REFRINGENCE OF GARNETS AND HYDROGARNETS

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Abstract

Using the Lorentz-Lorenz relation, refractive indexes for the garnets and hydrogarnets were calculated from the unit-cell dimensions and the ionic refractivities, as follows: grossular 1.731, andradite 1.886, almandine 1.832, spessartine 1.807, pyrope 1.723, uvarovite 1.868, $Ca_4Al_2(OH)_{12}$ 1.603, $Ca_3Fe_2(OH)_{12}$ 1.724, and plazolite 1.675. Simultaneously, values for the ionic refractivities of Fe'' (5.90), Cr'' (5.20), Si (0.18), Al (0.65), and H₄ (0.70) were calculated. These ionic refractivities are commensurate with values previously given for other cations and probably are applicable to other orthosilicates. The calculated refringences for grossular, andradite, and uvarovite are somewhat lower than previously published values while others are higher. That of pyrope is considerably higher. The calculated and observed values of *n* are compared for 75 chemically analyzed garnets.

INTRODUCTION

The refractive indexes of the end-member garnets have attracted considerable attention. Ford (1915) published an elaborate study which interrelated the chemical compositions, specific gravities and refractive indexes of the garnets. At that time x-ray diffraction data, of course, were not available; thus his investigations were closely coupled with experimental measurements of the specific gravities.

With Ford's work as a starting point, Fleischer (1937) reconsidered the entire topic, giving densities based on averages from published determinations and adding calculated densities based on his calculated values for a. He compared his unit-cell dimensions with those obtained by Stockwell (1927).

Skinner (1956) subsequently measured a dimensions for several synthetic end members (except uvarovite). His work can be taken as a basis for calculating the refringences directly from the unit-cell dimensions and the ionic refractivities, insofar as the ionic refractivities are known.

The problem, then, consists of re-evaluating the refringences of the several garnet end members and simultaneously ascertaining appropriate ionic refractivities for the purpose. This cannot be accomplished by a simple, straightforward procedure, but must take into account comparative polarizabilities of the ions and any other data which will lead to reasonable and mutually compatible results. Nevertheless, the garnets constitute a relatively coherent group with distinct advantages: (i) they are isotropic (or nearly so) so that vectorial components of the electrical dipoles need not be considered, (ii) they are orthosilicates of fairly simple compositions insofar as the end members are concerned, and (iii) the structures of the six common end members are not complicated by hydrogen bonds.

THEORETICAL CONSIDERATIONS

According to the Lorentz-Lorenz theory each atom (or ion) should have its own characteristic contribution (R) to the refractive index, in such a way that

$$\frac{M}{\rho} \cdot \frac{n^2 - 1}{n^2 + 2} = N_1 R_1 + N_2 R_2 + \dots$$
(1)

where M is the molecular weight of the unit-cell contents; ρ is the density; n is the refractive index; N_1 , N_2 , etc. are the numbers of atoms of each species per unit cell; and R_1 , R_2 , etc. are the characteristics of these atoms known as "ionic refractivities."*

Inasmuch as the density (specific gravity) is a difficult measurement to make with precision, for several reasons which need not be discussed here, this term should be eliminated from equation (1). A well-established relation is as follows:

$$\rho = \frac{M}{V \cdot A} \text{ or } \frac{M}{\rho} = V \cdot A$$

where ρ and M are the same as before, V is the volume of the unit cell in cm.³, and A is Avogadro's number. In the cubic case, then, by substitution in equation (1):

$$\frac{a^3}{1.6602} \cdot \frac{n^2 - 1}{n^2 + 2} = N_1 R_1 + N_2 R_2 + \dots$$
 (2)

where the unit-cell dimension a (in angstroms) is the only experimental factor involved in the calculation of the refractive index of an ideal structure for which R_1 , R_2 , etc. are known.

For the ideal end-member garnets:

$$N_1 = 96$$
 (oxygen)
 $N_2 = 24$ (silicon)
 $N_3 = 24$ (Ca, Mg, Fe'', or Mn'')
 $N_4 = 16$ (Al, Fe''', or Cr''')

so that the complete expression (for a simple garnet) becomes:

*One of the alternative empirical relations is that of Gladstone & Dale; its application to minerals has been discussed by Jaffe (1956) in Am. Min. 41, 757-777.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1.6602}{a^3} \cdot (96R_1 + 24R_2 + 24R_3 + 16R_4).$$
(3)

The greatest contribution (more than 70 per cent of the total) is that of the oxygen atoms of the 24 SiO₄ groups. Each of these oxygens can be assumed to have a contribution of 3.5, *i.e.* $96R_1 = 336$. On this basis other values of *R* have been established (see Bragg, 1937) and are listed in Table 1.

Ion	R	Uncertainty	Ion	R	Uncertainty
Al Fe"'' Cr"'' Si H ₄	$\begin{array}{c} 0.65 \\ 5.90 \\ 5.20 \\ 0.18 \\ 0.70 \end{array}$	$\begin{array}{c} 0.06 \\ 0.25 \\ 0.15 \\ 0.05 \\ 0.20 \end{array}$	Ca Mg Fe" Mn"	2.08* 0.36* 2.29* 2.33*	$\begin{array}{c} 0.10 \\ 0.08 \\ 0.10 \\ 0.10 \end{array}$

TABLE 1. EMPIRICAL IONIC REFRACTIVITIES

*Values previously assigned (see Bragg, 1937) are the same for Fe'' and Mn'', but are 1.99 and 0.44 for Ca and Mg, respectively.

Table 1 contains 7 new values for R which were obtained from calculations involving the garnets and hydrogarnets themselves, although numerous supplemental clues to these values have been sought elsewhere. The value for Si, being comparatively insignificant in garnets, was calculated from quartz. The value for Cr'' was assigned through consideration of the relative polarizing forces of Al, Fe'' and Cr'' and various other empirical data; the value calculated from chromite (*ca.* 4) is entirely unsatisfactory when applied to garnets.

REFRINGENCES OF THE END MEMBERS

The *a* dimensions of the synthetic end-member garnets (except uvarovite) are given by Skinner (1956). My determination of the *a* dimension for synthetic uvarovite is 12.012 ± 0.006 Å on the material synthesized by Hummel (1950); it is comparable with the measurement of Geller & Miller (1959), who found $a = 12.02 \pm 0.01$ Å.

The refractive indexes of the garnets, calculated from the unit-cell dimensions, are compared with previously recorded values in Table 2. These calculations have been extended (with some uncertainty) to the synthetic hydrogarnets and plazolite for which the *a* dimensions are taken from Flint *et al.* (1941) for $Ca_3Al_2(OH)_{12}$ and $Ca_3Fe_2(OH)_{12}$ and from Pabst (1937) for $Ca_3Al_2(SiO_4)_2(OH)_4$ (plazolite).

There is (Table 2) an appreciable difference between my calculated n for pyrope (1.723) and those of Skinner (1956) and Ford (1915), as is true also of their values (1.714 and 1.705, respectively). These differences

		Norr	Compara	ative data
	a (Å)	n	n	Reference
Grossular(GR) Andradite(AN) Almandine(AL) Spessartine(SP) Pyrope(PY) Uvarovite(UV) C ₂ AH ₆ (syn.) C ₃ FH ₆ (syn.) Plazolite	$\begin{array}{c} 11.851*\\ 12.048*\\ 11.526*\\ 11.621*\\ 11.459*\\ 12.012*\\ 12.585*\\ 12.765\\ 12.765\\ 12.164* \end{array}$	$\begin{array}{c} 1.731 \\ 1.886 \\ 1.832 \\ 1.807 \\ 1.723 \\ 1.868 \\ 1.603 \\ 1.724 \\ 1.675 \end{array}$	$1.734; 1.735 \\ 1.887; 1.895 \\ 1.830; 1.830 \\ 1.800; 1.800 \\ 1.714; 1.705 \\ 1.870 \\ 1.605 \\ 1.710 \\ 1.675$	Skinner; Ford idem idem idem Ford Flint et al. idem Pabst

TABLE 2. CALCULATED INDEXES OF REFRACTION FOR GARNETS AND HYDROGARNETS AND UNIT-CELL DIMENSIONS

*Skinner (1956), all \pm 0.002 Å. †This work, \pm 0.006 Å.

 $\pm Op.$ cit., converted from kX units, ± 0.02 Å except plazolite which is ± 0.01 Å.

are essentially coupled with R_{Mg} inasmuch as the values of R_{Al} , and R_{Sl} and R_0 yield consistent results for other garnets and hydrogarnets. Consequently, unless the value of R_{Mg} is appreciably in error, n for pyrope must be considerably greater than has been suggested in previous works.

The hydrogarnets involve an evaluation of the 4 protons which are capable of substitution for Si. The major discrepency is for "tricalcium ferrite hexahydrate" (abbreviated $C_{3}FH_{6}$ in Table 2) which yields a calculated value 1.724 as compared with a measured 1.710. In this connection it is noteworthy that, although the calculated value for $C_{3}FH_{6}$ is too great, n for and radius is low compared with previous values (1.886) vs. 1.887 and 1.895). Since the other hydrogarnet yields a low value, the fault cannot be with R for H₄ but must be the consequence of an error in the experimental value of a or n or both.

It should be indicated that the *a* dimension given by Skinner is not the only basis for calculating *n*. Abrahams & Geller (1958) give a = 11.874 ± 0.004 Å for grossular, for example, and this yields n = 1.726(as compared with 1.731 shown in Table 2). However, these differences are minor and have little influence on the assigned values for R. When one recalls that at least 70 per cent of the contribution to the optical properties of such orthosilicates is the result of the characteristics of the packing of the oxygen atoms, it becomes apparent that reasonable ionic refractivities can be deduced without dependency upon precision measurements of either n or a for any particular composition. It is essential. however, that the errors be random rather than systematic.

Applications to Analyzed Garnets

The most severe test of the newly assigned R values should arise from

examples high in pyrope and uvarovite, but it is here, unfortunately, that a dearth of experimental data is to be found.

Table 3 shows the detailed calculations for a Finnish uvarovite-grossular reported by von Knorring (1951). My measurement on analyzed

Oxides	Wt. (%)	Mol. ratios	Ratios of atoms	Ratios of charges (+)	Charges of cations $(\sum = 192)$	Number of cations	N·R
SiO ₂	38.40	0.6390	63,90	255.6	97.1	24.3	4.4
Al ₂ Õ ₃	10.77	0.1056	21.12	63.4	24.1	8.0	5.2
Cr ₂ O ₈	14.97	0.0985	19.70	59.1	22.4	7.5	39.0
Fe ₂ O ₃	1.89	0.0118	2.36	7.1	2.7	0.9	5.3
MnO	n.d.	. <u> </u>					
MgO	0.48	0.0119	1.19	2.4	0.9	0.5	0.2
CaO	33.08	0.5899	58.99	118.0	44.8	22.4	46.6
ign.	0.40					oxygen	336.0
					<u> </u>		
	99.99			505.6	192.0		436.7

 TABLE 3. CALCULATION OF THE REFRINGENCE OF UVAROVITE-GROSSULAR FROM

 LUIKONLAHTI, FINLAND (ANALYST: O. VON KNORRING)

material (supplied by von Knorring) is $a = 11.928 \pm 0.006$ Å. For some unexplained reason this measurement is not in good agreement with von Knorring's measurement (a = 11.892 Å), but his reputation as a chemical analyst is most outstanding, so this garnet should afford a reasonable example.

The sum of the products $(N \cdot R)$ (last column, Table 3) is 436.7, which yields a calculated n = 1.800; von Knorring reported 1.798 to 1.804. (Using his unit-cell dimension the calculated n = 1.810.) It is noticeable that the calculation yields 24.3 rather than 24 silicon atoms within the unit cell; the contribution of 0.3 of a silicon atom $(R_{\rm SI} = 0.18)$, however, is so small as to produce no change in the calculated n. Also, the ignition loss (0.40) has been disregarded.

My determination gave $a = 11.530 \pm 0.002$ Å for a sample of Kb1 (supplied by von Knorring) as compared with a = 11.528 reported by Nixon, von Knorring & Rooke (1963). Direct calculation of n (by the method illustrated in Table 3) for this pyrope from Kimberley yields n = 1.742, whereas the observed n = 1.748. (The analysis reports 0.27 per cent of TiO₂; 6.0 was estimated as the approximate ionic refractivity for Ti.)

The refractive indexes can be calculated from the molecular percentages of the end-member garnets. This is an indirect method insofar as it disregards such constituents as TiO_2 and H_2O , and circumvents the use of the unit-cell dimension. Tables 4 and 5 are based on such indirect calculations.

Identification*	GR	AN	AL	ΡY	SP	UV	Observed	Calculated	Difference
L-A	41.4	3.4	12.4	1	42.8	1	1.780	1.781	+0.001
L-B	54.3	1.9	9.9	I	34.0	I	1.773	1.772	-0.001
r-c	56.1	7.2	11.4	[25.3	[1.773	1.773	0
P-1943	5.7	l	69.6	21.2	3.5		1.806	1.802	-0.004
P-1938	0.8	0.8	69.3	0.6	28.5	1	1.824	1.824	0
N-E15	4.6	5.3	15.0	73.3	0.5	1.3	1.749	1.751	+0.002
N-Kbl	12.3	l	15.3	71.0	0.6	0.8	1.748	1.742	-0.006
N-A80	12.4	Ĭ	16.1	69.8	0.4	1.3	1.734	1.744	+0.010
N-E16	80 90	4.8	28.5	57.0	0.5	0.4	1.753	1.764	+0.011
N-E1	4.7	0.1	14.3	72.1	0.6	8.2	1.749	1.752	+0.003
N-E3	2.7	4.2	9.6	77.5	0.3	5.7	1.747	1.749	+0.002
N-E11	3.1	3.3	13.9	73.7	0.6	5.4	1.743	1.752	+0.009
N-A79	1.3	2.1	13.6	74.2	0.6	8.2	1.746	1.754	+0.008
N-G12	5.9	1.0	16.4	70.6	0.7	5.4	1.746	1.751	+0.005
N-E10		3.3	12.4	61.7	1.2	2.8	1.758	1.753	-0.005
N-E7	6.8	3.6	55.2	33.5	0.9		1.784	1.790	+0.006
N-E4	13.6	4.5	36.6	44.6	0.7	I	1.761	1.772	+0.011
*The prefix letter designations are tho because of a non-ga	s indicate re se of the orig	ferences: L final author ent; the cal	(Lee, 1962), s, and all mol culated <i>n</i> has	P (Pabst, 1 lecular perce	943 or 1938), ntages are th ted according	, and N (N ose calcula gly.)	ixon, von Kn ted by them. (orring & Rooke (The total for N	1963). Other E10 is 81.4%

Examination of Table 4 might suggest, on first consideration, that the new n for pyrope is too high, inasmuch as many of the specimens with the N prefix show + differences and all (except the last two) are primarily pyrope. The observed values do not appear to be completely consistent, however. Garnets N-Kb1 and N-A80 are closely similar in composition, but show a difference of 0.014 for their observed values of n, whereas the calculated difference (0.002) is much closer to what would be expected. Similarly N-E4 contains about three times as much AL as N-E10 (PY being proportionally less), but the observed difference for n is merely 0.003 whereas the calculated difference is 0.019. Again, the calculated difference is closer to expectation.

The GR-SP garnets (prefix L, Table 4) give excellent correspondence between calculated and observed values as does the AL-SP (P-1938).

Table 5 contains the 57 calculations made by Fleischer (1937); it compares his values with the observed values and with the calculated values obtained from the new end-member indexes. The last two columns indicate the qualitative departures from observed values for his calculation and for mine: + meaning a higher calculated value and zero meaning a departure of 0.001 or less.

Certain anomalies appear for specimens numbered 10, 12, 13, 26, 27, 35, and 52, all of which fall in the ++ category and show observed values considerably below either calculated value. Some of these garnets may contain water that was not reported in the analyses, and which might account for the low observed indexes inasmuch as the index of a hydrogarnet is much lower than that of its anhydrous analogue (see Table 2).

Those numbered 54, 56 and 57 fall in the double minus class. No. 56 is reported as containing 1.45 per cent ZnO and 0.80 per cent H₂O. Nos. 54 and 57 had reported *n* values 1.88 and 1.92, respectively. Although No. 57 appears to be andradite, its index of refraction suggests that a significant amount of TiO₂ might be present inasmuch as 1.92 is significantly above the highest value that has ever been assigned to any of the six end-member garnets (1.895 for AN, by Ford).

In general the newly calculated values for n tend to be slightly higher, particularly for almandines, spessartines and pyropes. A comment by Frietsch (1957) is interesting: "... the agreement between the observed and calculated values of the refractive indices is better for spessartite and almandite than for grossularite and andradite. The calculated values for the first-mentioned are too low; for the latter they are too high." It will be noted that the new values (Table 2) are such as to improve both of these situations.

The calculated density for uvarovite (based on a = 12.012 Å) is 3.835, as compared with Fleischer's value 3.775. It should be noted that Skinner

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ARNETS	This Work	1.733	1.735	1.752	1.743	1.757	1.751	1.752	1.747	1.762	1.777	1.770	1.771	1.792	1.787	1.787	1.792	1.791	1.793	1.792	1.797	1.791	1.807	1.811	1.803	1.797	1.803	1.809	1.807	1.810
DNS OF 57 G	Obsd.	1.734	1.737	1.748	1.750	1.750	1.750	1.752	1.756	1.756	1.758	1.766	1.766	1.777	1.782	1.785	1.786	1.787	1.787	1.789	1.791	1.792	1.794	1.794	1.796	1.797	1.797	1.797	1.800	1.804
COMPOSITIG	Fleischer- Ford	1.737	1.740	1.756	1.745	1.746	1.755	1.756	1.749	1.753	1.767	1.763	1.771	1.794	1.781	1.783	1.786	1.789	1.791	1.786	1.794	1.788	1.802	1.805	1.797	1.794	1.802	1.805	1.800	1.805
NDEXES, ANI	UV J	l	0.39	I	ļ	0.61	1	[1	I]	!	1	[ł	[[l]	l				[[1	[
EFRACTIVE I	SP	0.32	I	0.89	0.71	0.68	[0.32	0.14	0.72	0.35	1.19	1.50	0.92	3.04	2.58	1.72	0.10	4.15	1.39	1.60	5.09	40.16	83.85	89.77	3.88	17.76	1.39	89.12	4.32
DBSERVED R	ΡΥ	1.02	[0.72	1.31	59.83	1	1.07	7.32	48.72	52.24	43.78	43.16	7.51	27.44	18.05	25.13	15.53	13.99	32.07	16.09	15.29	6.95	0.85	1.02	15.69	1.61	19.80	1.98	20.37
JLATED AND	AL	2.06	0.59	3.63	8.07	27.31	1	0.52	3.82	28.89	41.66	36.53	40.93	45.13	55.35	54.87	61.08	50.32	49.12	52.46	57.56	54.17	41.12	10.68	4.14	63.99	56.51	61.10	0.53	73.20
BLE 5. CALCI	AN	1	2.27	10.80	2.03	1.26	12.71	12.88	7.88	2.94	5.75	3.33	5.93	11.24	1	1	1	6.77	6.46	6.22	5.18	1.50	2.61	3.26	[1	1.22	10.76	1.07	2.11
TAJ	GR	96.60	96.75	83.96	87.88	10.31	87.29	85.21	80.85	18.74	1	15.17	8.43	35.19	14.17	24.50	12.07	27.29	26.28	7.86	19.58	23.96	9.16	1.36	5.07	16.44	22.89	6.95	1.30	1
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This Work	1.807	1.8.1	1.811	1,813	1 814	1 893	1 810	1 214	1 820	1.810	1.815	1 817	1.817	1.817	1.825	1.814	1.821	1.819	1.820	1 826	1.820	1.820	1.862	1 855	1 854	1 880	1 847	1.876	resumably re-
Obsd.	1.805	1.805	1.806	1.808	1 808	1 808	1 810	1 811	1 812	1.813	1.813	1,813	1.814	1.815	1.816	1.817	1.817	1.818	1.818	1.818	1.819	1.821	1.847	1 855	1 88	1 887	1.80	1.92	O. Water, n
Fleischer- Ford	1.802	1.806	1.808	1.805	1 810	1 821	1 807	1 800	1.816	1.804	1.809	1.812	1.812	1.813	1.822	1.809	1.817	1.815	1.817	1.823	1.817	1.816	1.864	1.857	1.861	1 888	1.851	1.884	e Fe ₀ 0, as Fe
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SP	76.92	61.60	5.41	4.62	38.82	1.67	2 20	64.29	56.72	79.26	69.35	5.51	52.54	37.48	7.42	58.67	19.97	32.83	19.89	16.76	4.51	15.63	0.07		2.06	0.05	13.87	2.69	Fleischer cal
ΡY	2.23	l	17.50	11.30	1.91	2.85	10.04	1.20		2.03	0.59	14.25	1.21	3.02	3.50	3.36	5.21	4.19	4.97	3.89	8.76	7.90	0.17	2.05		3.36	5.30	2.49	se for which
AL	16.89	32.86	74.89	73.74	52.57	90.43	73.21	33.84	37.86	15.15	29.24	77.36	45.44	57.42	83.82	36.58	74.08	62.98	74.12	74.84	85.84	75.00		[	7.19	1.36	I	[	erisk are tho
AN	0.89	I	2.11	1		[	1	I	5.42	2.29	0.82	2.88	[	1	2.51	1.39	[	I	1	4.52	[	1.48	7.52	1.27	73.70	95.23	68.05	92.25	with an ast
GR	3.07	5.54	1	10.61	6.70	5.05	8.64	0.67	ļ	1.26	[	I	0.82	2.08	2.74		0.74	[	1.01	].	0.89	[	5.20	7.32	17.05	1	12.78	2.56	lyses marked
	30	31	32*	ŝ	34*	35	36*	37	38*	39	<del>4</del> 0	$41^{*}$	42*	43*	44	45*	46*	47	48*	49	50 <b>*</b>	51	52	53	54	55	56	57	*Ana

repracing SIU4 as ŝ מוכו, הו H4O4, has not been taken into account for any of these analyses (see text).

APPENDIX

GARNETS
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$n^{2}-1$
VALUES OF (
TABLE 6.

					.						
	$\frac{n^2-1}{n^2+2}$	u	$\frac{n^2-1}{n^2+2}$								
	39497	1 750	40741	1.780	.41955	1.810	.43140	1.840	.44296	1.870	.45424
~	39581	2	40823	2	.42035	5	.43217	57	.44372	2	.45498
ı ج <del>ا</del>	.39665	4	40904	4	.42115	4	.43296	4	.44448	4	.45572
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	39915	1.760	41149	1.790	42353	1.820	.43528	1.850	.44675	1.880	.45794
5	39998	0	41229	2	42433	5	.43606	7	.44750	7	.45867
4	40081	4	.41311	4	.42511	4	.43683	4	.44826	4	.45941
i co	40164	9	41393	9	.42590	9	.43760	9	.44901	9	.46014
) oc	40246	00	.41473	8	.42669	×	.43837	œ	.44976	×	.46087
	40329	1.770	41554	1.800	.42748	1.830	.43914	1.860	.45051	1.890	.46160
2	40412	2	41634	57	.42827	53	.43990	5	.45125	2	.46234
. <del>م</del>	40494	4	.41715	₹	.42905	4	.44067	4	.45200	4	.46306
5	40576	ų	41795	9	.42983	9	.44143	9	.45275	9	.46379
00	40659	) oc	.41875	00	.43062	æ	.44219	×	.45349	×	.46452

gives the density for pyrope as 3.582, which is erroneous if a = 11.459 Å. The correct density for pyrope (based on a = 11.459 Å) is 3.559.

#### CONCLUSIONS

The Lorentz-Lorenz relation appears to be applicable with sufficient reliability to permit calculation of the refringences of the six common end-member garnets. The n values of Ford (1915) have been modified on this basis (Table 2).

Empirical data of various sorts can be used in order to extend the values of ionic refractivities in connection with such calculations; commensurate values for Si, Al, Fe''', Cr''', and H₄ (for hydrogarnets) are supplied (Table 1). Values for Ca and Mg have been modified.

Some situations where the calculated n exceeds the observed n are probably best explained as the result of replacement of SiO₄ by H₄O₄, inasmuch as the indexes of hydrogarnets are appreciably lower than those of the corresponding anhydrous analogues. All chemical analyses of garnets should include a determination of water.

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