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Appendix 1: Depository item AM-14-503

**Incorporation of Y and REEs in aluminosilicate garnet:
Energetics from atomistic simulation**

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MINIMUM-ENERGY CONFIGURATIONS FOR DEFECTS

In order to compare the energetics of different possible substitution schemes for the incorporation of large trivalent ions, it was necessary first to determine for each scheme which of the possible defect configurations represented the arrangement with the lowest energy, and should therefore be the one most favored in nature. For each scheme, a variety of possible arrangements—chosen as described below—was evaluated for the case of Y incorporation at 1200 K and 2 GPa.

Two-atom substitutions: YAG, $\text{Y}^{\text{III}}\text{Na}$, $\text{Y}^{\text{III}}\text{Li}$, MNZ-MG, and MNZ-Fe

Only two ions are introduced into the garnet structure in substitution schemes that involve YAG, $\text{Y}^{\text{III}}\text{alkali}$, or menzerite-type components, so the sole factor affecting the defect energy in these cases is the separation between the two substituents. Table A1 compares defect free energies at 1200 K and 2 GPa for five possibilities. Configurations 1 through 4 place the charge-compensating ion in the first-nearest through fourth-nearest site to the Y-bearing dodecahedron, respectively. Configuration 5 approximates the free energy of a totally dissociated defect, in which the charge-compensating ions are separated by a distance sufficient to produce only negligible interactions between them. For each ion, the free energy for a defect consisting of only that ion was calculated, then the two results were summed. Because this calculation was carried out for a 2x2x2 supercell, it will overestimate the free energy of the dissociated defect somewhat, as the interactions between uncompensated ions in the supercell will raise the computed energy compared to the value for a single ion in complete isolation. Although these effects should be somewhat larger than those resulting from supercell interactions for compensating ion pairs, these interactions are believed to alter the defect energies by at most a few $\text{kJ}\cdot\text{mol}^{-1}$, as described in the main body of this article.

The results confirm the expectation that the defect free energy for these two-atom substitutions is lowest when the charge-compensating ions occupy nearest-neighbor sites.

Vacancy substitution: $\text{Y}^{\text{III}}\square$

Three sites are involved in the vacancy substitution scheme, so the number of possible arrangements of two substituent ions plus one vacancy is large. Based on the insight garnered from the comparative energies for the two-atom substitution schemes, the number of possible $\text{Y}^{\text{III}}\square$ configurations to be investigated was reduced by considering only those arrangements in which the vacancy was immediately adjacent to an Y ion. Free energies were then calculated for defects with varying separation between the two Y ions. Bosenick et al. (2000, their Fig. 4) determined that there are only seven unique distances between pairs of dodecahedral sites in a single (1x1x1) unit cell of garnet. Configurations with Y ions in these pairs of sites were labeled 1 through 7, in order of increasing Y-Y separation. For each such Y-Y separation, four different possibilities exist for siting of the vacancy, as each dodecahedron has four nearest-neighbor dodecahedra. Configurations with each of these possible locations of the vacancy were then labeled "a" through "d". (For configuration 1, in which the two Y atoms are themselves adjacent, one of the four possible sites for the vacancy is eliminated; thus there is no "configuration 1a".) The free energy for a fully dissociated defect was approximated by summing the free energies in the 2x2x2 supercell for a single Y ion and for an Y- \square pair in adjacent dodecahedra; as above, this

likely overestimates the free energy of the dissociated defect by a few $\text{kJ}\cdot\text{mol}^{-1}$. Table A2 compares free energies for the 28 configurations that were evaluated.

The results identify two configurations (4b and 5b) with essentially identical energy as the arrangements that minimize the energetic cost of the vacancy substitution scheme. As illustrated in Figure A1, in both of these configurations the vacant dodecahedron shares an edge with each of the two Y-bearing dodecahedra. In configuration 4b the Y-□-Y angle is smaller, bringing the two Y ions closer together and resulting in a very slightly higher defect energy in comparison to configuration 5b.

Octahedral Li substitution: $^{\text{VI}}\text{Li}$

Three sites are also involved in the $^{\text{VI}}\text{Li}$ substitution scheme, so again the number of possibilities to be investigated was limited by considering only those arrangements in which the Li ion occupied an octahedron that was either the first-nearest site (configurations 1-3) or second-nearest site (configurations 4-9) to the Y-bearing dodecahedron. In each case, the second Y ion was placed in progressively more distant sites. The free energy for a fully dissociated defect was approximated by summing the free energies in the $2\times 2\times 2$ supercell for a single Y ion and for an Y-Li pair in adjacent dodecahedra; as above, this likely overestimates the free energy of the dissociated defect by a few $\text{kJ}\cdot\text{mol}^{-1}$. Table A3 compares free energies for the 10 configurations that were evaluated.

The results are similar to those for the $^{\text{VIII}}\square$ case, in that they identify two configurations (2 and 3) with essentially identical energy as the arrangements that minimize the energetic cost of the $^{\text{VI}}\text{Li}$ substitution scheme. As illustrated in Figure A1, in both of these configurations the Li-bearing octahedron shares an edge with each of the two Y-bearing dodecahedra. In configuration 2 the Y-Li-Y angle is smaller, bringing the two Y ions closer together. In pyrope and almandine, this results in a minute decrease in energy relative to configuration 3, in which the Y-Li-Y angle is larger and the Y-Y distance is greater. In spessartine and grossular, however, the effect is the opposite, with higher free energy for configuration 2 than for configuration 3. This difference—which is so small that it is quite possibly merely an artifact of the calculation—was not examined in detail, but it may be related to the differences in polyhedral distortion in more expanded vs. more contracted structures. Configuration 2 was selected for further calculations, as it has the minimum energy for both pyrope and almandine, the two end-members of greatest petrologic significance.

TABLE A1. Effects of configuration on two-atom defect free energies (kJ·mol⁻¹) for Y in garnet at 1200 K, 2 GPa

Host	Config	YAG		VIII _{NA}		VIII _{LI}		MNZ-MG		MNZ-FE	
		d [Y-Al]	ΔG_{def}	d [Y-Na]	ΔG_{def}	d [Y-Li]	ΔG_{def}	d [Y- ^{VI} Mg]	ΔG_{def}	d [Y- ^{VI} Fe]	ΔG_{def}
Pyp	1	0.2500	2329	0.3062	323	0.3062	52	0.2795	1366	0.2795	1470
Pyp	2	0.3062	2340	0.4677	338	0.4677	69	0.4507	1393	0.4507	1497
Pyp	3	0.4677	2358	0.5000	347	0.5000	63	0.5728	1398	0.5728	1502
Pyp	4	0.5000	2357	0.5863	343	0.5863	72	0.6731	1400	0.6731	1504
Pyp	5	∞	2541	∞	519	∞	249	∞	1575	∞	1679
Alm	1	0.2500	2223	0.3062	126	0.3062	-135	0.2795	1253	0.2795	1353
Alm	2	0.3062	2236	0.4677	141	0.4677	-119	0.4507	1277	0.4507	1377
Alm	3	0.4677	2253	0.5000	145	0.5000	-127	0.5728	1281	0.5728	1382
Alm	4	0.5000	2253	0.5863	144	0.5863	-117	0.6731	1284	0.6731	1384
Alm	5	∞	2435	∞	319	∞	59	∞	1457	∞	1557
Sps	1	0.2500	2064	0.3062	-171	0.3062	-421	0.2795	1082	0.2795	1178
Sps	2	0.3062	2080	0.4677	-158	0.4677	-405	0.4507	1102	0.4507	1198
Sps	3	0.4677	2097	0.5000	-157	0.5000	-414	0.5728	1105	0.5728	1201
Sps	4	0.5000	2097	0.5863	-156	0.5863	-404	0.6731	1108	0.6731	1204
Sps	5	∞	2276	∞	18	∞	-230	∞	1280	∞	1376
Grs	1	0.2500	1727	0.3062	-809	0.3062	-1038	0.2795	702	0.2795	787
Grs	2	0.3062	1751	0.4677	-798	0.4677	-1021	0.4507	711	0.4507	795
Grs	3	0.4677	1766	0.5000	-801	0.5000	-1001	0.5728	711	0.5728	794
Grs	4	0.5000	1765	0.5863	-796	0.5863	-1023	0.6731	717	0.6731	801
Grs	5	∞	1938	∞	-627	∞	-829	∞	884	∞	968

Note: Interatomic distances d are given as fractions of the unit-cell dimension. Fully dissociated defects are signified by " ∞ " for the d value. **Bold** highlights minimum-energy configurations.

TABLE A2. Effects of configuration on $^{\text{VIII}}\square$ -defect free energies ($\text{kJ}\cdot\text{mol}^{-1}$) for Y in garnet at 1200 K, 2 GPa

Config	d [Y-Y]	Pyp	Alm	Sps	Grs
		ΔG_{def}	ΔG_{def}	ΔG_{def}	ΔG_{def}
1b	0.3062	-583	-871	-1308	-2253
1c	0.3062	-508	-798	-1239	-2197
1d	0.3062	-496	-785	-1226	-2182
2a	0.4677	-561	-850	-1288	-2232
2b	0.4677	-583	-871	-1308	-2244
2c	0.4677	-508	-798	-1239	-2191
2d	0.4677	-506	-796	-1237	-2187
3a	0.5000	-551	-845	-1288	-2238
3b	0.5000	-542	-836	-1280	-2229
3c	0.5000	-491	-787	-1233	-2192
3d	0.5000	-542	-836	-1280	-2229
4a	0.5590	-567	-857	-1295	-2239
4b	0.5590	-610	-896	-1331	-2265
4c	0.5590	-561	-850	-1287	-2231
4d	0.5590	-520	-811	-1252	-2202
5a	0.5863	-571	-860	-1298	-2241
5b	0.5863	-611	-898	-1332	-2266
5c	0.5863	-511	-802	-1243	-2194
5d	0.5863	-509	-799	-1240	-2189
6a	0.7071	-568	-857	-1294	-2238
6b	0.7071	-563	-852	-1290	-2233
6c	0.7071	-541	-830	-1268	-2214
6d	0.7071	-568	-857	-1294	-2238
7a	0.8660	-563	-852	-1290	-2232
7b	0.8660	-564	-852	-1290	-2234
7c	0.8660	-521	-811	-1252	-2202
7d	0.8660	-569	-857	-1294	-2236
8	∞	-393	-683	-1122	-2070

Note: Interatomic distances d are given as fractions of the unit-cell dimension. Fully dissociated defects are signified by " ∞ " for the d value. **Bold** highlights minimum-energy configurations.

TABLE A3. Effects of configuration on $^{\text{VI}}\text{Li}$ -defect free energies ($\text{kJ}\cdot\text{mol}^{-1}$) for Y in garnet at 1200 K, 2 GPa

Config			Pyp	Alm	Sps	Grs
	d [Y-Li]	d [Y-Y]	ΔG_{def}	ΔG_{def}	ΔG_{def}	ΔG_{def}
1	0.2795	0.3062	1453	1241	921	212
2	0.2795	0.4677	1426	1217	901	201
3	0.2795	0.5590	1429	1218	899	199
4	0.4507	0.3062	1504	1290	964	234
5	0.4507	0.4677	1487	1273	948	226
6	0.4507	0.5000	1510	1289	957	229
7	0.4507	0.5590	1486	1271	946	224
8	0.4507	0.5863	1485	1269	944	223
9	0.4507	0.6847	1480	1265	941	220
10	0.2795	∞	1679	1557	1376	968

Note: Interatomic distances d are given as fractions of the unit-cell dimension. Fully dissociated defects are signified by " ∞ " for the d value. **Bold** highlights minimum-energy configurations.

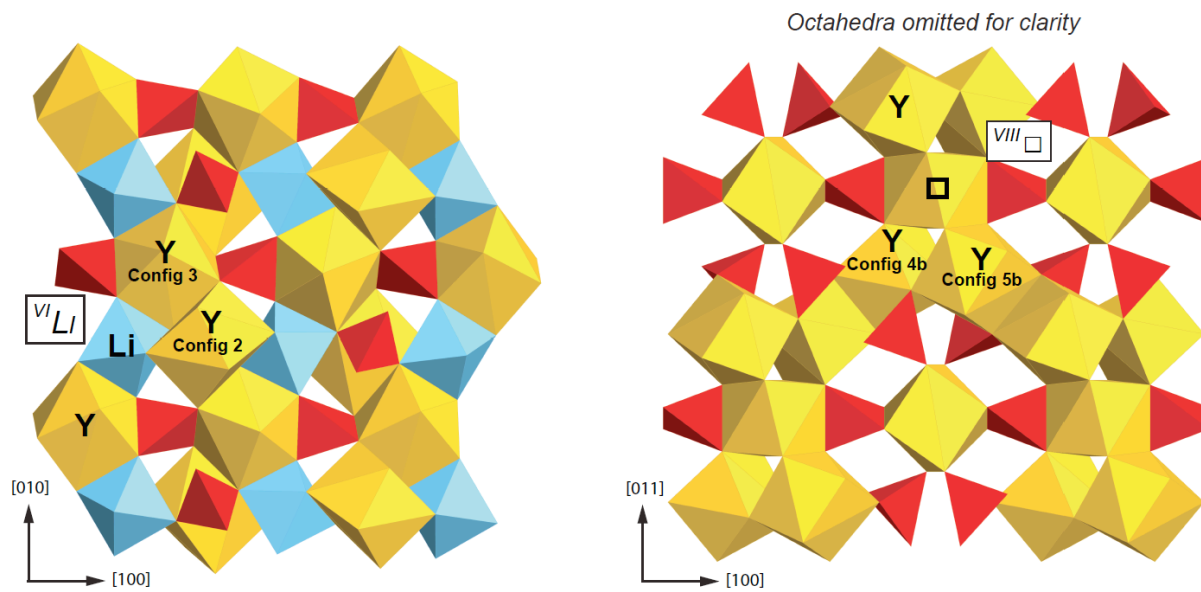


FIGURE A1. Portions of garnet structure illustrating alternative near-equivalent minimum-energy configurations for Y incorporation by means of ^{VI}Li substitution scheme (*left*) and $^{VIII}\square$ substitution scheme (*right*). In the unmodified structure, red tetrahedra are occupied by Si; blue octahedra are occupied by Al; and yellow dodecahedra are occupied by divalent cations Mg, Fe, Mn, and Ca. Labels on polyhedra indicate occupancy for substitution schemes (in boxes) described in text; “ \square ” indicates a vacant (unoccupied) dodecahedron. Structures are redrawn with modification from Bosenick et al. (2000) Figs. 1 (*left*) and 4 (*right*).