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SUPPLEMENTARY INFORMATION:
Ab initio investigation of majorite and pyrope garnets: Lattice dynamics and vibrational spectra

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#	$\nu_{TO,calc}$	II_{calc}	$\nu_{TO,exp}$				$\nu_{TO,calc}$	$\nu_{LO,calc}$	$\nu_{LO,exp}$		$\nu_{LO,calc}$
			McMillan '89	Hofmeister '91	Hofmeister '96	Hofmeister '04	Chaplin '98		Hofmeister '91	Hofmeister '96	Chaplin '98
1	119.4	2968	--	--	134.4	--	153.1	137.7	--	152.2	156.0
2	139.0	24	--	140	134.4	138	170.4	140.8	152	152.2	172.8
3	187.3	3366	--	200	194.6	196	230.9	213.0	218	218.1	231.0
4	214.6	0	--	238	220.8	220	234.6	214.6	240	223.0	257.4
5	260.0	603	--	260	258.5	259	273.3	263.5	263	263.0	273.4
	--	--	--	279	--	--	--	--	280	--	--
6	333.2	6427	340	339	336.2	337	316.9	346.2	353	357.3	318.8
7	346.3	28	--	365	336.2	--	380.7	353.1	370	357.3	402.5
8	379.9	3677	390	385	383.0	384	417.1	395.4	400	399.9	431.5
9	421.5	1361	--	423	421.7	420	432.1	425.3	422	423.0	442.9
10	458.1	13381	466	458	454.8	456	475.5	481.6	474	475.4	486.3
11	483.6	1048	485	478	478.3	478	493.8	527.1	528	529.6	532.3
12	532.2	711	538	536	535.4	535	556.1	563.7	556	557.4	610.5
13	582.7	1456	584	583	580.9	582	610.6	621.5	618	620.4	636.5
14	674.3	4	--	664	650	700	681.4	674.4	667	650	709.6
15	867.9	13959	877	878	871.0	875	841.2	887.7	889	890.0	877.4
16	898.6	5793	907	906	901.7	904	878.3	942.2	940	941.3	913.4
17	972.8	5920	976	976	972.0	976	973.8	1063.6	1063	1060.0	1068.1

Table S1 Calculated and experimental IR properties of pyrope. ν and II are the frequencies [cm^{-1}] and absorption integrated intensities [km/mol], respectively. Frequencies of both TO and LO modes are given. All IR active modes have F_{1u} symmetry.

		McMillan '89	Hofmeister '91	Hofmeister '96	Hofmeister '04	Chaplin '98
This work	M	9	16	17	15	17
	$\overline{\lvert\Delta\rvert}$	6.0	6.8	5.6	5.2	22.0
	$\overline{\Delta}$	-6.0	-4.8	0.5	-3.6	-14.6
	$\lvert\Delta\rvert_{max}$	10.1	23.4	24.3	25.7	43.6
McMillan '89	M	--	9	9	9	9
	$\overline{\lvert\Delta\rvert}$	--	2.9	5.5	4.0	20.0
	$\overline{\Delta}$	--	2.7	5.5	4.0	0.0
	$\lvert\Delta\rvert_{max}$	--	8.0	11.2	10.0	35.8
Hofmeister '91	M	--	--	16	15	16
	$\overline{\lvert\Delta\rvert}$	--	--	6.3	5.1	19.1
	$\overline{\Delta}$	--	--	6.2	0.3	-7.5
	$\lvert\Delta\rvert_{max}$	--	--	28.8	36.0	36.8
Hofmeister '96	M	--	--	--	15	17
	$\overline{\lvert\Delta\rvert}$	--	--	--	4.9	23.6
	$\overline{\Delta}$	--	--	--	-4.4	-15.1
	$\lvert\Delta\rvert_{max}$	--	--	--	50.0	44.5
Hofmeister '04	M	--	--	--	--	15
	$\overline{\lvert\Delta\rvert}$	--	--	--	--	20.6
	$\overline{\Delta}$	--	--	--	--	-7.2
	$\lvert\Delta\rvert_{max}$	--	--	--	--	34.9

Table S2 Statistics on the calculated and experimental IR-TO frequencies [cm^{-1}] of pyrope (data in Table S1). Statistical indices are defined in the Computational Method Section.

#	Sym	ν_{calc}	II_{calc}	ν_{exp} Hofmeister '91	ν_{exp} Kolesov '98	ν_{exp} Kolesov '00	ν_{exp} Hofmeister '04	ν_{calc} Chaplin '98
1	A_{1g}	356.8	827	362	364.1	363.4	363.4	342.7
2		566.0	724	562	562.8	561.4	561.6	524.0
3		926.6	3072	925	928.0	926.6	925.5	850.5
4	E_g	210.5	12	203	210.9	--	208.0	207.2
5		310.4	1	--	284.0	--	290.9	307.7
6		338.2	306	342	344.5	342.5	342.5	363.8
7		376.7	83	365	--	--	363.4	430.6
		--	--	439	--	--	--	--
8		527.8	33	524	525.0	--	524.6	506.8
9		636.6	44	626	--	--	--	633.2
10		865.0	48	911	--	--	--	816.3
11		939.2	19	938	--	--	--	943.1
12	F_{2g}	105.1	52	--	136.5	127.1	131	192.6
13		172.3	26	--	--	--	175	227.4
14		207.7	135	208	212.5	209.4	208.0	246.6
		--	--	230	--	--	--	--
15		269.3	10	272	--	273.0	271.2	297.2
		--	--	285	--	--	--	--
16		320.0	40	318	322.0	320.2	318.9	323.1
17		350.7	18	350	353.2	352.1	342.5	353.1
18		382.5	85	379	383.2	383.6	379.5	367.3
19		494.1	48	490	492.4	491.6	490.6	473.2
20		514.9	212	510	512.1	511.3	511	514.9
21		610.2	25	598	--	--	598.9	607.2
22		657.1	474	648	650.6	648.2	647.7	643.8
23		863.9	510	866	878.8	870.2	867.0	844.4
24		899.2	47	899	--	--	899.4	875.8
25		1072.3	295	1062	1066.0	1066.1	1061.4	1061.8

Table S3 Calculated and experimental Raman properties of pyrope. ν and II are the frequencies [cm^{-1}] and isotropic integrated intensities (in arbitrary units), respectively.

		Hofmeister '91	Kolesov '98	Kolesov '00	Hofmeister '04	Chaplin '98
This work	M	22	17	15	22	25
	$\overline{\lvert\Delta\rvert}$	6.7	7.1	4.9	6.4	24.6
	$\overline{\Delta}$	1.2	-1.3	-1.4	2.3	0.7
	$\lvert\Delta\rvert_{max}$	46.0	31.4	22.0	25.9	87.5
Hofmeister '91	M	--	15	14	19	22
	$\overline{\lvert\Delta\rvert}$	--	3.8	1.9	1.3	23.2
	$\overline{\Delta}$	--	-3.8	-1.8	-0.1	6.0
	$\lvert\Delta\rvert_{max}$	--	12.8	4.6	7.5	94.7
Kolesov '98	M	--	--	14	17	17
	$\overline{\lvert\Delta\rvert}$	--	--	2.4	3.9	22.2
	$\overline{\Delta}$	--	--	2.4	3.1	6.1
	$\lvert\Delta\rvert_{max}$	--	--	9.4	11.8	77.5
Kolesov '00	M	--	--	--	15	15
	$\overline{\lvert\Delta\rvert}$	--	--	--	2.2	23.9
	$\overline{\Delta}$	--	--	--	1.7	3.2
	$\lvert\Delta\rvert_{max}$	--	--	--	9.6	76.1
Hofmeister '04	M	--	--	--	--	22
	$\overline{\lvert\Delta\rvert}$	--	--	--	--	24.7
	$\overline{\Delta}$	--	--	--	--	-3.6
	$\lvert\Delta\rvert_{max}$	--	--	--	--	75.0

Table S4 Statistics on the calculated and experimental Raman frequencies [cm^{-1}] of pyrope (data in Table S3). Statistical indices are defined in the Computational Method Section.

#	Sym	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	#	Sym	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	#	Sym	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	#	Sym	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}
1	A_{1u}	312.7	2.45	1.34	16	E_u	210.4	1.10	0.89	31		325.4	2.67	1.40	46		346.1	2.24	1.11
2		374.3	2.21	1.01	17		299.6	2.80	1.60	32		347.3	1.20	0.59	47		401.9	2.79	1.19
3		464.8	2.57	0.95	18		349.1	2.27	1.11	33		383.5	1.69	0.75	48		451.8	2.83	1.07
4		718.4	3.46	0.82	19		375.7	2.25	1.03	34		477.5	1.97	0.71	49		503.8	2.84	0.96
5		1052.5	4.79	0.78	20		437.2	1.74	0.68	35		506.4	1.73	0.58	50		534.0	3.12	1.00
6	A_{2g}	238.1	1.52	1.09	21		501.4	3.57	1.22	36		583.4	2.62	0.77	51		641.5	3.88	1.03
7		307.3	3.49	1.94	22		559.9	2.90	0.89	37		847.7	5.26	1.06	52		660.4	2.59	0.67
8		452.0	2.34	0.89	23		664.0	2.13	0.55	38		887.1	3.75	0.72	53		869.8	4.54	0.89
9		585.5	1.01	0.29	24		912.8	3.99	0.75	39		975.5	4.63	0.81	54		915.0	4.59	0.86
10		1032.9	4.67	0.77	25		937.1	4.73	0.86	40	F_{2u}	114.1	1.93	2.89	55		956.1	4.92	0.88
11	A_{2u}	143.4	1.07	1.28	26	F_{1g}	153.4	1.72	1.92	41		209.5	1.54	1.25					
12		312.8	3.40	1.86	27		167.8	2.09	2.13	42		222.6	1.97	1.51					
13		395.5	1.37	0.59	28		197.6	2.81	2.44	43		269.2	1.32	0.84					
14		519.7	2.54	0.84	29		275.6	2.68	1.66	44		288.4	1.39	0.82					
15		907.2	4.37	0.82	30		289.7	1.44	0.85	45		336.8	2.13	1.08					

Table S5 Calculated frequencies [cm^{-1}], mode Grüneisen parameters γ (dimensionless) and pressure dependences $d\nu/dP$ [cm^{-1}/GPa] for the silent modes of pyrope.

#	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	#	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	#	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}
1	145.7	2.54	2.72	11	361.3	3.54	1.53	21	542.0	3.01	0.87
2	171.9	0.61	0.55	12	364.8	2.60	1.11	22	576.4	2.45	0.66
3	196.9	1.12	0.89	13	384.4	1.90	0.77	23	648.9	3.33	0.80
4	213.7	1.08	0.79	14	391.3	2.68	1.07	24	676.2	2.20	0.51
5	247.6	0.96	0.61	15	424.7	2.48	0.91	25	725.7	4.88	1.05
6	258.8	0.96	0.58	16	439.2	1.43	0.51	26	821.2	3.15	0.60
7	276.9	1.49	0.84	17	458.8	2.70	0.92	27	878.5	3.07	0.55
8	302.2	3.98	2.05	18	479.8	3.04	0.99	28	925.5	5.74	0.97
9	314.7	1.09	0.54	19	492.4	2.64	0.84	29	937.7	5.32	0.89
10	327.5	3.15	1.50	20	516.1	2.69	0.81	30	951.9	5.06	0.83
								31	980.4	5.60	0.89

Table S6 Calculated frequencies [cm^{-1}], mode Grüneisen parameters γ (dimensionless) and pressure dependences $d\nu/dP$ [cm^{-1}/GPa] for the silent modes of majorite. All modes have B_u symmetry.

Prp							
			Δν %				
ν_{calc}	Sym	II_{calc}	Mg	Al	Si	O	Description
119.4	F_{1u}	2968	-2.8	-0.4	-0.1	-0.4	Mg t
187.3	F_{1u}	3366	-2.8	-0.1	-0.3	-0.5	Mg t
333.2	F_{1u}	6427	-1.5	-0.2	-0.4	-1.5	Mg t + SiO_4 t
379.9	F_{1u}	3677	0.0	-1.2	-0.3	-2.2	Al t + SiO_4 r
458.1	F_{1u}	13381	-0.1	-2.2	-0.1	-1.3	Al t + SiO_4 r
Maj							
			Δν %				
ν_{calc}	Sym	II_{calc}	Mg(dod)	Mg(oct)	Si(oct)	Si(tet)	O	Description
341.4	E_u	1119	-0.6	-0.4	-0.3	-0.5	-1.9	Mg(dod) t + Mg(oct) t + SiO_4 l/t
345.1	A_u	1234	-1.3	-0.3	-0.1	-0.5	-1.5	Mg(dod) t + Mg(oct) t + SiO_4 l/t
360.5	A_u	1596	-0.5	-1.1	0.0	-0.4	-1.6	Mg(dod) t + Mg(oct) t + SiO_4 l/r
368.8	E_u	1052	-0.6	-0.4	-0.3	-0.5	-1.8	Mg(dod) t + Mg(oct) t + SiO_4 l/r
384.9	E_u	2453	-0.1	-0.8	-0.2	-0.4	-2.0	Mg(oct) t + SiO_4 l/r
396.5	E_u	1174	-0.2	-0.8	-0.4	-0.4	-1.8	Mg(oct) t + SiO_4 l/r
399.0	A_u	980	-0.1	-0.5	-0.2	-0.5	-2.4	Mg(oct) t + SiO_4 l/r
440.5	E_u	4968	-0.4	-0.4	-0.4	-0.3	-2.1	All subunits
510.3	A_u	2172	0.0	-0.2	-1.5	0.0	-1.9	Si(oct) + SiO_4 l/r
550.1	E_u	2112	-0.1	-0.1	-1.4	-0.3	-1.7	Si(oct) + SiO_4 l/r

Table S7 Percent isotopic shifts Δν % and structural contributions for the most intense IR modes in the low frequency range (below 750 cm^{-1}) of pyrope and majorite. To compute isotopic shifts, masses of each species have been in turn increased by 7.5%. Description labels refer to: "t" translation, "r" rocking, "l" libration.

Prp							
			Δν %				
ν_{calc}	Sym	II_{calc}	Mg	Al	Si	O	Description
207.7	F_{2g}	135	-0.8	0.0	-0.5	-2.3	Mg t + SiO_4 l
338.2	E_g	306	-1.3	0.0	-0.1	-2.2	Mg t + SiO_4 l
356.8	A_{1g}	827	0.0	0.0	0.0	-3.6	SiO_4 l
514.9	F_{2g}	212	0.0	0.0	-0.8	-2.7	SiO_4 r
566.0	A_{1g}	724	0.0	0.0	0.0	-3.6	SiO_4 l
657.1	F_{2g}	474	0.0	0.0	-0.7	-2.9	SiO_4 r

Maj								
			Δν %					
ν_{calc}	Sym	II_{calc}	Mg(dod)	Mg(oct)	Si(oct)	Si(tet)	O	Description
154.2	B_g	147	-0.7	0.0	0.0	-0.2	-2.8	Mg(dod) + SiO_4 l
154.5	A_g	165	-2.7	0.0	0.0	-0.3	-0.8	Mg(dod) + SiO_4 l
177.5	A_g	265	-0.6	0.0	0.0	-0.5	-2.4	Mg(dod) + SiO_4 l
229.7	A_g	369	-2.3	0.0	0.0	-0.1	-1.4	Mg(dod) + SiO_4 l
317.1	A_g	146	-0.3	0.0	0.0	-0.1	-2.3	SiO_4 l
368.9	A_g	229	-0.7	0.0	0.0	-0.1	-2.7	Mg(dod) + SiO_4 l
402.3	A_g	113	-0.4	0.0	0.0	-0.2	-2.4	SiO_4 l
458.0	A_g	116	0.0	0.0	0.0	-0.8	-2.8	SiO_4 r
540.6	E_g	110	-0.1	0.0	0.0	-0.5	-3.0	SiO_4 r
602.0	A_g	1667	0.0	0.0	0.0	-0.2	-3.3	SiO_4 l
653.2	E_g	197	0.0	0.0	0.0	-0.7	-2.8	SiO_4 r

Table S8 Percent isotopic shifts Δν % and structural contributions for the most intense Raman modes in the low frequency range (below 750 cm^{-1}) of pyrope and majorite. See caption to Table S7 for more details.

#	Sym	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	γ_{exp} Chopelas '06
1	A_g	356.8	3.42	1.64	1.5
2		566.0	2.65	0.80	0.85
3		926.6	4.06	0.75	0.6
4	E_g	210.5	1.16	0.95	1.2
5		310.4	2.71	1.49	1.4
6		338.2	3.31	1.67	1.5
7		376.7	2.52	1.15	1.5
8		527.8	2.38	0.77	0.85
9		636.6	1.38	0.37	0.85
10		865.0	3.74	0.74	0.8
11		939.2	4.97	0.91	0.7
12	F_{2g}	105.1	2.29	3.73	1.4
13		172.3	2.23	2.21	1.4
14		207.7	2.37	1.95	1.2
15		269.3	2.46	1.56	1.2
16		320.0	1.64	0.88	1.3
17		350.7	2.38	1.16	1.5
18		382.5	2.98	1.33	1.5
19		494.1	2.53	0.87	0.9
20		514.9	1.44	0.48	0.85
21		610.2	2.44	0.68	0.85
22		657.1	1.97	0.51	0.85
23		863.9	5.26	1.04	0.8
24		899.2	5.01	0.95	0.6
25		1072.3	4.62	0.74	0.8
$\overline{\gamma}$				1.14	1.11

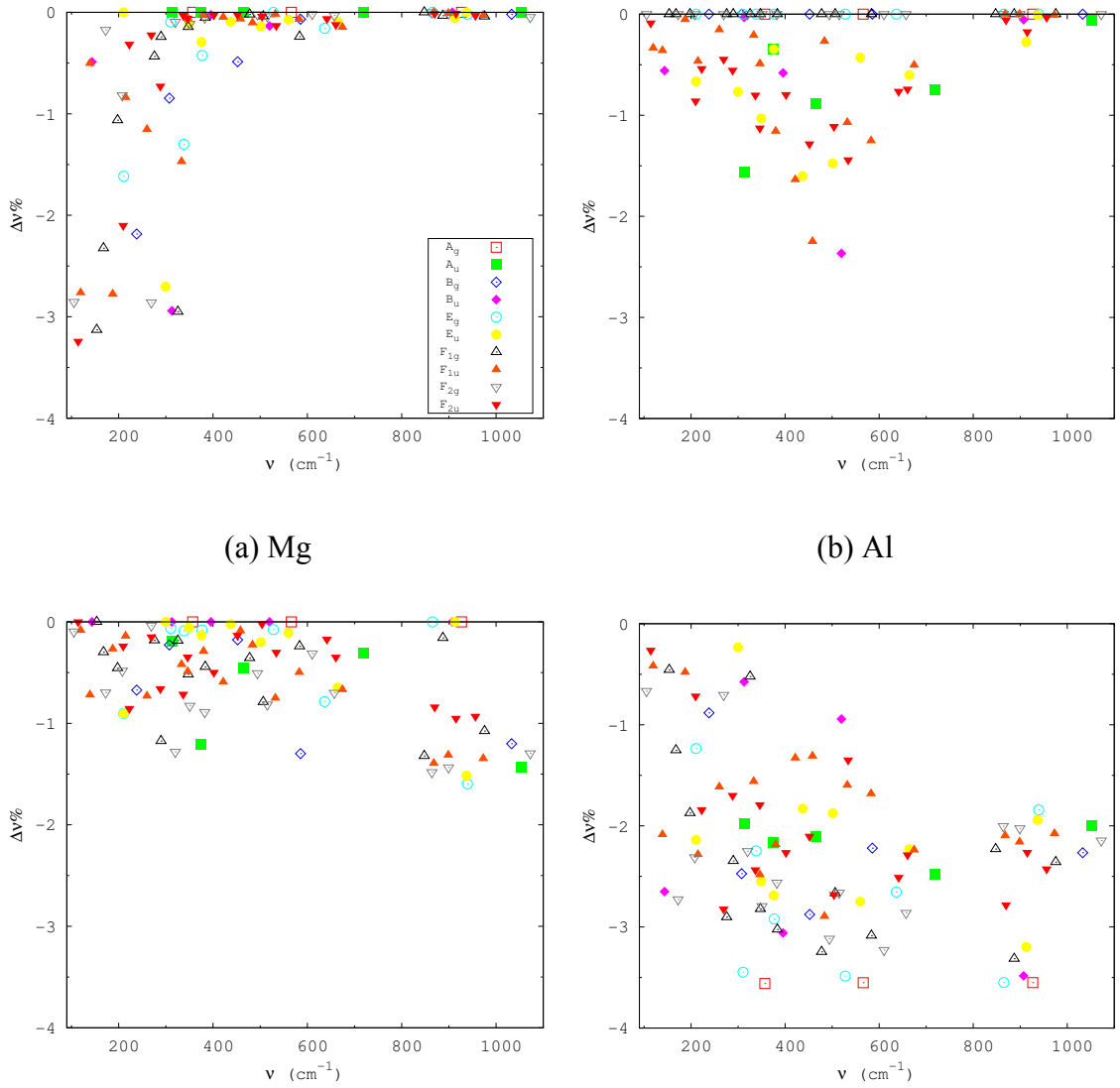
Table S9 Calculated and experimental mode Grüneisen parameters γ (dimensionless) and pressure dependences dν/dP [cm^{-1}/GPa] for the Raman active modes of pyrope. $\overline{\gamma}$ is the mean value computed over each set of γ data.

#	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	#	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}
1	119.4	1.14	1.64	11	483.6	2.10	0.74
2	139.0	1.37	1.68	12	532.2	3.68	1.18
3	187.3	2.23	2.03	13	582.7	3.62	1.06
4	214.6	2.88	2.29	14	674.3	2.62	0.66
5	260.0	1.47	0.97	15	867.9	4.84	0.95
6	333.2	1.84	0.95	16	898.6	5.03	0.96
7	346.3	1.90	0.94	17	972.8	4.93	0.87
8	379.9	2.19	0.99				
9	421.5	1.60	0.65				
10	458.1	2.62	0.98				

Table S10 Calculated mode Grüneisen parameters γ (dimensionless) and pressure dependences $d\nu/dP$ [cm^{-1}/GPa] for the IR active modes of pyrope. All modes have F_{1u} symmetry.

#	Sym	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	#	Sym	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	#	Sym	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}	#	Sym	ν_{calc}	$d\nu/dP_{calc}$	γ_{calc}
1	E_u	101.3	2.28	3.51	16	A_u	289.8	1.80	0.97	31	A_u	399.0	2.54	0.99	46	E_u	583.2	2.21	0.59
2	E_u	130.9	2.33	2.78	17	E_u	300.3	1.84	0.96	32	E_u	417.1	2.31	0.86	47	A_u	599.6	3.36	0.88
3	A_u	142.4	2.13	2.33	18	A_u	312.1	2.21	1.11	33	A_u	425.5	3.54	1.30	48	E_u	636.8	4.04	0.99
4	A_u	156.4	1.04	1.04	19	A_u	322.6	1.94	0.94	34	E_u	440.5	2.77	0.98	49	A_u	656.7	2.71	0.64
5	E_u	172.3	1.74	1.58	20	E_u	325.8	1.65	0.79	35	A_u	452.7	1.49	0.51	50	E_u	684.8	3.43	0.78
6	A_u	191.8	0.90	0.73	21	E_u	341.4	2.54	1.16	36	E_u	457.6	2.33	0.79	51	A_u	701.6	3.08	0.68
7	E_u	197.7	1.56	1.23	22	A_u	345.1	4.70	2.12	37	A_u	464.0	1.90	0.64	52	E_u	706.8	4.29	0.95
8	E_u	206.8	1.37	1.04	23	A_u	360.5	0.98	0.43	38	A_u	479.8	2.32	0.75	53	A_u	730.4	3.84	0.82
9	A_u	213.4	1.72	1.26	24	E_u	361.7	2.38	1.03	39	E_u	491.1	2.10	0.67	54	E_u	826.3	3.48	0.66
10	E_u	222.5	2.67	1.87	25	E_u	368.8	2.10	0.89	40	E_u	504.3	2.17	0.67	55	A_u	845.1	3.63	0.67
11	E_u	240.2	1.56	1.02	26	A_u	372.4	2.52	1.06	41	A_u	510.3	2.66	0.81	56	E_u	876.1	5.97	1.06
12	A_u	247.1	2.24	1.41	27	A_u	379.6	2.03	0.84	42	E_u	522.5	3.21	0.96	57	A_u	886.4	5.47	0.96
13	E_u	257.3	1.33	0.81	28	E_u	384.9	2.90	1.18	43	E_u	550.1	3.58	1.02	58	E_u	901.4	4.60	0.80
14	A_u	258.8	1.09	0.66	29	A_u	392.1	2.76	1.10	44	A_u	563.2	3.43	0.95	59	E_u	915.1	4.59	0.78
15	E_u	277.0	1.29	0.73	30	E_u	396.5	2.57	1.01	45	A_u	579.7	2.68	0.72	60	A_u	928.4	4.99	0.84
															61	A_u	950.4	5.13	0.84
															62	E_u	954.2	6.10	1.00
															63	A_u	974.5	5.41	0.87
															64	E_u	989.1	5.74	0.91
															65	A_u	1055.5	5.24	0.77

Table S11 Calculated mode Grüneisen parameters γ (dimensionless) and pressure dependences $d\nu/dP$ [cm^{-1}/GPa] for the IR active modes of majorite.



(a) Mg (b) Al

(c) Si (d) O

Figure S1 Percentage isotopic shifts Δν % on the vibrational frequencies of pyrope. Masses of each species have been in turn increased by 7.5%.