRD/NPD	[S11]
$HfMo_2O_8$ ‡	-12	77	573	496	-0.60		[S12]
ThP_2O_7	-10.5	473	1174	701	-0.74	PXRD	[S13]
CeP_2O_7	-5.7	718	1078	360	-0.21	PXRD	[S14]
$CaMn_7O_{12}$	-85.92	430	488	58	-0.50	PXRD	[S15]
ScF_3†	-12.3	10	1100	1090	-1.34	PXRD/NPD	[S16]
$MnZrF_6$	-13.41	300	673	373	-0.50	PXRD	[S17]
$FeZrF_6$	-9.72	300	673	373	-0.36	PXRD	[S17]
$Sc_{0.9}Al_{0.05}Fe_{0.05}F_3$	-4.8	300	800	500	-0.24	PXRD	[S18]
$Sc_{0.85}Al_{0.05}Fe_{0.1}F_3$	-2.31	300	800	500	-0.12	PXRD	[S18]
$Li_{0.04}(Sc_{0.94}Fe_{0.06})F_3$	-2.25	150	425	275	-0.06	NPD	[S19]
$Li_{0.02}(Sc_{0.97}Fe_{0.03})F_3$	-7.77	150	425	275	-0.21	NPD	[S19]
$(Sc_{0.9}Fe_{0.1})F_3$	-15.03	150	425	275	-0.41	NPD	[S19]
$CaNbF_6$†	-37.92	10	900	890	-3.37	PXRD/NPD	[S20]
$MgZrF_6$	-8	125	500	375	-0.30	PXRD	[S20]
$CaZrF_6$†	-21.0144	10	1022	1012	-2.13	PXRD/NPD	[S21]
$CaHfF_6$†	-49.5534	10	285	275	-1.36	NPD	[S21]
$Fe_{0.7}Ni_{0.3}ZrF_6$	-5.97	300	675	375	-0.22	PXRD	[S22]
$(Sc_{0.9}Zr_{0.1})F_{3+\delta}$*	$-23(2)$	300	650	350	-0.81	PXRD	[S23]
$Sc_{0.75}Y_{0.25}F_3$[1]*	$-10.39(12)$	250	800	550	-0.57	PXRD	[S24]
$TiZrF_6$	-18.27	300	623	323	-0.59	PXRD	[S25]

* Data digitised online and α_V calculated using PASCal [S2]

†α_V calculated from data in S.I.

‡ Values quoted from Ref. S26, experimental method unknown

Table S2: Cyanide framework

Compound	α_V (MK^{-1})	T_1 (K)	T_2 (K)	ΔT (K)	χ_α (%)	Exp.	Ref.
$Zn(CN)_2$	-50.7	25	375	350	-1.77	SCXRD	[S27]
$Cd(CN)_2$	-61.2	150	375	225	-1.38	SCXRD	[S27]
$Cd(CN)_2$ (single-network)	-100.5	170	375	205	-2.06	SCXRD	[S28]
$FeCo(CN)_6$	-4.41	4.2	300	295.8	-0.13	PXRD	[S29]
$Zn_3[Fe(CN)_6]_2$	-118.8	123	298	175	-2.08	PXRD	[S30]
$Cu_3[Fe(CN)_6]_2$	-59.7	123	298	175	-1.04	PXRD	[S30]
$Mn_3[Co(CN)_6]_2$	-87.6	123	298	175	-1.53	PXRD	[S30]
$Fe_3[Co(CN)_6]_2$	-58.8	123	298	175	-1.03	PXRD	[S30]
$Co_3[Co(CN)_6]_2$	-119.1	123	298	175	-2.08	PXRD	[S30]
$Ni_3[Co(CN)_6]_2$	-90	123	298	175	-1.58	PXRD	[S30]
$Cu_3[Co(CN)_6]_2$	-60	123	298	175	-1.05	PXRD	[S30]
$Zn_3[Co(CN)_6]_2$	-89.1	123	298	175	-1.56	PXRD	[S30]
$MnPt(CN)_6$	-19.74	100	400	300	-0.59	PXRD	[S31]
$FePt(CN)_6$	-12	100	400	300	-0.36	PXRD	[S31]
$CoPt(CN)_6$	-4.8	100	400	300	-0.14	PXRD	[S31]
$NiPt(CN)_6$	-3.06	100	400	300	-0.09	PXRD	[S31]
$ZnPt(CN)_6$	-10.59	100	400	300	-0.32	PXRD	[S31]
$CdPt(CN)_6$	-30.06	100	400	300	-0.90	PXRD	[S31]
$Cs_{0.91}Zn[Fe(CN)_6]_{0.97} \cdot 0.4H_2O$	-12.3	100	300	200	-0.25	PXRD	[S32]
$CsCd[Fe(CN)_6]\cdot 0.5H_2O$	-26.4	100	300	200	-0.53	PXRD	[S32]
$Rb_{0.78}Fe[Fe(CN)_6]_{0.83} \cdot 2.8H_2O$	-6.3	100	300	200	-0.13	PXRD	[S32]
$Rb_{0.64}Zn[Fe(CN)_6]_{0.88} \cdot 2.3H_2O$	-17.7	100	300	200	-0.35	PXRD	[S32]

Table S3: Zeolites

Framework	Topology	α_V (MK^{-1})	T_1 (K)	T_2 (K)	ΔT (K)	χ_α (%)	Exp.	Ref.
FAU	Zeolite Y (siliceous)	-12.6	25	572	547	-0.69	PXRD	[S33]
LTA	ITQ-29	-22.11	100	300	200	-0.44	PXRD	[S34]
LTA	Na-A (dehyd)	-6.34	100	300	200	-0.13	PXRD	[S35]
LTA	Ag-A (dehyd)	-7.68	100	300	200	-0.15	PXRD	[S34]
FAU	SiY	-12.06	298	923	625	-0.75	PXRD	[S36]
FAU	NaX (dry)	-5.28	423	723	300	-0.16	PXRD	[S37]
	NaY (hyd)	-3.87	461	613	152	-0.06	PXRD	[S37]
LTA	NaA (dry)	-8.94	373	723	350	-0.31	PXRD	[S37]
MTN	dodecasil 3C	-5.1	463	1002	539	-0.27	PXRD	[S38]
FAU	Na-zeolite X*	$-3.3(6)$	25	293	268	0.09	PXRD	[S39]
FAU	SAPO-37	-10.71	303	773	470	-0.50	PXRD	[S40]

* Numerical data obtained from paper and α_V calculated using PASCal.[S2]

Table S4: Metal-Organic Frameworks

Compound	α_V (MK^{-1})	T_1 (K)	T_2 (K)	ΔT (K)	χ_α (%)	Exp.	Ref.
HKUST-1	$-12.3(3)$	80	500	420	-0.52	SCXRD/PXRD	[S41]
MOF-14	-18.5	3	395	392	-0.72	PXRD/NPD	[S42]
MOF-5	$-39.3(3)$	80	500	420	-1.65	PXRD	[S43]
d-UiO-66(Hf) $n = 5$	$-70(2)$	473	653	180	-1.26	PXRD	[S44]
d-UiO-66(Hf) $n = 4.5$	$-81(4)$	473	653	180	-1.45	PXRD	[S44]
d-UiO-66(Hf) $n = 4$	$-95(2)$	473	653	180	-1.71	PXRD	[S44]
d-UiO-66(Hf) $n = 3.5$	$-88(5)$	473	653	180	-1.58	PXRD	[S44]
d-UiO-66(Hf) $n = 3$	$-94(5)$	473	653	180	-1.68	PXRD	[S44]
d-UiO-66(Hf) $n = 2.5$	$-97(4)$	473	653	180	-1.75	PXRD	[S44]

n = defect concentration

Table S5: Magnetic NTE

Compound	α_V (MK^{-1})	T_1 (K)	T_2 (K)	ΔT (K)	χ_α (%)	Exp.	Ref.
$(Ga_{0.7}Cu_{0.3})_{0.85}Mn_{0.15}NMn_3$	-436.2	210	230	20	-0.87	SG	[S45]
$(Ga_{0.7}Cu_{0.3})_{0.8}Mn_{0.2}NMn_3$	-176.1	170	215	45	-0.79	SG	[S45]
$(Ga_{0.7}Cu_{0.3})_{0.75}Mn_{0.25}NMn_3$	-57.3	10	175	165	-0.95	SG	[S45]
$(Ga_{0.7}Cu_{0.3})_{0.7}Mn_{0.3}NMn_3$	-68.4	10	125	115	-0.79	SG	[S45]
$(Ga_{0.7}Cu_{0.3})_{0.69}Mn_{0.31}NMn_3$	-76.2	10	90	80	-0.61	SG	[S45]
$(Ga_{0.7}Cu_{0.3})_{0.68}Mn_{0.32}NMn_3$	-77.1	10	80	70	-0.54	SG	[S45]
$Ag_{0.7}Mn_{0.3}NMn_3$	-171	213	233	20	-0.34	SG	[S46]
$Ag_{0.6}Mn_{0.4}NMn_3$	-50.1	175	212	37	-0.19	SG	[S46]
$Ag_{0.5}Mn_{0.5}NMn_3$	-15.3	135	185	50	-0.08	SG	[S46]
$Ga_{0.9}Cr_{0.1}N_{0.83}Mn_3$	-138	256	318	62	-0.86	SG	[S47]
$Ga_{0.8}Cr_{0.2}N_{0.83}Mn_3$	-67.8	151	232	81	-0.55	SG	[S47]
$Ga_{0.8}Mn_{0.2}N_{0.8}Mn_3$	-153	294	339	45	-0.69	SG	[S48]
$Ga_{0.75}Mn_{0.25}N_{0.8}Mn_3$	-126	255	309	54	-0.68	SG	[S48]
$Ga_{0.7}Mn_{0.3}N_{0.8}Mn_3$	-75	206	279	73	-0.55	SG	[S48]
$Zn_{0.5}Ge_{0.5}N(Mn_{0.96}Fe_{0.04})_3$	-75	316	386	70	-0.53	SG	[S49]
$Zn_{0.55}Sn_{0.45}N_{0.85}C_{0.1}B_{0.05}Mn_3$	-111	270	325	55	-0.61	SG	[S50]
$Zn_{0.5}Sn_{0.5}N_{0.85}C_{0.1}B_{0.05}Mn_3$	-90	280	340	60	-0.54	SG	[S50]
$Cu_{0.53}Ge_{0.47}NMn_3$	-36	280	365	85	-0.31	SG	[S49]
$Cu_{0.5}Ge_{0.5}NMn_3$	-48	267	342	75	-0.36	SG	[S49]
$Cu_{0.5}Sn_{0.5}NMn_3$	-84	296	332	36	-0.30	D/PXRD	[S51]
$Cu_{0.6}Si_{0.15}Ge_{0.25}NMn_3$	-48	120	184	64	-0.31	SG	[S52]
$Ga_{0.6}Ge_{0.4}NMn_3$	-55.2	370	430	60	-0.33	D/PXRD	[S53]
$Ga_{0.75}Si_{0.25}NMn_3$	-42	272	420	148	-0.62	PXRD	[S54]
$Ga_{0.7}Ge_{0.3}N_{0.88}C_{0.12}Mn_3$	-54	197	319	122	-0.66	SG	[S49]
$Ga_{0.8}Ge_{0.2}NMn_3$	-104.7	300	370	70	-0.73	D/PXRD	[S53]
$Ga_{0.9}Sn_{0.1}NMn_3$	-82.5	279	338	59	-0.49	D	[S55]
$Zn_{0.4}Sn_{0.6}NMn_3$	-114	410	440	30	-0.34	D/PXRD	[S51]
$Zn_{0.4}Sn_{0.6}N_{0.85}C_{0.15}Mn_3$	-69	270	336	66	-0.46	D/PXRD	[S51]
$Zn_{0.9}Ge_{0.1}NMn_3$	-684	202	222	20	-1.37	PXRD	[S56]
$Zn_{0.7}Ge_{0.3}NMn_3$	-93	299	373	74	-0.69	PXRD	[S56]
$Zn_{0.5}Ge_{0.5}NMn_3$	-21.45	348	448	100	-0.21	PXRD	[S56]
$Zn_{0.8}Mn_{0.2}NMn_3$	-174.6	94	155	61	-1.07	SG	[S57]
$Zn_{0.75}Mn_{0.25}NMn_3$	-87.6	78	152	74	-0.65	SG	[S57]
$Zn_{0.7}Mn_{0.3}NMn_3$	-49.5	52	150	98	-0.49	SG	[S57]

Table S6: Magnetic NTE, continued

Compound	α_V (MK^{-1})	T_1 (K)	T_2 (K)	ΔT (K)	χ_α (%)	Exp.	Ref.
$Zn_{0.8}Co_{0.2}NMn_3$	-165.9	125	180	55	-0.91	PXRD	[S58]
$Zn_{0.6}Co_{0.4}NMn_3$	-93	180	230	50	-0.47	PXRD	[S58]
$Zn_{0.5}Co_{0.5}NMn_3$	-50.1	150	240	90	-0.45	PXRD	[S58]
$Zn_{0.3}Co_{0.7}NMn_3$	-20.4	153	223	70	-0.14	PXRD	[S58]
$La(Fe_{0.96}Co_{0.04})_{11.4}Al_{1.6}$	-50.19	138	290	152	-0.76	SG	[S59]
$La(Fe_{0.94}Co_{0.06})_{11.4}Al_{1.6}$	-49.65	150	325	175	-0.87	SG	[S59]
$La(Fe_{0.92}Co_{0.08})_{11.4}Al_{1.6}$	-38.88	160	350	190	-0.74	SG	[S59]
$LaFe_{10.5}CoSi_{1.5}$	-78.3	240	350	110	-0.86	D	[S60]
$LaFe_{10.6}Si_{2.4}$	-15.12	77	300	223	-0.34	D	[S60]
$LaFe_{11.3}Co_{0.2}Si_{1.5}$	-167.4	200	274	74	-1.24	D	[S60]
$LaFe_{11.5}Si_{1.5}$	-45.6	77	300	223	-1.02	D	[S60]
$LiGaCr_4S_8$*	-14.7	12	111	99	-0.15	PXRD/NPD	[S61]
$LaPrFe_{10.7}Co_{0.8}Si_{1.5}$	-97.5	200	300	100	-0.98	SG	[S62]
$La_{0.9}Pr_{0.1}Fe_{10.7}Co_{0.8}Si_{1.5}$	-101.4	200	300	100	-1.01	SG	[S62]
$La_{0.7}Pr_{0.3}Fe_{10.7}Co_{0.8}Si_{1.5}$	-110.4	200	300	100	-1.10	SG	[S62]
$La_{0.5}Pr_{0.5}Fe_{10.7}Co_{0.8}Si_{1.5}$	-115.5	200	300	100	-1.16	SG	[S62]
$LaFe_{11.5}Si_{1.5}Co_{1.6}$	-149.1	180	250	70	-1.04	SG/PXRD	[S63]

* Data digitised online and α_V calculated using PASCal [S2]

Table S7: Charge transfer NTE

Compound	α_V (MK^{-1})	T_1 (K)	T_2 (K)	ΔT (K)	χ_α (%)	Exp.	Ref.
$YbInCu_4$*	-57.9	9	80	71	-0.41	PXRD	[S64]
$Sm_{0.55}Y_{0.45}S$*	-65.4	9	250	241	-1.58	PXRD	[S65]
$Sm_{0.7}Y_{0.3}S$*	-96.9	9	250	241	-2.34	PXRD	[S65]
$SrCu_3Fe_4O_{12}$†	-40.23	170	270	100	-0.40	PXRD	[S66]
$LaCu_3Fe_{3.25}Mn_{0.75}O_{12}$	-66(3)	300	340	40	-0.26	PXRD	[S67]
$Ca_{0.2}Sr_{0.8}Cu_3Fe_4O_{12}$*	-30(3)	191	271	80	-0.24	PXRD	[S68]
$Ca_{0.4}Sr_{0.6}Cu_3Fe_4O_{12}$*	-23(3)	180	240	60	-0.14	PXRD	[S68]
$SrCu_3Fe_{3.5}Mn_{0.5}O_{12}$	-19.2(6)	240	350	110	-0.21	PXRD	[S69]
$SrCu_3Fe_3MnO_{12}$	-17.1(15)	300	370	70	-0.12	PXRD	[S69]

* Data digitised online and α_V calculated using PASCal [S2]

S1 References

[S1] A. Rohatgi, *WebPlotDigitizer*, https://automeris.io/WebPlotDigitizer, 2018.

[S2] M. J. Cliffe and A. L. Goodwin, *J. Appl. Crystallogr.*, 2012, **45**, 1321–1329.

[S3] E. E. Rodriguez, A. Llobet, T. Proffen, B. C. Melot, R. Seshadri and P. B. Littlewood, *J. Appl. Phys.*, 2009, **105**, 114901.

[S4] B. J. Kennedy, Y. Kubota and K. Kato, *Solid State Commun.*, 2005, **136**, 177–180.

[S5] A. Sanson, F. Rocca, G. Dalba, P. Fornasini, R. Grisenti, M. Dapiaggi and G. Artioli, *Phys. Rev. B*, 2006, **73**, 214305.

[S6] J. S. O. Evans, T. A. Mary, T. Vogt, M. A. Subramanian and A. W. Sleight, *Chem. Mater.*, 1996, **8**, 2809–2823.

[S7] T. A. Mary, J. S. O. Evans, T. Vogt and A. W. Sleight, *Science*, 1996, **272**, 90–92.

[S8] M. Zhang, Y. Mao, J. Guo, W. Zhou, M. Chao, N. Zhang, M. Yang, X. Kong, X. Kong and E. Liang, *RSC Adv.*, 2017, **7**, 3934–3940.

[S9] E. Bourova and P. Richet, *Geophys. Res. Lett.*, 1998, **25**, 2333–2336.

[S10] Y. Yamamura, N. Nakajima and T. Tsuji, *Phys. Rev. B*, 2001, **64**, 184109.

[S11] C. Lind, A. P. Wilkinson, Z. Hu, S. Short and J. D. Jorgensen, *Chem. Mater.*, 1998, **10**, 2335–2337.

[S12] C. A. Kennedy, M. A. White, A. P. Wilkinson and T. Varga, *Appl. Phys. Lett.*, 2007, **90**, 151906.

[S13] G. Wallez, P. E. Raison, N. Dacheux, N. Clavier, D. Bykov, L. Delevoye, K. Popa, D. Bregiroux, A. N. Fitch and R. J. M. Konings, *Inorg. Chem.*, 2012, **51**, 4314–4322.

[S14] K. M. White, P. L. Lee, P. J. Chupas, K. W. Chapman, E. A. Payzant, A. C. Jupe, W. A. Bassett, C.-S. Zha and A. P. Wilkinson, *Chem. Mater.*, 2008, **20**, 3728–3734.

[S15] K. Gautam, D. K. Shukla, S. Francoual, J. Bednarcik, J. R. L. Mardegan, H.-P. Liermann, R. Sankar, F. C. Chou, D. M. Phase and J. Strempfer, *Phys. Rev. B*, 2017, **95**, 144112.

[S16] B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas, K. W. Chapman and A. P. Wilkinson, *J. Am. Chem. Soc.*, 2010, **132**, 15496–15498.

[S17] L. Hu, J. Chen, J. Xu, N. Wang, F. Han, Y. Ren, Z. Pan, Y. Rong, R. Huang, J. Deng, L. Li and X. Xing, *J. Am. Chem. Soc.*, 2016, **138**, 14530–14533.

[S18] F. Han, J. Chen, L. Hu, Y. Ren, Y. Rong, Z. Pan, J. Deng and X. Xing, *J. Am. Ceram. Soc.*, 2016, **99**, 2886–2888.

[S19] J. Chen, Q. Gao, A. Sanson, X. Jiang, Q. Huang, A. Carnera, C. G. Rodriguez, L. Olivi, L. Wang, L. Hu, K. Lin, Y. Ren, Z. Lin, C. Wang, L. Gu, J. Deng, J. P. Attfield and X. Xing, *Nat. Commun.*, 2017, **8**, 14441.

[S20] B. R. Hester, J. C. Hancock, S. H. Lapidus and A. P. Wilkinson, *Chem. Mater.*, 2017, **29**, 823–831.

[S21] J. C. Hancock, K. W. Chapman, G. J. Halder, C. R. Morelock, B. S. Kaplan, L. C. Gallington, A. Bongiorno, C. Han, S. Zhou and A. P. Wilkinson, *Chem. Mater.*, 2015, **27**, 3912–3918.

[S22] J. Xu, L. Hu, L. Wang, J. Deng, J. Chen and X. Xing, *Acta Phys. Chem. Sin.*, 2018, **34**, 339–343.

[S23] T. Wang, J. Xu, L. Hu, W. Wang, R. Huang, F. Han, Z. Pan, J. Deng, Y. Ren, L. Li, J. Chen and X. Xing, *Appl. Phys. Lett.*, 2016, **109**, 181901.

[S24] C. R. Morelock, B. K. Greve, L. C. Gallington, K. W. Chapman and A. P. Wilkinson, *J. Appl. Phys.*, 2013, **114**, 213501.

[S25] C. Yang, Y. Zhang, J. Bai, B. Qu, P. Tong, M. Wang, J. Lin, R. Zhang, H. Tong, Y. Wu, W. Song and Y. Sun, *J. Mater. Chem. C*, 2018, **6**, 5148–5152.

[S26] C. Lind, A. P. Wilkinson, C. J. Rawn and E. A. Payzant, *J. Mater. Chem.*, 2001, **11**, 3354–3359.

[S27] A. L. Goodwin and C. J. Kepert, *Phys. Rev. B*, 2005, **71**, 140301.

[S28] A. E. Phillips, A. L. Goodwin, G. J. Halder, P. D. Southon and C. J. Kepert, *Angew. Chem. Int. Ed.*, 2008, **47**, 1396–1399.

[S29] S. Margadonna, K. Prassides and A. N. Fitch, *J. Am. Chem. Soc.*, 2004, **126**, 15390–15391.

[S30] S. Adak, L. L. Daemen, M. Hartl, D. Williams, J. Summerhill and H. Nakotte, *J. Solid State Chem.*, 2011, **184**, 2854–2861.

[S31] K. W. Chapman, P. J. Chupas and C. J. Kepert, *J. Am. Chem. Soc.*, 2006, **128**, 7009–7014.

[S32] T. Matsuda, J. E. Kim, K. Ohoyama and Y. Moritomo, *Phys. Rev. B*, 2009, **79**, 172302.

[S33] M. P. Attfield and A. W. Sleight, *Chem. Commun.*, 1998, 601–602.

[S34] T. Carey, A. Corma, F. Rey, C. C. Tang, J. A. Hriljac and P. A. Anderson, *Chem. Commun.*, 2012, **48**, 5829–5831.

[S35] T. Carey, C. C. Tang, J. A. Hriljac and P. A. Anderson, *Chem. Mater.*, 2014, **26**, 1561–1566.

[S36] L. Leardini, S. Quartieri, G. Vezzalini and R. Arletti, *Micro. Meso. Mater.*, 2015, **202**, 226–233.

[S37] M. Noack, M. Schneider, A. Dittmar, G. Georgi and J. Caro, *Micro. Meso. Mater.*, 2009, **117**, 10–21.

[S38] S. H. Park, R. W. Große-Kunstleve, H. Graetsch and H. Gies, *Stud. Surf. Sci. and Catal.*, 1997, **105**, 1989–1994.

[S39] J. W. Couves, R. H. Jones, S. C. Parker, P. Tschaufeser and C. R. A. Catlow, *J. Phys.: Condens. Matter*, 1993, **5**, 329.

[S40] V. R. Buragadda, L. Yu, F. G. Alabarse, A. Haidoux, C. Levelut, A. van der Lee, O. Cambon and J. Haines, *RSC Adv.*, 2013, **3**, 9911–9915.

[S41] Y. Wu, A. Kobayashi, G. Halder, V. Peterson, K. Chapman, N. Lock, P. Southon and C. Kepert, *Angew. Chem. Int. Ed.*, 2008, **47**, 8929–8932.

[S42] Y. Wu, V. K. Peterson, E. Luks, T. A. Darwish and C. J. Kepert, *Angew. Chem. Int. Ed.*, 2014, **53**, 5175–5178.

[S43] N. Lock, Y. Wu, M. Christensen, L. J. Cameron, V. K. Peterson, A. J. Bridgeman, C. J. Kepert and B. B. Iversen, *J. Phys. Chem. C*, 2010, **114**, 16181–16186.

[S44] M. J. Cliffe, J. A. Hill, C. A. Murray, F.-X. Coudert and A. L. Goodwin, *Phys. Chem. Chem. Phys.*, 2015, **17**, 11586–11592.

[S45] X. Guo, P. Tong, J. Lin, C. Yang, K. Zhang, M. Wang, Y. Wu, S. Lin, W. Song and Y. Sun, *Scripta Mater.*, 2017, **128**, 74–77.

[S46] J. C. Lin, P. Tong, W. Tong, S. Lin, B. S. Wang, W. H. Song, Y. M. Zou and Y. P. Sun, *Appl. Phys. Lett.*, 2015, **106**, 082405.

[S47] X. Guo, P. Tong, J. Lin, C. Yang, K. Zhang, S. Lin, W. Song and Y. Sun, *Front. Chem.*, 2018, **6**, 75.

[S48] X. G. Guo, J. C. Lin, P. Tong, M. Wang, Y. Wu, C. Yang, B. Song, S. Lin, W. H. Song and Y. P. Sun, *Appl. Phys. Lett.*, 2015, **107**, 202406.

[S49] K. Takenaka and H. Takagi, *Appl. Phys. Lett.*, 2005, **87**, 261902.

[S50] T. Hamada and K. Takenaka, *J. Appl. Phys.*, 2011, **109**, 07E309.

[S51] K. Takenaka, K. Asano, M. Misawa and H. Takagi, *Appl. Phys. Lett.*, 2008, **92**, 011927.

[S52] R. Huang, L. Li, F. Cai, X. Xu and L. Qian, *Appl. Phys. Lett.*, 2008, **93**, 081902.

[S53] L. Huiqing, S. Ying, D. Sihao, S. Kewen, W. Lei, Z. Wenjun, H. Huimin, D. Shenghua and W. Cong, *J. Am. Ceram. Soc.*, 2017, **100**, 5739–5745.

[S54] S. Ying, W. Cong, W. Yongchun, C. Lihua, N. Man and L. Fusheng, *J. Am. Ceram. Soc.*, 2010, **93**, 650–653.

[S55] Z. Liqiang, W. Daolian, T. Jie, L. Wen, W. Wei, H. Rongjin and L. Laifeng, *Rare Metal Mater. Eng.*, 2014, **43**, 1304–1307.

[S56] Y. Sun, C. Wang, Y. Wen, K. Zhu and J. Zhao, *Appl. Phys. Lett.*, 2007, **91**, 231913.

[S57] J. Lin, P. Tong, W. Tong, Y. Zou, C. Yang, F. Zhu, X. Zhang, L. Li, M. Wang, Y. Wu, S. Lin, W. Song, X. Zhu and Y. Sun, *Scripta Mater.*, 2018, **152**, 6–10.

[S58] L. Chu, L. Ding, C. Wang, M. Li, Y. Guo and Z. Liu, *Materials*, 2018, **11**, 286.

[S59] Y. Zhao, R. Huang, S. Li, W. Wang, X. Jiang, Z. Lin, J. Li and L. Li, *Phys. Chem. Chem. Phys.*, 2016, **18**, 20276–20280.

[S60] R. Huang, Y. Liu, W. Fan, J. Tan, F. Xiao, L. Qian and L. Li, *J. Am. Chem. Soc.*, 2013, **135**, 11469–11472.

[S61] G. Pokharel, A. F. May, D. S. Parker, S. Calder, G. Ehlers, A. Huq, S. A. J. Kimber, H. S. Arachchige, L. Poudel, M. A. McGuire, D. Mandrus and A. D. Christianson, *Phys. Rev. B*, 2018, **97**, 134117.

[S62] W. Li, R. Huang, W. Wang, J. Tan, Y. Zhao, S. Li, C. Huang, J. Shen and L. Li, *Inorg. Chem.*, 2014, **53**, 5869–5873.

[S63] S. Li, R. Huang, Y. Zhao, W. Wang and L. Li, *Phys. Chem. Chem. Phys.*, 2015, **17**, 30999–31003.

[S64] B. Kindler, D. Finsterbusch, R. Graf, F. Ritter, W. Assmus and B. Lüthi, *Phys. Rev. B*, 1994, **50**, 704–707.

[S65] P. A. Alekseev, J.-M. Mignot, E. V. Nefeodova, K. S. Nemkovski, V. N. Lazukov, N. N. Tiden, A. P. Menushenkov, R. V. Chernikov, K. V. Klementiev, A. Ochiai, A. V. Golubkov, R. I. Bewley, A. V. Rybina and I. P. Sadikov, *Phys. Rev. B*, 2006, **74**, 035114.

[S66] Y. Ikuya, T. Kazuki, O. Kenya, H. Naoaki, K. Jungeun, T. Naruki, T. Ryoji, M. Masafumi, N. Norimasa, I. Toru, I. Tetsuo, K. Kenichi, T. Masaki and T. Mikio, *Angew. Chem. Int. Ed.*, 2011, **50**, 6579–6582.

[S67] I. Yamada, S. Marukawa, M. Murakami and S. Mori, *Appl. Phys. Lett.*, 2014, **105**, 231906.

[S68] I. Yamada, K. Shiro, N. Hayashi, S. Kawaguchi, T. Kawakami, R. Takahashi and T. Irifune, *J. Asian Ceram. Soc.*, 2017, **5**, 169–175.

[S69] I. Yamada, S. Marukawa, N. Hayashi, M. Matsushita and T. Irifune, *Appl. Phys. Lett.*, 2015, **106**, 151901.