Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Quantifying rigidity for thermally stable Cr^{3+} phosphors

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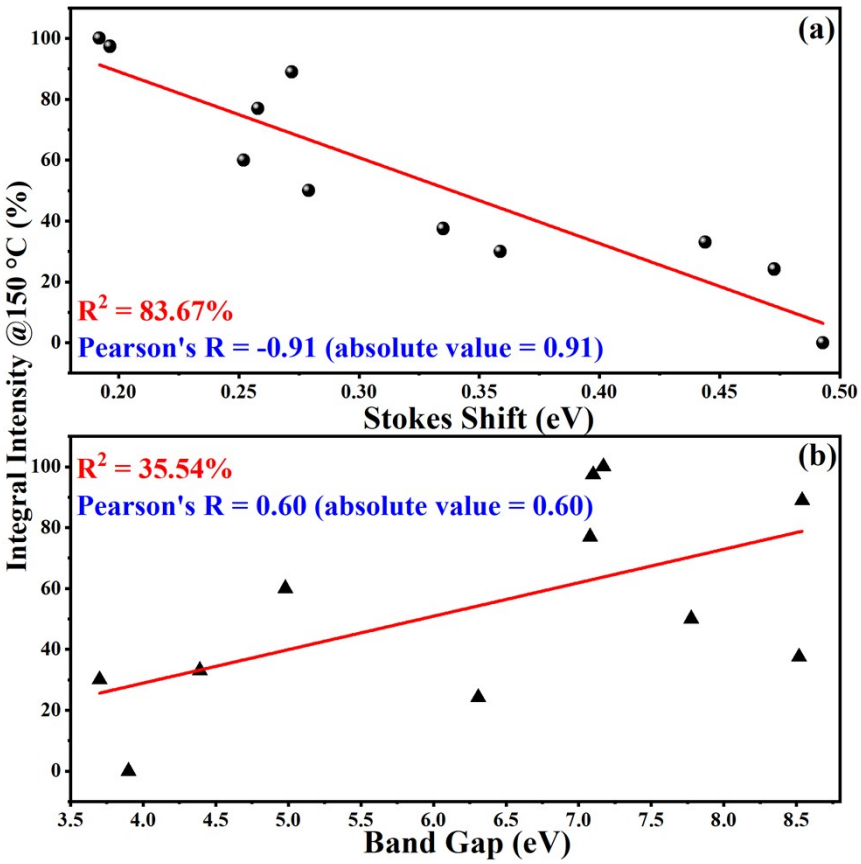

Figure S1. Correlation analysis of (a) Stokes shift vs thermal stability and (b) band gap vs thermal stability for Cr^{3+}-doped phosphors ($SrAl_{12}O_{19}$, $Ca_3Sc_2Si_3O_{12}$, CaMgSi2O6, $KAlP_2O_7$, $GaTaO_4$, $ScBO_3$, $Mg_2B_2O_5$, $Mg_2Ge_2O_6$, $Mg_4Ta_2O_9$, $LaSc_3(BO_3)_4$ and $LiIn_2SbO_6$). Pearson's R, also known as Pearson correlation coefficient, is a measure of linear correlation between two sets of data. Pearson's R ranged from -1 to 1, representing the negative to a positive correlation. The high absolute Pearson's R-value (close to -1 or 1) implies a strong correlation between the two sets of data while the low absolute Pearson's R-value (close to 0) implies a weak correlation.

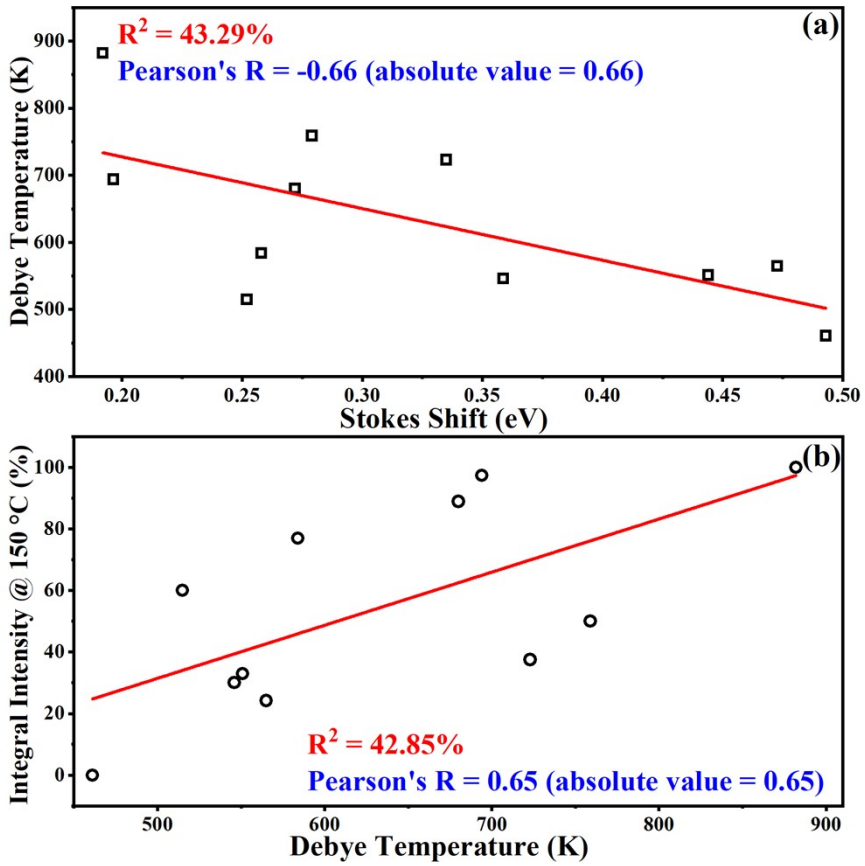

Figure S2. Correlation analysis of (a) Stokes shift vs Debye temperature and (b) Debye temperature and thermal stability for Cr^{3+}-doped phosphors ($SrAl_{12}O_{19}$, $Ca_3Sc_2Si_3O_{12}$, CaMgSi2O6, $KAlP_2O_7$, $GaTaO_4$, $ScBO_3$, $Mg_2B_2O_5$, $Mg_2Ge_2O_6$, $Mg_4Ta_2O_9$, $LaSc_3(BO_3)_4$ and $LiIn_2SbO_6$).

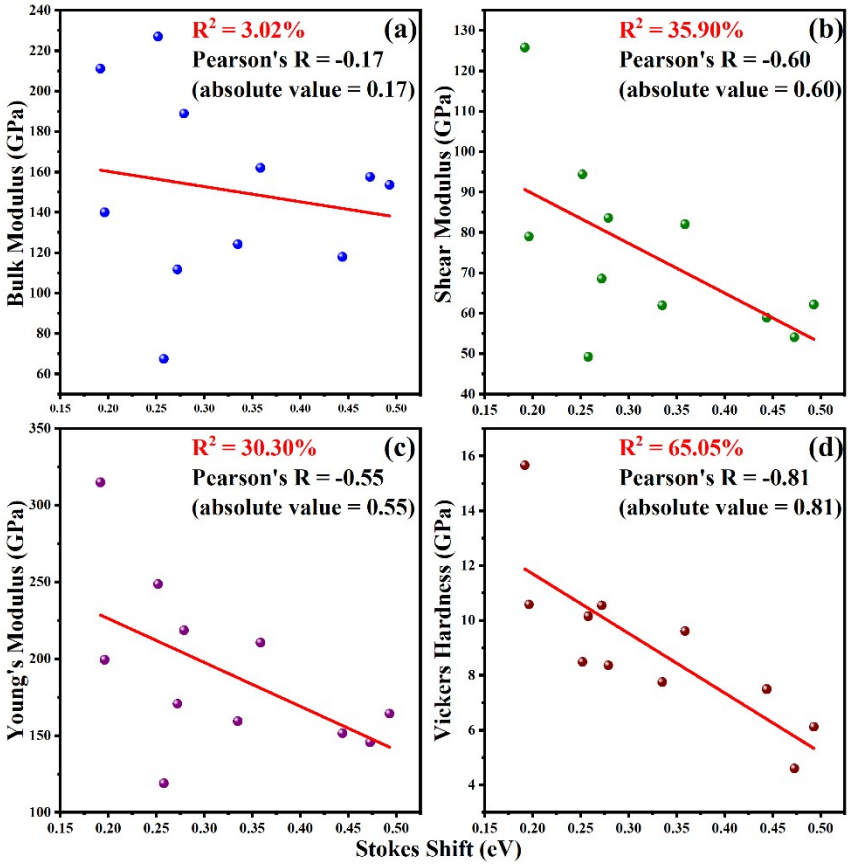

Figure S3. Correlation analysis of (a) Stokes vs Bulk modulus, (b) Stokes vs shear modulus, (c) Stokes vs Young's modulus and (d) Stokes vs Vickers hardness for Cr^{3+}-doped phosphors ($SrAl_{12}O_{19}$, $Ca_3Sc_2Si_3O_{12}$, $CaMgSi_2O_6$, $KAlP_2O_7$, $GaTaO_4$, $ScBO_3$, $Mg_2B_2O_5$, $Mg_2Ge_2O_6$, $Mg_4Ta_2O_9$, $LaSc_3(BO_3)_4$ and $LiIn_2SbO_6$).

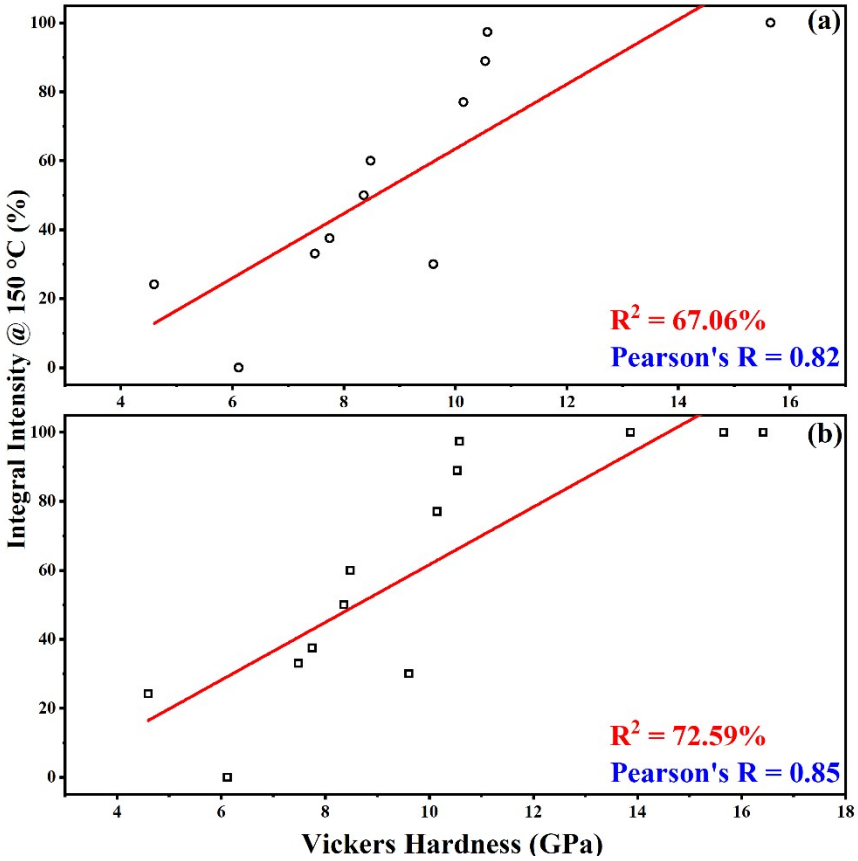

Figure S4. Correlation analysis of Vickers hardness vs thermal stabilities of for Cr^{3+}-doped phosphors (a) $SrAl_{12}O_{19}$, $Ca_3Sc_2Si_3O_{12}$, $CaMgSi_2O_6$, $KAlP_2O_7$, $GaTaO_4$, $ScBO_3$, $Mg_2B_2O_5$, $Mg_2Ge_2O_6$, $Mg_4Ta_2O_9$, $LaSc_3(BO_3)_4$ and $LiIn_2SbO_6$, (b) $Lu_3Al_5O_{12}$, $Y_3Al_5O_{12}$, $SrAl_{12}O_{19}$, $Ca_3Sc_2Si_3O_{12}$, $CaMgSi_2O_6$, $KAlP_2O_7$, $GaTaO_4$, $ScBO_3$, $Mg_2B_2O_5$, $Mg_2Ge_2O_6$, $Mg_4Ta_2O_9$, $LaSc_3(BO_3)_4$ and $LiIn_2SbO_6$.

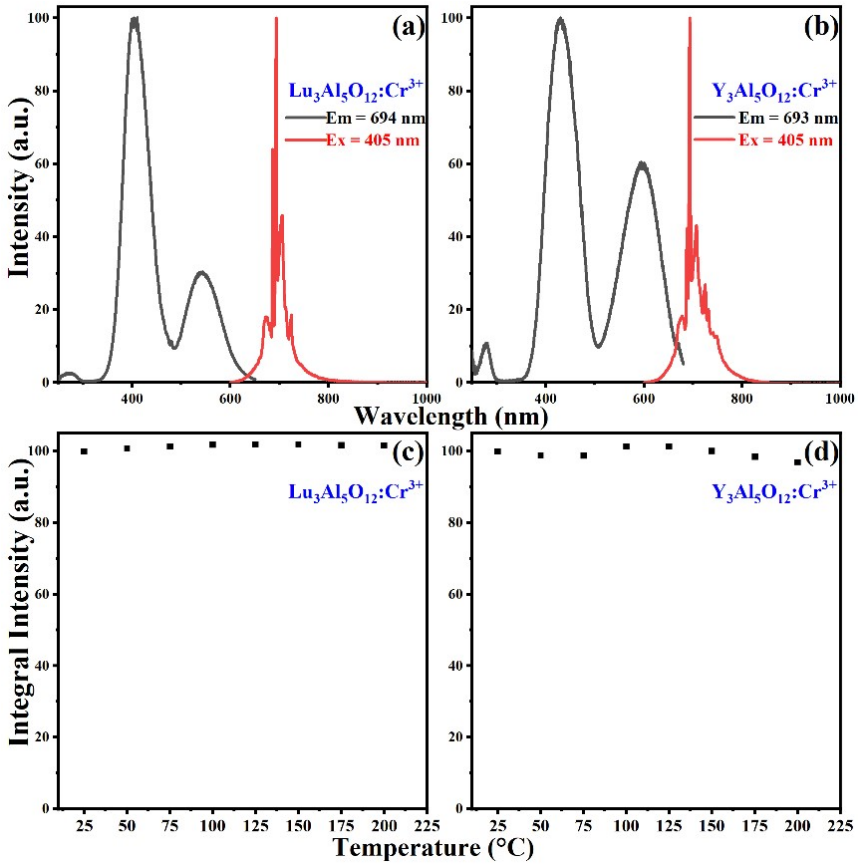

Figure S5. (a) PL and PLE spectra of $Lu_3Al_5O_{12}:Cr^{3+}$, (b) PL and PLE spectra of $Y_3Al_5O_{12}:Cr^{3+}$, (c) integral emission intensity of $Lu_3Al_5O_{12}:Cr^{3+}$ dependent on temperature, (d) integral emission intensity of $Y_3Al_5O_{12}:Cr^{3+}$ dependent on temperature.

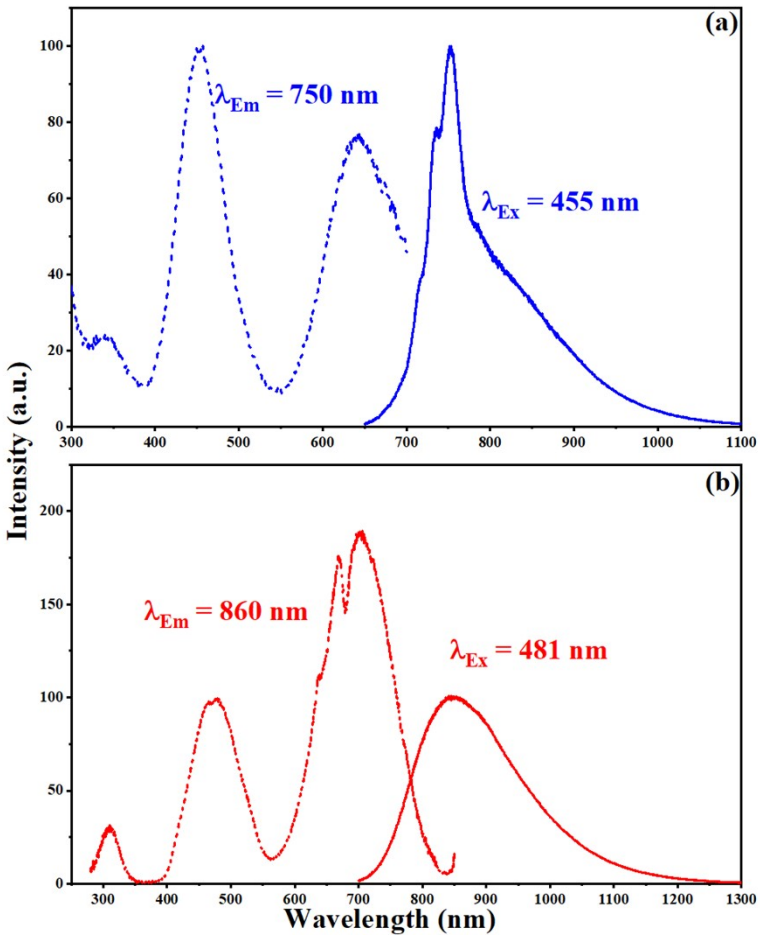

Figure S6. PL and PLE spectra of (a) $La_2MgSnO_6:Cr^{3+}$ and (b) $KMg(PO_3)_3:Cr^{3+}$.

Table S1. K-points setting of the systems.

System	K-point mesh (for PBEsol)	K-point mesh (for HSE06)
$Lu_3Al_5O_{12}$	2×2×2	-
$Y_3Al_5O_{12}$	2×2×2	-
$SrAl_{12}O_{19}$	5×5×1	-
$Ca_3Sc_2Si_3O_{12}$	2×2×2	-
$CaMgSi_2O_6$	3×3×5	-
$KAlP_2O_7$	4×3×3	1×1×1
$GaTaO_4$	5×4×5	-
$ScBO_3$	9×9×2	-
$Mg_2B_2O_5$	4×3×8	2×2×2
$Mg_2Ge_2O_6$	1×3×5	1×3×5
$Mg_4Ta_2O_9$	9×9×2	-
$LaSc_3(BO_3)_4$	3×3×2	1×1×1
$LiIn_2SbO_6$	5×5×3	-
$KMg(PO_3)_3$	4×4×3	2×2×1
La_2MgSnO_6	6×6×4	3×3×2

Table S2. Electron configurations for atoms in the calculations.

Atom	Configuration
Li	$2s^1$
B	$2s^2 2p^1$
O	$2s^2 2p^4$
Mg	$3s^2$
Al	$3s^2 3p^1$
Si	$3s^2 3p^2$
P	$3s^2 3p3$
K	$3p^6 4s^1$
Ca	$3p^6 4s^2$
Sc	$3d^2 4s^1$
Ga	$4s^2 4p^1$
Ge	$4s^2 4p^2$
Sr	$4s^2 4p^6 5s^2$
Y	$4s^2 4p^6 4d^2 5s^1$
In	$5s^2 5p^1$
Sn	$5s^2 5p^2$
Sb	$5s^2 5p^3$
La	$5p^6 5d^1 6s^2$
Lu	$4f^{14} 5s^2 5p^6 5d^1 6s^2$
Ta	$5d^4 6s^1$

Table S3. Cell parameters of $Y_3Al_5O_{12}$, $Ca_3Sc_2Si_3O_{12}$, $CaMgSi_2O_6$, $GaTaO_4$, $ScBO_3$ and $LaSc_3(BO_3)_4$ from experimental data (Exp) and calculations by PBE and PBEsol functionals.

		a (Å)	b (Å)	c (Å)	V (Å3)	
$Y_3Al_5O_{12}$	Exp[1]	11.9900	11.9900	11.9900	1723.6835	
	PBE	12.1075	12.1075	12.1075	1774.8581	
	PBEsol	11.9958	11.9958	11.9958	1726.1871	
	PBE-Error	+0.98%	+0.98%	+0.98%	+2.97%	
	PBEsol-Error	+0.05%	+0.05%	+0.05%	+0.14%	
		a (Å)	b (Å)	c (Å)	V (Å3)	
$Ca_3Sc_2Si_3O_{12}$	Exp[2]	12.2500	12.2500	12.2500	1838.2656	
	PBE	12.3281	12.3281	12.3281	1873.6430	
	PBEsol	12.2008	12.2008	12.2008	1816.1975	
	PBE-Error	+0.64%	+0.64%	+0.64%	+1.92%	
	PBEsol-Error	-0.40%	-0.40%	-0.40%	-1.20%	
		a (Å)	b (Å)	c (Å)	β (°)	V (Å3)
$CaMgSi_2O_6$	Exp[3]	9.7500	8.9260	5.2510	105.90	439.5029
	PBE	9.8588	9.0017	5.3080	106.06	452.6815
	PBEsol	9.7658	8.8985	5.2624	105.99	439.6119
	PBE-Error	+1.12%	+0.85%	+1.08%	+0.15%	+3.00%
	PBEsol-Error	+0.16%	-0.31%	+0.22%	+0.08%	+0.02%
		a (Å)	b (Å)	c (Å)	β (°)	V (Å3)
$GaTaO_4$	Exp[4]	4.5879	5.5673	4.9589	90.20	126.6606
	PBE	4.6490	5.6495	5.0324	90.33	132.1715
	PBEsol	4.6093	5.5882	4.9863	90.51	128.4324
	PBE-Error	+1.33%	+1.48%	+1.48%	+0.15%	+4.35%
	PBEsol-Error	+0.47%	+0.38%	+0.55%	+0.35%	+1.40%
		a (Å)	b (Å)	c (Å)	V (Å3)	
$ScBO_3$	Exp[5]	4.7480	4.7480	15.2620	297.9638	
	PBE	4.7816	4.7816	15.3386	303.7162	
	PBEsol	4.7425	4.7425	15.1669	295.4189	
	PBE-Error	+0.71%	+0.71%	+0.50%	+1.93%	
	PBEsol-Error	-0.12%	-0.12%	-0.62%	-0.85%	

Table S4. Vickers hardness and Debye temperature data of the materials.

Material	Vickers Hardness (Gpa)	Debye Temperature (K)
$Lu_3Al_5O_{12}$	16.42	675
$Y_3Al_5O_{12}$	13.87	728
$SrAl_{12}O_{19}$	15.66	882
$Ca_3Sc_2Si_3O_{12}$	10.58	694
$CaMgSi_2O_6$	10.54	680
$KAlP_2O_7$	10.15	584
$GaTaO_4$	8.49	515
$ScBO_3$	8.36	759
$Mg_2B_2O_5$	7.75	723
$Mg_2Ge_2O_6$	7.49	551
$Mg_4Ta_2O_9$	9.61	546
$LaSc_3(BO_3)_4$	4.60	565
$LiIn_2SbO_6$	6.11	461

Table S5. Elastic parameters and band gap values of La_2MgSnO_6 and $KMg(PO_3)_3$.

Material	Bulk modulus (GPa)	Shear modulus (GPa)	Young modulus (GPa)	Poisson ratio	Vickers hardness (Gpa)	Debye Temp (K)	Band Gap (eV)
La_2MgSnO_6	149.996	77.332	197.973	0.28	9.410	480.83	5.77
$KMg(PO_3)_3$	59.494	38.574	95.157	0.23	7.463	529.58	6.62

References:

1. Ł. Dobrzycki, E. Bulska, D. A. Pawlak, Z. Frukacz and K. Woźniak, *Inorg. Chem.*, 2004, **43**, 7656-7664.
2. R. Oberti, S. Quartieri, M. C. Dalconi, F. Boscherini, G. Iezzi, M. Boiocchi and S. G. Eeckhout, *Am. Mineral.*, 2006, **91**, 1230-1239.
3. E. Bruno, S. Carbonin and G. Molin, *Tschermaks mineralogische und petrographische Mitteilungen*, 1982, **29**, 223-240.
4. L. Perfler, V. Kahlenberg, D. Többens, A. Schaur, M. Tribus, M. Orlova and R. Kaindl, *Inorg. Chem.*, 2016, **55**, 5384-5397.
5. D. A. Keszler and H. Sun, *Acta Crystallogr. C*, 1988, **44**, 1505-1507.