



STRUCTURAL
CHEMISTRY

Volume 75 (2019)

Supporting information for article:

Tolerance factor and phase stability of the garnet structure

Zhen Song, Dandan Zhou and Quanlin Liu

Tolerance Factor and Phase Stability of the Garnet Structure

Zhen Song, Dandan Zhou, and Quanlin Liu*

Beijing Key Laboratory for New Energy Materials and Technologies, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

E-mail: qlliu@ustb.edu.cn

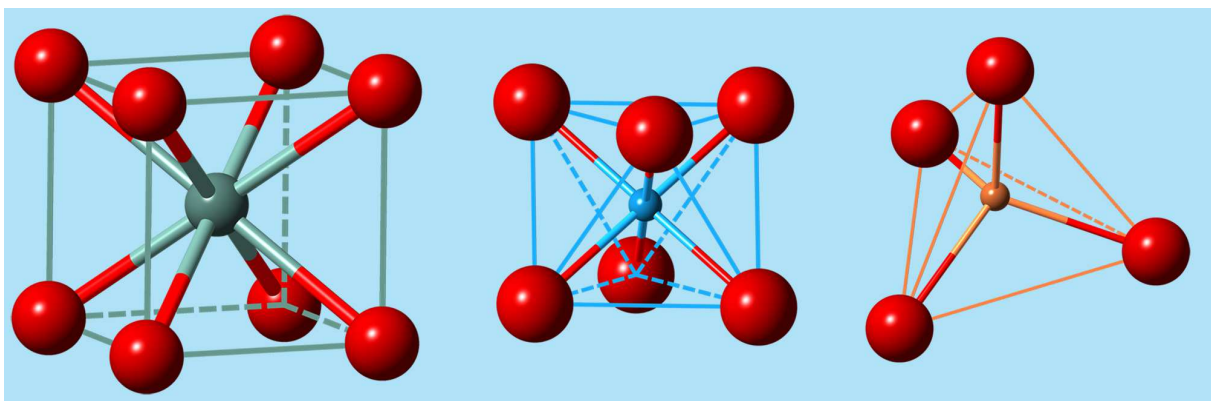


Figure S1: Geometrical relationships used to express the Tolerance Factor

Table S1: Tolerance Factor of End-Member Garnets

ID Num.	Formula	Ref.	τ
80352390	$(Y)_3\{Te\}_2[Li]_3 < O >_{12}$	1	0.836
80352590	$(Pr)_3\{Te\}_2[Li]_3 < O >_{12}$	1	0.751

Continuation on next page

Continuation of Table S1

Num.	Formula	Ref.	τ
80352600	(Nd) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.765
80352620	(Sm) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.790
80352630	(Eu) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.800
80352640	(Gd) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.810
80352650	(Tb) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.820
80352660	(Dy) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.830
80352670	(Ho) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.839
80352680	(Er) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.847
80352690	(Tm) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.854
80352700	(Yb) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.861
80352710	(Lu) ₃ {Te} ₂ [Li] ₃ < O > ₁₂	1	0.866
80374590	(Pr) ₃ {W} ₂ [Li] ₃ < O > ₁₂	1	0.809
80374600	(Nd) ₃ {W} ₂ [Li] ₃ < O > ₁₂	1	0.823
81313390	(Y) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	2–4	0.893
81313630	(Eu) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	5	0.851
81313640	(Gd) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	3,6	0.863
81313650	(Tb) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	7,8	0.874
81313660	(Dy) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	9	0.886
81313670	(Ho) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	9	0.896
81313680	(Er) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	10–12	0.905
81313690	(Tm) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	13	0.914
81313700	(Yb) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	3,11,12	0.921
81313710	(Lu) ₃ {Al} ₂ [Al] ₃ < O > ₁₂	3,14	0.928
81321390	(Y) ₃ {Sc} ₂ [Al] ₃ < O > ₁₂	15	1.186

Continuation on next page

Continuation of Table S1

Num.	Formula	Ref.	τ
81321640	(Gd) ₃ {Sc} ₂ [Al] ₃ < O > ₁₂	16	1.163
81352110	(Na) ₃ {Te} ₂ [Al] ₃ < O > ₁₂	1	0.782
81413120	(Mg) ₃ {Al} ₂ [Si] ₃ < O > ₁₂	17–21	1.073
81413200	(Ca) ₃ {Al} ₂ [Si] ₃ < O > ₁₂	17,19,22–24	0.863
81413250	(Mn) ₃ {Al} ₂ [Si] ₃ < O > ₁₂	22,23,25,26	1.016
81413260	(Fe) ₃ {Al} ₂ [Si] ₃ < O > ₁₂	20,27,28	1.049
81413270	(Co) ₃ {Al} ₂ [Si] ₃ < O > ₁₂	29–31	1.065
81413380	(Sr) ₃ {Al} ₂ [Si] ₃ < O > ₁₂	Non-Existence 18,32	0.690
81413480	(Cd) ₃ {Al} ₂ [Si] ₃ < O > ₁₂	18	0.884
81413560	(Ba) ₃ {Al} ₂ [Si] ₃ < O > ₁₂	Non-Existence 18,32	0.391
81421200	(Ca) ₃ {Sc} ₂ [Si] ₃ < O > ₁₂	33,34	1.206
81423200	(Ca) ₃ {V} ₂ [Si] ₃ < O > ₁₂	35	1.044
81423250	(Mn) ₃ {V} ₂ [Si] ₃ < O > ₁₂	18	1.174
81423480	(Cd) ₃ {V} ₂ [Si] ₃ < O > ₁₂	36	1.061
81424120	(Mg) ₃ {Cr} ₂ [Si] ₃ < O > ₁₂	22	1.189
81424200	(Ca) ₃ {Cr} ₂ [Si] ₃ < O > ₁₂	37–39	1.003
81424250	(Mn) ₃ {Cr} ₂ [Si] ₃ < O > ₁₂	18,22	1.137
81424260	(Fe) ₃ {Cr} ₂ [Si] ₃ < O > ₁₂	22	1.167
81425200	(Ca) ₃ {Mn} ₂ [Si] ₃ < O > ₁₂	18	0.943
81425250	(Mn) ₃ {Mn} ₂ [Si] ₃ < O > ₁₂	40	1.085
81426120	(Mg) ₃ {Fe} ₂ [Si] ₃ < O > ₁₂	41	1.096
81426200	(Ca) ₃ {Fe} ₂ [Si] ₃ < O > ₁₂	18,19,41	0.890
81426250	(Mn) ₃ {Fe} ₂ [Si] ₃ < O > ₁₂	18,22	1.039
81426260	(Fe) ₃ {Fe} ₂ [Si] ₃ < O > ₁₂	22	1.072

Continuation on next page

Continuation of Table S1

Num.	Formula	Ref.	τ
81431200	(Ca) ₃ {Ga} ₂ [Si] ₃ < O > ₁₂	18	1.011
81439200	(Ca) ₃ {Y} ₂ [Si] ₃ < O > ₁₂	Orthorhombic 42,43	1.423
81449200	(Ca) ₃ {In} ₂ [Si] ₃ < O > ₁₂	18,44	1.285
82321110	(Na) ₃ {Sc} ₂ [V] ₃ < O > ₁₂	45,46	1.095
82626390	(Y) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	3,47–50	0.867
82626590	(Pr) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	51,52	0.775
82626600	(Nd) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	52,53	0.791
82626620	(Sm) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	3,54	0.817
82626630	(Eu) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	54	0.828
82626640	(Gd) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	54–56	0.839
82626650	(Tb) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	54,57	0.850
82626660	(Dy) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	3	0.860
82626670	(Ho) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	58	0.870
82626680	(Er) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	54	0.878
82626690	(Tm) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	58	0.886
82626700	(Yb) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	3	0.893
82626710	(Lu) ₃ {Fe} ₂ [Fe] ₃ < O > ₁₂	3	0.899
83121390	(Y) ₃ {Sc} ₂ [Ga] ₃ < O > ₁₂	59	1.134
83121570	(La) ₃ {Sc} ₂ [Ga] ₃ < O > ₁₂	59	1.041
83121640	(Gd) ₃ {Sc} ₂ [Ga] ₃ < O > ₁₂	59–61	1.113
83121710	(Lu) ₃ {Sc} ₂ [Ga] ₃ < O > ₁₂	59	1.160
83131390	(Y) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	3,48,50	0.974
83131590	(Pr) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	62	0.891
83131600	(Nd) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	63	0.905

Continuation on next page

Continuation of Table S1

Num.	Formula	Ref.	τ
83131620	(Sm) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	63,64	0.929
83131630	(Eu) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	62	0.939
83131640	(Gd) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	63,65–67	0.949
83131650	(Tb) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	7,63,68	0.958
83131660	(Dy) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	69	0.968
83131670	(Ho) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	69	0.977
83131680	(Er) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	70	0.984
83131700	(Yb) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	3	0.998
83131710	(Lu) ₃ {Ga} ₂ [Ga] ₃ < O > ₁₂	3	1.003
83152110	(Na) ₃ {Te} ₂ [Ga] ₃ < O > ₁₂	1	0.748
83212391	(Y _{2/3} Mg _{1/3}) ₃ {Mg} ₂ [Ge] ₃ < O > ₁₂	71	1.181
83213200	(Ca) ₃ {Al} ₂ [Ge] ₃ < O > ₁₂	72	0.799
83213250	(Mn) ₃ {Al} ₂ [Ge] ₃ < O > ₁₂	73	0.941
83213480	(Cd) ₃ {Al} ₂ [Ge] ₃ < O > ₁₂	44,73	0.819
83221200	(Ca) ₃ {Sc} ₂ [Ge] ₃ < O > ₁₂	33,44,74	1.117
83221380	(Sr) ₃ {Sc} ₂ [Ge] ₃ < O > ₁₂	75,76	1.009
83221480	(Cd) ₃ {Sc} ₂ [Ge] ₃ < O > ₁₂	33,44,73	1.131
83223200	(Ca) ₃ {V} ₂ [Ge] ₃ < O > ₁₂	77	0.967
83223480	(Cd) ₃ {V} ₂ [Ge] ₃ < O > ₁₂	77	0.984
83224200	(Ca) ₃ {Cr} ₂ [Ge] ₃ < O > ₁₂	78	0.929
83224250	(Mn) ₃ {Cr} ₂ [Ge] ₃ < O > ₁₂	79	1.054
83224480	(Cd) ₃ {Cr} ₂ [Ge] ₃ < O > ₁₂	73	0.946
83225200	(Ca) ₃ {Mn} ₂ [Ge] ₃ < O > ₁₂	77	0.874
83226200	(Ca) ₃ {Fe} ₂ [Ge] ₃ < O > ₁₂	71	0.825

Continuation on next page

Continuation of Table S1

Num.	Formula	Ref.	τ
83226250	(Mn) ₃ {Fe} ₂ [Ge] ₃ < O > ₁₂	80	0.963
83226480	(Cd) ₃ {Fe} ₂ [Ge] ₃ < O > ₁₂	73	0.844
83231200	(Ca) ₃ {Ga} ₂ [Ge] ₃ < O > ₁₂	81	0.937
83231250	(Mn) ₃ {Ga} ₂ [Ge] ₃ < O > ₁₂	72	1.061
83231480	(Cd) ₃ {Ga} ₂ [Ge] ₃ < O > ₁₂	44,73	0.954
83239120	(Mg) ₃ {Y} ₂ [Ge] ₃ < O > ₁₂	Not Reported	1.445
83239200	(Ca) ₃ {Y} ₂ [Ge] ₃ < O > ₁₂	71,75	1.319
83239380	(Sr) ₃ {Y} ₂ [Ge] ₃ < O > ₁₂	75,82	1.228
83245200	(Ca) ₃ {Rh} ₂ [Ge] ₃ < O > ₁₂	77	1.004
83249200	(Ca) ₃ {In} ₂ [Ge] ₃ < O > ₁₂	44	1.191
83249380	(Sr) ₃ {In} ₂ [Ge] ₃ < O > ₁₂	76	1.090
83249480	(Cd) ₃ {In} ₂ [Ge] ₃ < O > ₁₂	44	1.204
83266200	(Ca) ₃ {Dy} ₂ [Ge] ₃ < O > ₁₂	76	1.333
83267200	(Ca) ₃ {Ho} ₂ [Ge] ₃ < O > ₁₂	76	1.320
83267380	(Sr) ₃ {Ho} ₂ [Ge] ₃ < O > ₁₂	76	1.230
83268200	(Ca) ₃ {Er} ₂ [Ge] ₃ < O > ₁₂	76	1.306
83268380	(Sr) ₃ {Er} ₂ [Ge] ₃ < O > ₁₂	76	1.215
83269200	(Ca) ₃ {Tm} ₂ [Ge] ₃ < O > ₁₂	76	1.294
83269380	(Sr) ₃ {Tm} ₂ [Ge] ₃ < O > ₁₂	76	1.201
83270200	(Ca) ₃ {Yb} ₂ [Ge] ₃ < O > ₁₂	76	1.278
83270380	(Sr) ₃ {Yb} ₂ [Ge] ₃ < O > ₁₂	76	1.185
83271200	(Ca) ₃ {Lu} ₂ [Ge] ₃ < O > ₁₂	76	1.270
83271380	(Sr) ₃ {Lu} ₂ [Ge] ₃ < O > ₁₂	76	1.176
83324110	(Na) ₃ {Cr} ₂ [As] ₃ < O > ₁₂	83	0.904

Continuation on next page

Continuation of Table S1			
Num.	Formula	Ref.	τ
83326110	$(\text{Na})_3\{\text{Fe}\}_2[\text{As}]_3 < \text{O} >_{12}$	84	0.788
85031200	$(\text{Ca})_3\{\text{Ga}\}_2[\text{Sn}]_3 < \text{O} >_{12}$	76	0.859
90313110	$(\text{Na})_3\{\text{Al}\}_2[\text{Li}]_3 < \text{F} >_{12}$	85	0.636
90321110	$(\text{Na})_3\{\text{Sc}\}_2[\text{Li}]_3 < \text{F} >_{12}$	86	0.956
90322110	$(\text{Na})_3\{\text{Ti}\}_2[\text{Li}]_3 < \text{F} >_{12}$	87	0.852
90323110	$(\text{Na})_3\{\text{V}\}_2[\text{Li}]_3 < \text{F} >_{12}$	87	0.808
90324110	$(\text{Na})_3\{\text{Cr}\}_2[\text{Li}]_3 < \text{F} >_{12}$	87	0.769
90326110	$(\text{Na})_3\{\text{Fe}\}_2[\text{Li}]_3 < \text{F} >_{12}$	87,88	0.662
90327110	$(\text{Na})_3\{\text{Co}\}_2[\text{Li}]_3 < \text{F} >_{12}$	87	0.654
90349110	$(\text{Na})_3\{\text{In}\}_2[\text{Li}]_3 < \text{F} >_{12}$	86	1.028
End of Table			

References

- (1) Kasper, H. A New Series of Rare Earth Garnets $\text{Ln}_3\text{M}_2\text{Li}_3\text{O}_{12}$ ($\text{M} = \text{Te}, \text{W}$). *Inorg. Chem.* **1969**, *8*, 1000–1002.
- (2) Emiraliev, A.; Kocharov, A.; Bakradze, R.; Karimov, U.; Ahmetzhanov, Z. The Neutron Diffraction Redefinition of the Coordinates of the Atoms of Oxygen in Yttrio-Aluminium Garnet. *Kristallografiya* **1976**, *21*, 211–213.
- (3) Euler, F.; Bruce, J. A. Oxygen Coordinates of Compounds with Garnet Structure. *ACTA Crystallogr.* **1965**, *19*, 971–978.
- (4) Bagdasarov, K. S.; Bolotina, N. B.; Kalinin, V. I.; Karyagin, V. F.; Kuz'min, B. V.; Muradyan, L. A.; Ryadnov, S. N.; Uyukin, E. M.; Chernaya, T. S.; Fedorov, E. A.

- Photoinduced Effects and Real Structure of Crystals of Yttrium Aluminum Garnet. *Sov. Phys. Crystallogr.* **1991**, *36*, 398–405.
- (5) Garskaite, E.; Sakirzanovas, S.; Kareiva, A.; Glaser, J.; Meyer, H.-J. Synthesis and Structure of Europium Aluminium Garnet (EAG). *Z. Für Anorg. Allg. Chem.* **2007**, *633*, 990–993.
- (6) Hamilton, A. S.; Lampronti, G. I.; Rowley, S. E.; Dutton, S. E. Enhancement of the Magnetocaloric Effect Driven by Changes in the Crystal Structure of Al-Doped GGG, $\text{Gd}_3\text{Ga}_{5-x}\text{Al}_x\text{O}_{12}$ ($0 \leq X \leq 5$). *J. Phys.: Condens. Matter* **2014**, *26*, 116001.
- (7) Bi, J.; Wang, X.; Molokeev, M. S.; Zhu, Q.; Li, X.; Chen, J.; Sun, X.; Kim, B.-N.; Li, J.-G. The Effects of Ga^{3+} Substitution on Local Structure and Photoluminescence of $\text{Tb}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ Garnet Phosphor. *Ceram. Int.* **2018**, *44*, 8684–8690.
- (8) Zorenko, Y.; Gorbenko, V.; Voznyak, T.; Zorenko, T.; Kuklinski, B.; Turos-Matysyak, R.; Grinberg, M. Luminescence Properties of Phosphors Based on $\text{Tb}_3\text{Al}_5\text{O}_{12}$ (TbAG) Terbium-Aluminum Garnet. *Opt. Spectrosc.* **2009**, *106*, 365–374.
- (9) Rubinstein, C.; Barns, R. Crystallographic Data for Rare-Earth Aluminum Garnets. *Am. Mineral. J. Earth Planet. Mater.* **1964**, *49*, 1489–1490.
- (10) Chernaya, T.; Muradyan, L.; Rusakov, A.; Kaminskii, A.; Simonov, V. Refinement and Analysis of Atomic Structures of $\text{Er}_3\text{Al}_5\text{O}_{12}$ and $(\text{Y}_{2.80}\text{Er}_{0.20})\text{Al}_5\text{O}_{12}$. *Kristallografiya* **1985**, *30*, 72–75.
- (11) Dobrzycki, L.; Bulska, E.; Pawlak, D. A.; Frukacz, Z.; Woźniak, K. Structure of YAG Crystals Doped/Substituted with Erbium and Ytterbium. *Inorg. Chem.* **2004**, *43*, 7656–7664.
- (12) Etschmann, B.; Streltsov, V.; Ishizawa, N.; Maslen, E. Synchrotron X-Ray Study of $\text{Er}_3\text{Al}_5\text{O}_{12}$ and $\text{Yb}_3\text{Al}_5\text{O}_{12}$ Garnets. *Acta Crystallogr. B* **2001**, *57*, 136–141.

- (13) Rubinstein, C.; Barns, R. Crystallographic Data for Rare-Earth Aluminum Garnets: Part II. *Am. Mineral. J. Earth Planet. Mater.* **1965**, *50*, 782–785.
- (14) Ahn, W.; Kim, Y. J. Effects of Flux on the Synthesis and the Luminescence of Lu₃Al₅O₁₂: Ce³⁺ Phosphors. *Sci. Adv. Mater.* **2016**, *8*, 904–908.
- (15) Allik, T. H.; Morrison, C. A.; Gruber, J. B.; Kokta, M. R. Crystallography, Spectroscopic Analysis, and Lasing Properties of Nd³⁺: Y₃Sc₂Al₃O₁₂. *Phys. Rev. B* **1990**, *41*, 21.
- (16) Yamazaki, S.; Marumo, F.; Tanaka, K.; Morikawa, H.; Kodama, N.; Kitamura, K.; Miyazawa, Y. A Structural Study of Facet and Off-Facet Parts of Rare-Earth Garnets, Gd₃Sc₂Al₃O₁₂, Gd₃Sc₂Ga₃O₁₂, and La₃Lu₂Ga₃O₁₂. *J. Solid State Chem.* **1994**, *108*, 94–98.
- (17) Meagher, E. The Crystal Structures of Pyrope and Grossularite at Elevated Temperatures. *Am. Mineral. J. Earth Planet. Mater.* **1975**, *60*, 218–228.
- (18) Novak, G. A.; Gibbs, G. V. The Crystal Chemistry of the Silicate Garnets. *Am. Mineral. J. Earth Planet. Mater.* **1971**, *56*, 791–825.
- (19) Sawada, H. Electron Density Study of Garnets:Z₃Al₂Si₃O₁₂(Z=Mg, Fe, Mn, Ca) and Ca₃Fe₂Si₃O₁₂. *J. Solid State Chem.* **1999**, *142*, 273–278.
- (20) Armbruster, T.; Geiger, C. A.; Lager, G. A. Single-Crystal X-Ray Structure Study of Synthetic Pyrope Almandine Garnets at 100 and 293 K. *Am. Mineral.* **1992**, *77*, 512–521.
- (21) Pavese, A.; Artioli, G.; Prencipe, M. X-Ray Single-Crystal Diffraction Study of Pyrope in the Temperature Range 30–973 K. *Am. Mineral.* **1995**, *80*, 457–464.
- (22) Ottonello, G.; Bokreta, M.; Sciuto, P. F. Parameterization of Energy and Interactions in Garnets: End-Member Properties. *Am. Mineral.* **1996**, *81*, 429–447.

- (23) Geiger, C. A.; Armbruster, T. Mn₃Al₂Si₃O₁₂ Spessartine and Ca₃Al₂Si₃O₁₂ Grossular Garnet: Structural Dynamic and Thermodynamic Properties. *Am. Mineral.* **1997**, *82*, 740–747.
- (24) PKANDL, W. Verfeinerung Der Kristallstruktur Des Grossulars Mit Neutronen-Und Röntgenstrahlbeugung. *Z. Für Krist.-Cryst. Mater.* **1966**, *123*, 81–116.
- (25) Geiger, C. A.; Rodehorst, U.; Armbruster, T. The Crystal Structures of Grossular and Spessartine between 100 and 600 K and the Crystal Chemistry of Grossular-Spessartine Solid Solutions. *American Mineralogist* **2002**, *87*, 542–549.
- (26) Gramaccioli, C. M.; Pilati, T.; Demartin, F. Atomic Displacement Parameters for Spessartine Mn₃Al₂Si₃O₁₂ and Their Lattice-Dynamical Interpretation. *Acta Crystallogr. B* **2002**, *58*, 965–969.
- (27) Prandl, W. Die Magnetische Struktur Und Die Atomparameter Des Almandins Al₂Fe₃(SiO₄)₃. *Z. Für Krist.-Cryst. Mater.* **1971**, *134*, 333–343.
- (28) Geiger, C.; Armbruster, T.; Lager, G.; Jiang, K.; Lottermoser, W.; Amthauer, G. A Combined Temperature Dependent ⁵⁷Fe Mössbauer and Single Crystal X-Ray Diffraction Study of Synthetic Almandine: Evidence for the Gol'danskii-Karyagin Effect. *Phys. Chem. Miner.* **1992**, *19*, 121–126.
- (29) OHASHI, H.; FUJITA, T.; OSAWA, T. Structure of Co₃Al₂Si₃O₁₂ Garnet. *J. Jpn. Assoc. Mineral. Petrol. Econ. Geol.* **1981**, *76*, 58–60.
- (30) Ohashi, H.; Osawa, T.; Sato, A. Low-Pressure Polymorph of Co₃Al₂Si₃O₁₂. *Acta Crystallogr. C* **1995**, *51*, 2213–2215.
- (31) Ross, C. R.; Keppler, H.; Canil, D.; O'Neill, H. S. C. Structure and Crystal-Field Spectra of Co₃Al₂(SiO₄)₃ and (Mg, Ni)₃Al₂(SiO₄)₃ Garnet. *Am. Mineral.* **1996**, *81*, 61–66.

- (32) Gentile, A.; Roy, R. Isomorphism and Crystalline Solubility in the Garnet Family. *Am. Mineral. J. Earth Planet. Mater.* **1960**, *45*, 701–711.
- (33) Mill, B. V.; Belokoneva, E. L.; Simonov, M. A.; Belov, N. V. Refined Crystal Structures of the Scandium Garnets $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$, and $\text{Cd}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$. *J. Struct. Chem.* **1977**, *18*, 321–323.
- (34) Quartieri, S.; Oberti, R.; Boiocchi, M.; Dalconi, M. C.; Boscherini, F.; Safonova, O.; Woodland, A. B. Site Preference and Local Geometry of Sc in Garnets: Part II. The Crystal-Chemistry of Octahedral Sc in the Andradite– $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ Join. *Am. Mineral.* **2006**, *91*, 1240–1248.
- (35) Righter, K.; Sutton, S.; Danielson, L.; Pando, K.; Schmidt, G.; Yang, H.; Berthet, S.; Newville, M.; Choi, Y.; Downs, R. T., et al. The Effect of f O₂ on the Partitioning and Valence of V and Cr in Garnet/Melt Pairs and the Relation to Terrestrial Mantle V and Cr Content. *Am. Mineral.* **2011**, *96*, 1278–1290.
- (36) Mill, B. Hydrothermal Synthesis of Garnets Containing V³⁺, In³⁺ and Sc³⁺. *Sov. Phys. Dokl.* **1964**, *9*, 414.
- (37) Geller, S.; Miller, C. E. The Synthesis of Uvarovite. *Am. Mineral.* **1959**, *44*, 0.
- (38) Carda, J.; Monros, G.; Esteve, V.; Amigo, J. Cation Distribution by Powder X-Ray Diffraction in Uvarovite-Grossularite Garnets Solid Solutions Synthesized by the Sol-Gel Method. *J. Solid State Chem.* **1994**, *108*, 24–28.
- (39) Andrut, M.; Wildner, M. The Crystal Chemistry of Birefringent Natural Uvarovites. Part III. Application of the Superposition Model of Crystal Fields with a Characterization of Synthetic Cubic Uvarovite. *Phys. Chem. Miner.* **2002**, *29*, 595–608.
- (40) Arlt, T.; Armbruster, T.; Miletich, R.; Ulmer, P.; Peters, T. High Pressure Single-

- Crystal Synthesis, Structure and Compressibility of the Garnet $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$. *Phys. Chem. Miner.* **1998**, *26*, 100–106.
- (41) Armbruster, T.; Geiger, C. A. Andradite Crystal Chemistry, Dynamic X-Site Disorder and Structural Strain in Silicate Garnets. *Eur. J. Mineral.* **1993**, *5*, 59–72.
- (42) Yamane, H.; Nagasawa, T.; Shimada, M.; Endo, T. $\text{Ca}_3\text{Y}_2(\text{SiO}_4)_3$. *Acta Crystallogr. Sect. C* **1997**, *53*, 1367–1369.
- (43) Piccinelli, F.; Speghini, A.; Mariotto, G.; Bovo, L.; Bettinelli, M. Visible Luminescence of Lanthanide Ions in $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Y}_2\text{Si}_3\text{O}_{12}$. *J. Rare Earths* **2009**, *27*, 555–559.
- (44) Li, H.-L.; Kuang, X.-Y.; Mao, A.-J.; Li, Y.; Wang, S.-J. Study of Local Structures and Optical Spectra for Octahedral Fe^{3+} Centers in a Series of Garnet Crystals $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$ (A=Cd, Ca; B=Al, Ga, Sc, In; C=Ge, Si). *Chem. Phys. Lett.* **2010**, *484*, 387–391.
- (45) Belokoneva, E.; Mill, B.; Simonov, M.; Belov, N. Refinement of Crystal-Structure of Vanadium Garnet $\text{Na}_3\text{Sc}_2\text{V}_3\text{O}_{12}$. *Kristallografiya* **1974**, *19*, 374–375.
- (46) Lobanov, N.; Butman, L.; Tsirel'son, V. Precision X-Ray Diffraction Study of the Garnets $\text{Na}_3\text{Sc}_2\text{V}_3\text{O}_{12}$ and $\text{Na}_{0.90}\text{Ca}_{2.38}\text{Mn}_{1.72}\text{V}_3\text{O}_{12}$. *J. Struct. Chem.* **1989**, *30*, 96–104.
- (47) Geller, S.; Gilleo, M. The Crystal Structure and Ferrimagnetism of Yttrium-Iron Garnet, $\text{Y}_3\text{Fe}_2(\text{FeO}_4)_3$. *J. Phys. Chem. Solids* **1957**, *3*, 30–36.
- (48) Nakatsuka, A.; Yoshiasa, A.; Takeno, S. Site Preference of Cations and Structural Variation in $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ ($0 \leq x \leq 5$) Solid Solutions with Garnet Structure. *Acta Crystallogr. B* **1995**, *51*, 737–745.

- (49) Bonnet, M.; Delapalme, A.; Fuess, H.; Thomas, M. Refinement of the Structure of Yttrium Iron Garnet (YIG). A Case of Severe Extinction and Absorption. *Acta Crystallogr. B* **1975**, *31*, 2233–2240.
- (50) Fischer, P.; Hälg, W.; Stoll, E.; Segmüller, A. X-Ray and Neutron Diffraction Study of the Substitutional Disorder in the Yttrium-Iron-Gallium Garnets. *Acta Crystallogr.* **1966**, *21*, 765–769.
- (51) Komori, T.; Sakakura, T.; Takenaka, Y.; Tanaka, K.; Okuda, T. Tripraseodymium Pentairon (III) Dodecaoxide, Pr₃Fe₅O₁₂: A Synchrotron Radiation Study. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2009**, *65*, i73–i73.
- (52) Guo, L.; Huang, K.; Chen, Y.; Li, G.; Yuan, L.; Peng, W.; Yuan, H.; Feng, S. Mild Hydrothermal Synthesis and Ferrimagnetism of Pr₃Fe₅O₁₂ and Nd₃Fe₅O₁₂ Garnets. *J. Solid State Chem.* **2011**, *184*, 1048–1053.
- (53) Komori, T.; Sakakura, T.; Takenaka, Y.; Tanaka, K.; Okuda, T. Trineodymium (III) Pentairon (III) Dodecaoxide, Nd₃Fe₅O₁₂. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2009**, *65*, i72–i72.
- (54) Dukhovskaya, E.; Saksonov, Y. G.; Titova, A. Oxygen Parameters of Certain Compounds of the Garnet Structure. *Izv. Akad. Nauk SSSR Neorganicheskie Mater.* **1973**, *9*, 809–813.
- (55) Weidenborner, J. Least Squares Refinement of the Structure of Gadolinium-Iron Garnet Gd₃Fe₂Fe₃O₁₂. *Acta Crystallogr.* **1961**, *14*, 1051–1056.
- (56) Bertraud, F.; Forret, F. Structure Des Ferrites Ferrimagnétiques Des Terres Rares. *Compt Rend Acad Sci Paris* **1956**, *242*, 382–383.
- (57) Fuess, H.; Bassi, G.; Bonnet, M.; Delapalme, A. Neutron Scattering Length of Terbium

- Structure Refinement and Magnetic Moments of Terbium Iron Garnet. *Solid State Commun.* **1976**, *18*, 557–562.
- (58) Espinosa, G. P. Crystal Chemical Study of the Rare-Earth Iron Garnets. *J. Chem. Phys.* **1962**, *37*, 2344–2347.
- (59) Malysa, B.; Meijerink, A.; Jüstel, T. Temperature Dependent Cr³⁺ Photoluminescence in Garnets of the Type X₃Sc₂Ga₃O₁₂ (X = Lu, Y, Gd, La). *J. Lumin.* **2018**, *202*, 523–531.
- (60) Kondratyuk, I.; Zharikov, E.; Simonov, V. Refinement of Atomic Structures of Gd₃ Sc₂ Ga₃ O₁₂ and (Gd_{0.8} Nd_{0.2}) Sc₂ Ga₃ O₁₂. *Kristallografiya* **1988**, *33*, 51–56.
- (61) Shao, S.; Zhang, Q.; Liu, W.; Sun, D.; Gu, C.; Yin, S. Preparation, Structure and Luminescence Properties of Nanocrystalline Eu: Gd₃Sc₂Ga₃O₁₂. *J. Alloys Compd.* **2009**, *471*, 263–267.
- (62) Bertaut, F.; Forrat, F. Etude Des Combinaisons Des Oxydes Des Terres Rares Avec Lalumine et La Galline. *COMPTES RENDUS Hebd. SEANCES Acad. Sci.* **1956**, *243*, 1219–1222.
- (63) Sawada, H. Electron Density Study of Garnets: Z₃Ga₅O₁₂; Z= Nd, Sm, Gd, Tb. *J. Solid State Chem.* **1997**, *132*, 300–307.
- (64) Sharma, A.; Silverstein, H.; Hallas, A.; Luke, G.; Wiebe, C. Sub-Kelvin Magnetic Order in Sm₃Ga₅O₁₂ Single Crystal. *J. Magn. Magn. Mater.* **2015**, *384*, 235–240.
- (65) Sharma, S.; Som, S.; Jain, R.; Kunti, A. Spectral and CIE Parameters of Red Emitting Gd₃Ga₅O₁₂:Eu³⁺ Phosphor. *J. Lumin.* **2015**, *159*, 317–324.
- (66) Asami, K.; Ueda, J.; Tanabe, S. Trap Depth and Color Variation of Ce³⁺-Cr³⁺ Co-Doped Gd₃(Al,Ga)₅O₁₂ Garnet Persistent Phosphors. *Opt. Mater.* **2016**, *62*, 171–175.

- (67) Sasvari, J.; Werner, P.; Faegri, K.; Haaland, A.; Schilling, B. E. R.; Seip, R.; Taugbol, K. Structural Studies of Gadolinium Gallium Garnet. *Acta Chem. Scand.* **1983**, 203–206.
- (68) Kuvaldin, B.; Bakradze, R.; Fykin, L.; Martyshchenko, V. Types of Diffraction Reflections for Garnet Structure. Refinement of Coordinates of Oxygen Ions in $Tb_3Ga_5O_{12}$. *Kristallografiya* **1980**, *25*, 1155–1161.
- (69) Patzke, G.; Wartchow, R.; Binnewies, M. Crystal Structure of Triholmium Pentagallium Dodecaoxide, $Ho_3Ga_2(GaO_4)_3$ and of Tridysprosium Pentagallium Dodecaoxide, $Dy_3Ga_2(GaO_4)_3$. *Z. Für Krist.-New Cryst. Struct.* **1999**, *214*, 143–144.
- (70) Schneider, S.; Roth, R.; Waring, J. Solid State Reactions Involving Oxides of Trivalent Cations. *J. Research Natl. Bur. Standards* **1961**,
- (71) Lévy, D.; Barbier, J. Normal and Inverse Garnets: $Ca_3Fe_2Ge_3O_{12}$, $Ca_3Y_2Ge_3O_{12}$ and $Mg_3Y_2Ge_3O_{12}$. *Acta Crystallogr. Sect. C* **1999**, *55*, 1611–1614.
- (72) Tauber, A.; Whinfrey, C.; Banks, E. The Crystal Chemistry of Some Germanium Garnets. *J. Phys. Chem. Solids* **1961**, *21*, 25–32.
- (73) Tauber, A.; Banks, E.; Kedesdy, H. Synthesis of Germanate Garnets. *Acta Crystallogr.* **1958**, *11*, 893–894.
- (74) Pinelli, S.; Bigotta, S.; Toncelli, A.; Tonelli, M.; Cavalli, E.; Bovero, E. Study of the Visible Spectra of $Ca_3Sc_2Ge_3O_{12}$ Garnet Crystals Doped with Ce^{3+} or Pr^{3+} . *Opt. Mater.* **2004**, *25*, 91–99.
- (75) Pasiński, D.; Sokolnicki, J. Luminescence Study of Eu^{3+} -Doped Garnet Phosphors: Relating Structure to Emission. *J. Alloys Compd.* **2017**, *695*, 1160–1165.
- (76) Mill, B. V. Synthesis of Garnets with Large Cations. *Sov. Phys. Dokl.* **1966**, *10*, 1015.
- (77) MILL, B.; LEVANIDOV, M.; BELOV, K. New Garnet Materials for Substrates. *Inorg. Mater.* **1979**, *15*, 1428–1431.

- (78) Prandl, W. Magnetic Structure and Space Group of the Garnet $\text{Ca}_3\text{Cr}_2(\text{GeO}_4)_3$. *Solid State Commun.* **1972**, *11*, 645–647.
- (79) Lipp, C.; Strobel, S.; Lissner, F.; Niewa, R. Garnet-Type $\text{Mn}_3\text{Cr}_2(\text{GeO}_4)_3$. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2012**, *68*, i35–i35.
- (80) Lind, M.; Geller, S. Crystal Structure of the Garnet $\{\text{Mn}_3\}[\text{Fe}_2](\text{Ge}_3)\text{O}_{12}$. *Z. Krist.* **1969**, *129*, 427–434.
- (81) Liu, C.; Xia, Z.; Molokeev, M. S.; Liu, Q. Synthesis, Crystal Structure, and Enhanced Luminescence of Garnet-Type $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$: Cr^{3+} by Codoping Bi^{3+} . *J. Am. Ceram. Soc.* **2015**, *98*, 1870–1876.
- (82) Marin, S. J.; O’Keeffe, M.; Young, V. G.; Von Dreele, R. B. The Crystal Structure of $\text{Sr}_3\text{Y}_2\text{Ge}_3\text{O}_{12}$. *J. Solid State Chem. Fr.* **1991**, *91*, 173–175.
- (83) Bouzemi, B.; Boughzala, H.; Jouini, T. $\text{Na}_3\text{Cr}_2(\text{AsO}_4)_3$: Trisodium Dichromium (III) Triarsenate. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2002**, *58*, i117–i118.
- (84) Ouerfelli, N.; Guesmi, A.; Mazza, D.; Zid, M. F.; Driss, A. L’arséniate $\text{Na}_3\text{Fe}_2(\text{AsO}_4)_3$: Étude Structurale de La Forme Basse Température et Simulation Des Propriétés de Conduction Des Cations Alcalins. *Acta Crystallogr. C* **2008**, *64*, i41–i44.
- (85) Geller, S. Refinement of the Crystal Structure of Cryolithionite, $\{\text{Na}_3\}[\text{Al}_2](\text{Li}_3)\text{F}_{12}$. *American Mineralogist* **1971**, *56*, 18–23.
- (86) De Pape, R.; Portier, J.; Granec, J.; Gauthier, G.; Hagenmuller, P. Sur Quelques Nouveaux Grenats Fluorés. *CR Acad Sc Paris Sér. C* **1969**, *269*, 1120–1121.
- (87) De Pape, R.; Portier, J.; Gauthier, G.; Hagenmuller, P. Les Grenats Fluorés Des Éléments de Transition $\text{Li}_3\text{Na}_3\text{In}_2\text{F}_{12}$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Fe}$ Ou Co). *CR Acad Sc Paris Sér. C* **1967**, *265*, 1244–1246.

- (88) Massa, W.; Post, B.; Babel, D. Verfeinerung Der Granatstruktur Des Natrium-Lithium-Eisen (III) Fluorids $\text{Na}_3\text{Li}_3\text{Fe}_2\text{F}_{12}$. *Z. Für Krist.-Cryst. Mater.* **1982**, *158*, 299–306.

Tolerance factors of over 130 different end-member garnets together with references, illustration of geometrical relationships used to express the tolerance factor are included in the supporting information.