PHYSICAL PROPERTIES OF END-MEMBERS OF THE GARNET GROUP*

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ABSTRACT

Unit cell size (a_0), molar volume (V_m), density (ρ), refractive index (n), and the linear (d_a) and volume (d_v) coefficients of thermal expansion from 298° to 1023° K. have been determined for synthetic pure end-member garnets. The following values were found for a_0, V_m, ρ, and n at 298.16° K. (25° C.):

	a_0, Å	V_m, cc./mole.	ρ, gm./cc.	n (Na)
Grossularite	11.851	125.31	3.594	1.734
Andradite	12.048	131.69	3.859	1.887
Almandite	11.526	115.28	4.318	1.830
Spessartite	11.621	118.15	4.190	1.800
Pyrope	11.459	113.29	3.582	1.714

The linear and volume coefficients of thermal expansion have been determined as polynomial functions of temperature. The constants of the equations are given in Table 10 in the body of the paper.

INTRODUCTION

The physical properties of the end-members of the garnet group have been predicted by Ford (1915) and later revised by Fleischer (1937). The predictions were made by extrapolating the properties of natural garnet solid solutions back to the pure end-members. Since insufficient variables have been measured to completely specify the compositions, it is desirable that the predicted properties of the pure end-members be checked.

For the present study, pure synthetic end-member garnets were available. The Norton Company supplied pyrope, spessartite and andradite, grown at unstated temperatures and pressures. The garnets were synthesized from the pure component oxides. Dr. H. S. Yoder of the Geophysical Laboratory, Carnegie Institute, supplied specimens of almandite grown at 10,000 bars and 800° C., and grossularite grown at 9,000 bars and 970° C. To both of these suppliers thanks are due for their ready cooperation and help.

Table 1 compares the values of the unit cell size (a_0), of the pure end-members with the values obtained by Fleischer (1937) and Stockwell (1927). The values of a_0 determined by Fleischer and Stockwell have been corrected from the old kX units to Ångstrom units, using Bragg's (1947) recommended conversion factor. Both Fleischer and Stockwell

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TABLE 1. VALUES OF a_0 FOR THE GARNETS AT 25° C.

	Fleischer a_0, Å	Stockwell a_0, Å	Skinner a_0, Å
Grossularite	11.864	11.864	11.851
Andradite	12.069	12.064	12.048
Almandite	11.518	11.516	11.526
Spessartite	11.613	11.600	11.621
Pyrope	11.463	11.453	11.459

obtained their values by extrapolation from garnets of mixed composition. Stockwell's values were determined from his own measurements, while Fleischer's values were derived from published data on the garnets. The agreements are reasonably good, except for andradite. Fleischer's value for andradite is 0.021 Å larger than the present author's value. It is interesting to note that the measured value of a_0 for a garnet containing ing 85% of the andradite end-member used by Fleischer in his work was 0.033 Å lower than the computed value from his extrapolated pure end-member values. For the only other high andradite garnet quoted by Fleischer, on which a_0 was determined, the agreement between measurement and prediction is exact. Considered as a group, the measurements show surprisingly good agreement with the extrapolated values.

Refractive indices were measured by matching the refractive index of the sample with that of an immersion liquid, then finding the refractive index of the liquid by the minimum deviation method. The only estimates available for the refractive indices were those of Ford (1915) who obtained them by extrapolation. They are compared with the values obtained in the present work in Table 2. The agreement between the two sets of data is excellent except for pyrope and andradite. A synthetic pyrope grown by Dr. E. C. Robertson at 950±10° C. and 20,000±1,000 bars had the same index as the sample used in the present study. It was not possible to get an independent check on the index of andradite. The discrepancy is probably due to the method of extrapolation used by Ford, since he used only two variables in a five component system.

TABLE 2. REFRACTIVE INDICES OF GARNETS IN SODIUM LIGHT AT 25° C.

	Ford	Skinner	Difference
Grossularite	1.735	1.734±0.002	−0.001
Andradite	1.895	1.887±0.002	−0.008
Almandite	1.830	1.830±0.002	0.000
Spessartite	1.800	1.800±0.002	0.000
Pyrope	1.705	1.714±0.002	+0.009

TABLE 3. DENSITIES OF GARNETS AT 25° C.

	Fleischer, measured S.G.	Skinner, calculated density, gm./cc.	Difference
Grossularite	3.530	3.594 ± 0.001	$+0.064$
Andradite	3.835	3.859 ± 0.001	$+0.024$
Almandite	4.325	4.318 ± 0.001	-0.007
Spessartite	4.180	4.190 ± 0.001	$+0.010$
Pyrope	3.510	3.582 ± 0.001	$+0.072$

Due to the fine grained nature of the samples direct measurements of the specific gravity could only be made for pyrope. The densities quoted are those determined from the volume of the unit cell, using Wichers' (1952) atomic weights. The specific gravity of pyrope was determined by selecting a 15 mg. sample of pure single crystals and weighing them in a metal basket on the Berman balance. Toluene was the immersion liquid used. The accuracy of the measurement is not good, since surface effects are large in the basket method. The measured specific gravity at 25° C. is 3.57 ± 0.03, and is perhaps fortuitously close to the value computed from the unit cell. The only good measured values available for comparison are those quoted by Fleischer (1937), and again these values were obtained by extrapolation from measurements on natural compound garnets. The big differences are difficult to explain. The measured specific gravity of pure pyrope on the Berman balance gives a much better check with the calculated density than does Fleischer's value. The big difference between the measured and calculated values of grossularite could not be checked.

The molar volumes (V_m) of the pure end-member garnets have not been previously determined. Table 4 gives the molar volumes at 298.16° K. (25° C.) and 1 atmosphere, with the unit cell sizes used to calculate them. Birge's (1944) value of $(6.02338 \pm 0.00043) \times 10^{23}$ mole^{-1} for Avogadro's number was used in the calculations. The probable accuracy of measurement for the values of a_0 is given as 0.001 Å. The precision of measurement is 0.0005 Å, but due to possible errors in the method of determina-

TABLE 4. UNIT CELL SIZE AND MOLAR VOLUMES OF THE GARNETS AT 298.16° K. AND 1 ATMOSPHERE

	a_0, Å	V_m, cc./mole.
Grossularite	11.851 ± 0.001	125.31 ± 0.03
Andradite	12.048 ± 0.001	131.69 ± 0.03
Almandite	11.526 ± 0.001	115.28 ± 0.03
Spessartite	11.621 ± 0.001	118.15 ± 0.03
Pyrope	11.459 ± 0.001	113.29 ± 0.03

tion it is not felt that the accuracy can be stated any closer than 0.001 Å (Skinner, 1955).

The presence of any $(OH)_4$ replacing (SiO_4) in a garnet would probably seriously alter the physical properties, so all possible care was taken to determine whether or not any $(OH)_4$ was present. The hydrogrossularites have a much lower density and refractive index than grossularite, according to Pabst (1932, 1942). It is very probable that the $(OH)_4$ radical in the other garnet molecules would have the same effect as in grossularite, and lower the refractive index and density. Belynakin and Petrov (1941) showed that a strong endothermic reaction occurred at 650° C. when the hydrogrossularite hibschite was heated. The effect is apparently not reversible and they suggest that the transition is "from the original crystalline phase into an amorphous phase." Their heating curves also show exothermic reactions at 870° and 940° C. Natural grossularites, containing no water, do not show any of these reactions. It is very probable that the endothermic reaction at 650° C. corresponds to a breakdown of the hibschite and a loss of water. The garnets used in the present study were individually heated to 750° and 850° for varying periods of time. If the garnets contained some of the hydrogarnet molecules it was expected that the indices of refraction would be increased after the heating, corresponding to a destruction of the hydrogarnet. No such change was found. In all cases the index of refraction was the same before and after heating. It was concluded that the synthetic garnets used do not contain any $(OH)_4$ groups in their structure.

The unit cell size (a_0) and molar volume (V_m) of each garnet was determined at temperatures up to 750° C. in a special 16 cm. diameter x-ray powder camera (Skinner 1955). From these data the linear and volume thermal expansion coefficients were determined as a function of temperature from 298° K. to 1023° K. The coefficients (Table 10) are given in the form,

$$\alpha_a = \frac{1}{a_s}\left(\frac{\partial a}{\partial T}\right)_P = b + cT - dT^{-2}$$

and

$$\alpha_v = \frac{1}{V_{ms}}\left(\frac{\partial V_m}{\partial T}\right)_P = b_1 + c_1T - d_1T^{-2}$$

where

α_a and α_v are the linear and volume thermal expansion coefficients respectively.
a_0 and a_s are the unit cell sizes at T° K. and 298.16° K. respectively.
V_m and V_{ms} are the molar volumes at T° K. and 298.16° K. respectively.
b, c, d and b_1, c_1, d_1 are constants of the equations.
P is a constant pressure of 1 atmosphere.
T is the temperature in degrees Kelvin.

TABLE 5. GROSSULARITE: MEASURED VALUES OF a_0 AND CALCULATED VALUES OF V_m AT DIFFERENT TEMPERATURES

Temperature, °C.	a_0, Å	V_m, cc./mole
19.0	11.8503	125.297
21.4	11.8504	125.301
25.0	11.8507	125.309
57.2	11.8529	125.380
94.1	11.8556	125.466
108.8	11.8566	125.497
185.5	11.8626	125.686
277.7	11.8705	125.938
387.9	11.8805	126.257
389.9	11.8807	126.265
480.1	11.8893	126.537
589.3	11.8996	126.866
707.7	11.9123	127.272

Since it is frequently desired to determine the unit cell size or the molar volume at a particular temperature the constants of integration for the above equations are also given. When the equations above are integrated, functions of the form below are obtained.

$$\frac{\Delta V_m}{V_{ms}} = I + b_1T + \tfrac{1}{2}c_1T^2 + d_1T^{-1}$$

where

ΔV_m is the total difference in molar volume from 298.16° K. to T° K.
I is the constant of integration.
T is the temperature in degrees Kelvin.

TABLE 6. ANDRADITE: MEASURED VALUES OF a_0 AND CALCULATED VALUES OF V_m AT DIFFERENT TEMPERATURES

Temperature, ° C.	a_0, Å	V_m, cc./mole
21.4	12.0481	131.676
25.0	12.0484	131.686
59.0	12.0513	131.781
109.1	12.0558	131.928
149.3	12.0593	132.043
208.9	12.0648	132.224
304.2	12.0740	132.527
349.0	12.0783	132.669
427.1	12.0861	132.926
501.8	12.0937	133.176
589.2	12.1032	133.491
629.9	12.1082	133.656
690.0	12.1144	133.862

TABLE 7. ALMANDITE: MEASURED VALUES OF a_0 AND CALCULATED VALUES OF V_m AT DIFFERENT TEMPERATURES

Temperature, ° C.	a_0, Å	V_m, cc./mole
21.5	11.5256	115.276
25.0	11.5258	115.283
50.5	11.5274	115.330
108.6	11.5314	115.451
146.9	11.5342	115.535
205.4	11.5388	115.673
243.8	11.5421	115.782
321.0	11.5490	115.980
361.6	11.5528	116.095
401.0	11.5565	116.206
455.5	11.5616	116.360
489.2	11.5653	116.472
543.2	11.5703	116.623
581.3	11.5740	116.735
644.0	11.5813	116.956
709.3	11.5885	117.174
771.0	11.5955	117.387

The details of measurement and method of determining the various parameters in the above equations are described by Skinner (1955).

Tables 5, 6, 7, 8, and 9 show the measured values of a_0 and the computed values of V at different temperatures. All measurements were made with both rising and lowering temperatures to detect any irreversible changes.

TABLE 8. SPESSARTITE: MEASURED VALUES OF a_0 AND CALCULATED VALUES OF V_m AT DIFFERENT TEMPERATURES

Temperature, ° C.	a_0, Å	V_m, cc./mole
18.7	11.6200	118.132
19.3	11.6203	118.141
25.0	11.6207	118.154
68.5	11.6242	118.260
129.7	11.6292	118.413
232.5	11.6390	118.713
299.3	11.6465	118.942
394.2	11.6555	119.218
443.5	11.6600	119.356
501.0	11.6675	119.587
557.5	11.6745	119.802
623.0	11.6825	120.049
702.0	11.6915	120.314

TABLE 9. PYROPE: MEASURED VALUES OF a_0 AND CALCULATED VALUES OF V_m AT DIFFERENT TEMPERATURES

Temperature, ° C.	a_0, Å	V_m, cc./mole
11.0	11.4578	113.254
25.0	11.4590	113.290
27.7	11.4592	113.296
56.0	11.4612	113.358
89.6	11.4642	113.444
122.3	11.4670	113.527
153.9	11.4697	113.608
195.5	11.4736	113.723
247.1	11.4780	113.854
270.5	11.4805	113.929
289.0	11.4822	113.979
328.1	11.4859	114.089
395.9	11.4924	114.283
441.0	11.4973	114.430
524.2	11.5050	114.660
597.1	11.5138	114.923
629.5	11.5163	114.997
698.5	11.5240	115.228
758.0	11.5305	115.422

The volume thermal expansions of the garnet group are shown in Fig. 1. Pyrope, grossularite and andradite are close to each other. Spessartite, though having a larger expansion than pyrope, grossularite or andradite, is essentially similar in behaviour in that the curves are roughly parallel above 200° C. Almandite is anomalous and the curve does not flatten out as with the other garnets. The effect is completely reversible and cannot be ascribed to strains in the structure being released as the temperature rises or to oxidation effects.

Insufficient data are available on the specific heats of the garnets to determine the characteristic temperatures. The compressibilities of almandite and grossularite have been determined by Adams and Gibson (1929), and of pyrope and andradite by Bridgman (1928). The only data on the elastic constants of the garnets are those by Ramachandra Rao (1945) who determined s_{11}, s_{12}, s_{44} for seven natural iron-bearing garnets.

Using Rao's data for a garnet containing 80% of the almandite end-member, and the molecular weight of pure almandite, a characteristic temperature of 350° K. was obtained for almandite. Since the compressibility alone is insufficient for determining the characteristic temperature, and other data on the elastic constants of the pure end-member garnets are not available, an assumption is necessary to calculate the characteristic temperature. The assumption used was that the ratio of the velocity

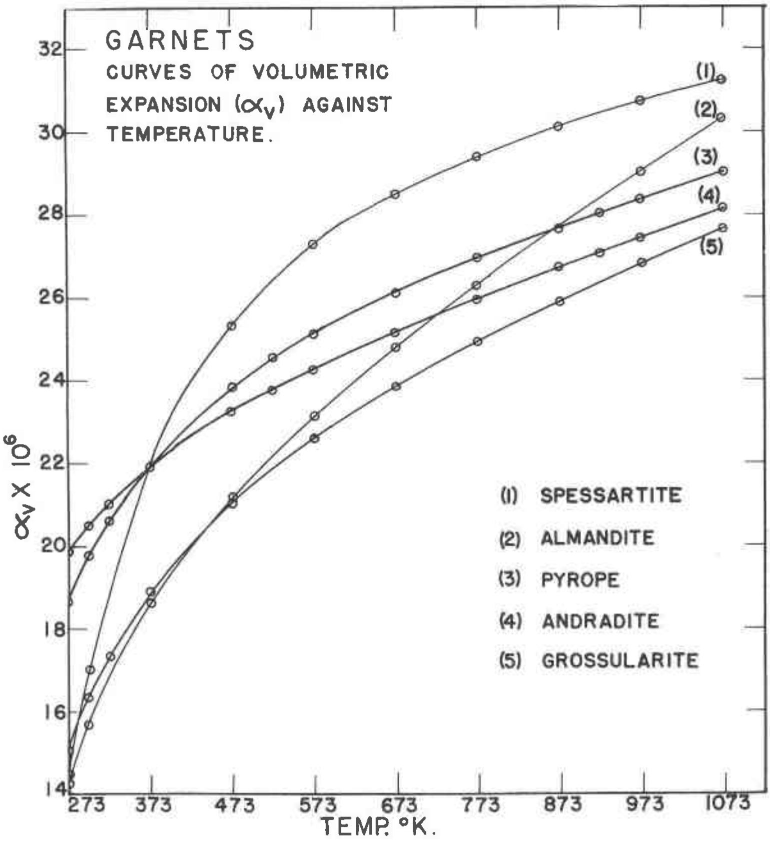

FIG. 1

TABLE 10. PARAMETERS OF FUNCTIONS GIVING THE LINEAR AND VOLUME COEFFICIENTS OF THERMAL EXPANSION

Substance	Function	Parameters				Accuracy	Temp. range
		b	*c*	*d*	*I*		
		$\times 10^{-5}$	$\times 10^{-9}$		$\times 10^{-3}$		298° K. to
Grossularite	α_a	0.6502	2.697	0.1658	−2.6137	0.3%	973° K.
	α_v	1.951	8.089	0.4972	−7.8406	0.5%	973° K.
Andradite	α_a	0.7010	2.280	0.07468	−2.4407	0.2%	973° K.
	α_v	2.103	6.839	0.2245	−7.3238	0.5%	973° K.
Almandite	α_a	0.5922	4.046	0.1690	−2.5115	0.3%	1023° K.
	α_v	1.776	12.14	0.5071	−7.5347	0.6%	1023° K.
Spessartite	α_a	0.9758	0.9087	0.3856	−4.2422	0.3%	973° K.
	α_v	2.927	2.726	1.156	−12.723	0.6%	973° K.
Byrope	α_a	0.7703	1.985	0.1513	−2.8912	0.3%	1023° K.
	α_v	2.311	5.956	0.4538	−8.6736	0.4%	1023° K.

of the dilational waves (V_p) to the velocity of the rotational waves (V_s) is 1.7 (Birch, 1952, p. 250). With this assumption and the compressibilities of Adams and Gibson (1929) and Bridgman (1928), the characteristic temperatures of andradite, grossularite and pyrope were determined as 270°, 300° and 320° K. respectively. The thermal expansion curves of the garnets (Fig. 1) suggest that these values are too low and that characteristic temperatures between 400° and 550° K. are more reasonable.

REFERENCES

Adams, L. H., and Gibson, R. E. (1929), The elastic properties of certain basic rocks and minerals: *Proc. Nat. Acad. Sci.*, **15**, 713–724.

Belyankin, D. S., and Petrov, V. P. (1941), The grossularoid group (hibschite, plazolite): *Am. Mineral.*, **26**, 450–453.

Birch, F. (1952), Elasticity and constitution of the earth's interior: *Jour. of Geophysics Research*, **57**, 227–286.

Birge, B. T. (1945), The 1944 values of certain atomic constants with particular reference to the electronic charge: *Am. Jour. Phys.*, **13**, 63–75.

Bragg, W. L. (1947), Letter to the editor. *Am. Mineral.*, **32**, 592.

Bridgman, P. W. (1928), The linear compressibility of thirteen natural crystals: *Am. Jour. Sci.*, **15**, 287–296.

Fleischer, M. H. (1937), The relation between chemical composition and physical properties in the garnet group: *Am. Mineral.*, **22**, 751–759.

Ford, W. E. (1915), A study of the relations existing between the chemical, optical and other properties of the garnet group: *Am. Jour. Sci.*, **40**, 33–49.

Pabst, A. (1937), The crystal structure of plazolite: *Am. Mineral.*, **22**, 861–868.

——— (1942), Re-examination of hibschite: *Am. Mineral.*, **27**, 783–792.

Ramachandra Rao, B. (1945), Elastic constants of garnets: *Proc. Indian Acad. Sci.*, **22**, 194–198.

Skinner, B. J. (1955), A new x-ray heating camera and the thermal expansions of thoria, periclase and diamond: In press.

Stockwell, C. H. (1927), An x-ray study of the garnet group: *Am. Mineral*, **12**, 327–344.

Wichers, E. (1952), Report of the committee on atomic weights of the American Chemical Society: *Jour. Am. Chem. Soc.*, **74**, 2447–2450.

Manuscript received May 25, 1955.