

Dielectric constants of silicate garnets and the oxide additivity rule

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ABSTRACT

The dielectric constants and dielectric loss values of a series of garnets were measured at 1 MHz using a two-terminal method and empirically determined edge corrections. The results are five intermediate pyrope-almandine samples, $\kappa' = 11.96$ – 12.35 ; spessartine, $\kappa' = 11.65$; two andradite samples, $\kappa' = 10.53$ – 10.59 ; and three grossular samples, $\kappa' = 8.53$ – 8.81 .

The deviations of measured dielectric polarizabilities as determined using the Clausius-Mosotti equation from those calculated using the sum of oxide polarizabilities according to $\alpha_D(M_2M'X_4) = 2\alpha_D(MX) + \alpha_D(M'X_2)$ is $+5.0$ to $+6.5\%$ for the pyrope-almandine samples, $+1.9\%$ for spessartine, -2.3% for the andradite samples, and -5.5 to -7.0% for grossular. These deviations from additivity are believed to result from garnet structural constraints leading to “rattling” Mg ions and “compressed” Ca ions.

INTRODUCTION

Dielectric polarizability, α_D , is related to the measured dielectric constant, κ' , by the Clausius-Mosotti equation:

$$\alpha_D = 1/b[(V_m)(\kappa' - 1)/(\kappa' + 2)] \quad (1)$$

where V_m is the molar volume in \AA^3 , b is assumed to be $4\pi/3$, and κ' , the real part of the complex dielectric constant, is measured in the range 1 KHz to 10 MHz (Roberts, 1950, 1951). The dielectric polarizability includes both ionic and electronic components. The electronic polarizability, α_e , is related to the refractive index, n , by the Lorenz-Lorentz equation (Lorentz, 1880; Lorenz, 1880):

$$\alpha_e = 1/b[(V_m)(n^2 - 1)/(n^2 + 2)]. \quad (2)$$

Assumption of point dipole ions and cubic symmetry leads to $b = 4\pi/3$ (Tessman et al., 1953; Kip, 1962; Anderson, 1974; Arndt and Hummel, 1988). Introduction of overlapping electron distribution (covalency) leads to $b = 1.2$ – 1.3 for silicates (Arndt and Hummel, 1988; Marler, 1988). The Clausius-Mosotti equation is strictly valid only for compounds in which the molecule or ion has cubic symmetry (Szigeti, 1949; Bosman and Havinga, 1963; Duffin, 1980; Kip, 1962; Megaw, 1957; Roberts, 1949, 1950, 1951; Dunmur, 1972) but is approximately valid for a number of noncubic crystals (Roberts, 1949, 1951; Lasaga and Cygan, 1982).

The concept of additivity of molecular polarizabilities, whereby the molecular polarizability of a complex substance can be broken up into the molecular polarizabilities of simpler substances according to

$$\alpha_D(M_2M'X_4) = 2\alpha_D(MX) + \alpha_D(M'X_2) \quad (3)$$

has been discussed by Heydweiller (1920), Cheng (1940), Jonker and Van Santen (1947), Roberts (1949, 1950, 1951), and Lasaga and Cygan (1982). This rule has been applied to both electronic and dielectric polarizabilities (Narayana Rao, 1949; Lasaga and Cygan, 1982; Arndt and Hummel, 1988), but in this paper we discuss the rule only insofar as it applies to dielectric polarizabilities. Earlier work (Jonker and Van Santen, 1947; Narayana Rao, 1949; Roberts, 1951; Lasaga and Cygan, 1982) found the oxide additivity rule to be accurate to 5–10%. However, our recent studies on Y and RE aluminates, chrysoberyl, spinel, olivine-type silicates, phenacite, zircon, and a group of beryllates, borates, and phosphates (Shannon et al., 1989, 1990, 1991a, 1991b, 1992; Shannon and Subramanian, 1989; Shannon, 1991; Subramanian and Shannon, 1989) show that these compounds form a class of well-behaved oxides whose dielectric polarizabilities follow the oxide additivity rule to ± 0.5 – 1.5% .

The purpose of this paper is to determine accurately the 1-MHz dielectric constants of a variety of silicate garnets and to evaluate the validity of the oxide additivity rule in these minerals.

EXPERIMENTAL

The samples were all gem-quality crystals. The grossular, andradite, and spessartine are relatively pure. We were unable to obtain end-member pyrope or almandine specimens suitable for dielectric measurements. All samples labeled as pyrope contain significant quantities of Ca; sample Py5, in addition to Ca, contains considerable Mn. The source and color of the samples are listed in Table 1.

TABLE 1. Electron microprobe analyses, cell dimensions, colors, and sources of garnets

	Gr1	Gr2	Gr3	An1	An2	Py1	Py2	Py3	Py4	Py5
Na ₂ O	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00
MgO	0.03	0.28	0.04	0.18	0.17	19.57	18.08	15.25	10.30	11.18
Al ₂ O ₃	22.26	22.21	22.47	0.09	0.11	23.63	23.16	23.39	22.60	22.60
SiO ₂	39.61	39.55	39.30	35.31	35.46	42.60	41.11	41.14	40.75	40.32
CaO	36.07	37.50	37.24	33.09	33.20	5.73	1.08	2.43	2.56	4.12
TiO ₂	0.54	0.53	0.02	0.05	0.01	0.08	0.00	0.02	0.05	0.03
V ₂ O ₅	0.13	0.01	0.10	0.00	0.01	0.02	na	0.02	—	0.28
Cr ₂ O ₃	0.02	0.00	0.00	0.00	0.00	0.61	0.00	0.00	—	0.24
MnO	0.51	0.14	0.15	0.01	0.03	0.28	0.19	0.40	0.54	8.91
FeO	1.27	0.15	0.51	—	—	9.08	16.37	19.48	21.88	14.51
Fe ₂ O ₃	—	—	—	31.24	31.55	—	—	—	—	—
Total	100.44	100.39	99.85	99.98	100.53	101.61	102.46	102.14	98.68	102.3
<i>a</i> , Å	11.8480(4)	11.8508(4)	11.8507(8)	12.0626(1)	12.0626(1)	11.5357(1)	11.4926(3)	11.5148(1)	11.5389(1)	11.56
<i>V_m</i> , Å ³	207.89	208.04	208.04	219.40	219.40	191.88	189.74	190.85	192.04	193
Color	rose	amber	colorless	l. green	l. green	rose	reddish purple	red	red	red
Source	Asbestos, Quebec	Umba River, Tanzania	Jeffrey Quarry, Quebec	Ala Valley, Italy	Val Malenco, Italy	Northeast AZ	Madagascar	Sri Lanka	No. Creek, NY	Tanzania

Samples were oriented for cutting to obtain the maximum area for capacitance measurement. Although no systematic effort was made to obtain information on possible chemical zonation, significant color variations were not observed in any crystal. Microprobe analyses of points on individual crystals did not reveal any significant chemical heterogeneities.

Electron microprobe analyses were made using a JEOL 733 electron microprobe. Data reduction methods are described by Armstrong (1982, 1988). X-ray diffraction patterns were obtained using a Guinier-type focusing camera, CuK α_1 radiation, and Si SRM 640 as an internal standard. Cell dimensions were obtained by least-squares refinement.

Rectangular-, triangular-, or trapezoidal-shaped samples were cut from the bulk crystals using a low-speed diamond wheel saw. Sample thickness and area varied from 0.09 to 0.13 cm and 0.10 to 1.0 cm², respectively. Sputtered Au electrodes were applied over the entire parallel surfaces of the sample using a Denton Vacuum Desk II sputtering unit. Sample preparation is described in de-

tail by Subramanian et al. (1989). Dielectric constant measurements were made with a parallel plate capacitance technique using Hewlett-Packard 4274A and 4275A LCR bridges and fixture 16034B (Test Tweezers) according to the procedure described by Subramanian et al. (1989) and Hewlett-Packard (1984). Edge corrections were made using the expression

$$C_e = (0.019 \ln P/t - 0.043)P \quad (4)$$

where *t* = sample thickness and *P* = perimeter in centimeters. The overall accuracy of the dielectric constant measurements using the above techniques is estimated to be 1.0–1.5%. Dielectric loss errors are estimated to be 5–20% at levels of $\tan \delta = 0.002$ and 50–100% at levels of 0.0004–0.0005.

RESULTS

Table 1 summarizes compositional data, unit-cell dimensions, colors, and sources of the garnets studied here. Table 2 lists all of the known garnet dielectric constants. There is good agreement among values found here and

TABLE 2. Cell dimensions, molar volumes, and dielectric constants of garnet single crystals

Garnet	Source	<i>a</i> , Å	<i>V_m</i> , Å ³	κ'	$\tan \delta$	Frequency	Reference
Pyrope-almandine	Northeastern AZ	11.5357(1)	191.88	12.00	<0.0005	1 MHz	This work
	Madagascar	11.4926(3)	189.74	12.20	<0.0005	1 MHz	This work
	Sri Lanka?	11.5148(1)	190.85	12.35	<0.0005	1 MHz	This work
	Tanzania	11.5635(1)	193.28	12.28	0.001	1 MHz	This work
	North Creek, NY	11.5389(2)	192.04	11.96	<0.0005	1 MHz	This work
	Warren, NY	—	—	11.5	0.009	1 MHz	Olhoeft (1981)
Spessartine	Mania, Madagascar	11.533	191.75	13	—	IR	Bliss (1989)
	Little 3 Mine, Ramona, CA	11.6135(1)	195.79	11.65	0.005	1 MHz	This work
Andradite	Haddam, CT	—	—	11.2	0.009	1 MHz	Olhoeft (1981)
	Val Malenco, Italy	12.0626(1)	219.40	10.59	0.010	1 MHz	This work
	Ala Valley, Italy	12.0626(1)	219.40	10.53	0.005	1 MHz	This work
Grossular	Graham Cty, AZ	—	—	10.5	0.063	1 MHz	Olhoeft (1981)
	Umba River	11.8508(4)	208.04	8.71	0.001	1 MHz	This work
	Jeffrey Quarry	11.8507(8)	208.04	8.53	0.002	1 MHz	This work
	Asbestos, Quebec	11.8480(4)	207.89	8.81	0.002	1 MHz	This work
	Transvaal	—	—	8.1	0.003	1 MHz	Olhoeft (1981)
Lake Jaco, Chihuahua	11.844	207.68	8.5	—	IR	Bliss (1989)	

TABLE 3. Dielectric constants and molar polarizabilities of MgO, CaO, MnO, FeO, Al₂O₃, Fe₂O₃, and SiO₂

Compound	Orientation	κ'	$\langle \kappa' \rangle$	$V_m, \text{\AA}^3$	$\alpha, \text{\AA}^3$	Reference
MgO		9.830	9.830	18.69	3.331	Fontanella et al. (1974)
CaO		11.95	11.95	27.83	5.22	Subramanian et al. (1989)
MnO		18.10	18.10	22.00	4.47	Chaudhury and Rao (1969)
		22.0	22.0	22.00	4.59	Plendl et al. (1969)
	E a	18.93	18.70	22.00	4.49	Seehra et al. (1986)
	E c	18.23				
FeO					4.18	Shannon et al. (1991a)
Al ₂ O ₃	E a	9.395	10.126	42.45	7.627	Fontanella et al. (1974)
	E c	11.589				
Fe ₂ O ₃					10.51	Shannon (1991b)*
SiO ₂	E a	4.520	4.559	37.66	4.878	Fontanella et al. (1974)
	E c	4.637				

* Obtained from $\alpha_o(\text{Fe}_2\text{O}_3) = [\alpha_o(\text{Y}_3\text{Fe}_5\text{O}_{12}) - 1.5\alpha_o(\text{Y}_2\text{O}_3)]/2.5$.

those of Bliss (1989) and Olhoeft (1981). The Olhoeft values for the Warren, New York, almandine and the Transvaal grossular are slightly lower than the values observed here for pyrope-almandine and grossular, but this could be caused by different compositions. The Bliss value for the Madagascar pyrope-almandine seems a little higher than those for the other pyrope-almandine but might be caused by the higher Fe content. The origin of the observed difference in dielectric constant of the Bliss pyrope-almandine may also lie in the inherent accuracies of the IR techniques used. Classical dispersion analyses of quartz and Al₂O₃ give differences of ± 1 –5% (Spitzer and Kleinman, 1961; Barker, 1963; Gaskell and Johnson, 1974) when comparing the long-wavelength dielectric constant from infrared data and the dielectric constant obtained from 1-MHz capacitance measurements.

DISCUSSION

Table 3 lists what we believe are the most accurate dielectric constants and polarizabilities of MgO, CaO,

FeO, MnO, Al₂O₃, Fe₂O₃, and SiO₂, which are used to calculate the polarizabilities of the garnets. Table 4 compares the total molecular dielectric polarizabilities determined from the measured dielectric constants using the Clausius-Mosotti relationship (Eq. 1) and the oxide additivity rule.

The deviation between the observed dielectric polarizabilities of spessartine and andradite and those calculated from the the sum of the oxide polarizabilities according to the oxide additivity rule (Eq. 3) is only slightly larger than the typical 1% variation observed previously for a series of aluminates, gallates, and silicates (Shannon and Subramanian, 1989; Subramanian and Shannon, 1989; Shannon et al., 1989, 1990, 1991a, 1991b, 1992). However, the agreement between observed and calculated polarizabilities of pyrope-almandine and grossular is significantly worse. Even more important perhaps is that the observed deviations are of opposite sign.

Similar deviations from additivity were found by Holland (1989) in a study of the thermodynamic quantities of silicate minerals; he found the entropy contributions

TABLE 4. Comparison of observed and predicted single-crystal dielectric polarizabilities of various garnets

Type	Composition	κ	Predicted α_r	Measured $\alpha_r(\text{exp})^*$	$\Delta, \%$	
Pyrope	Mg _{2.04} Fe _{0.53} Ca _{0.43} Mn _{0.02} Al _{1.96} Cr _{0.03} Fe _{0.01} Si ₃ O ₁₂	12.00	33.70	35.99	+6.4	
	Mg _{1.96} Fe _{0.96} Ca _{0.09} Mn _{0.01} Al _{1.96} Si ₃ O ₁₂	12.20	33.54	35.72	+6.1	
	Mg _{1.64} Fe _{1.17} Ca _{0.19} Mn _{0.03} Al _{2.00} Si ₃ O ₁₂	12.35	33.88	36.03	+6.0	
	Mg _{1.23} Fe _{0.90} Mn _{0.56} Ca _{0.33} Al _{1.98} V _{0.02} Cr _{0.01} Zn _{0.01} Si ₃ O ₁₂	12.28	34.63	36.45	+5.0	
	Fe _{1.45} Mg _{1.18} Ca _{0.20} Mn _{0.04} Al _{2.0} Si ₃ O ₁₂	11.96	33.65	35.99	+6.5	
Almandine	Fe _{2.03} Mg _{0.66} Ca _{0.14} Mn _{0.15} Al _{1.98} Fe _{0.03} Si ₃ O ₁₂	13	34.59	36.6	+5.5	
	Mn _{2.80} Fe _{0.17} Ca _{0.01} Al _{2.03} Si ₃ O ₁₂	11.65	35.79	36.47	+1.9	
Spessartine						
Source	Composition	κ	Predicted α_r (oxide rule)	Measured $\alpha_r(\text{exp})^*$	$\Delta, \%$	
Umba River, Tanzania	Grossular					
	Ca _{2.98} Al _{1.97} Mg _{0.04} Mn _{0.01} Ti _{0.02} Fe _{0.01} Si _{2.99} O _{11.98} (O ₄ H ₄) _{0.01}	8.71	37.87	35.75	-5.9	
	Ca _{2.98} Mn _{0.01} Fe _{0.01} Al _{1.97} Fe _{0.02} Si _{2.94} O ₁₂	8.53	37.59	35.67	-5.4	
	Ca _{2.98} Mn _{0.04} Fe _{0.135} Al _{2.0} Si _{3.0} O ₁₂	8.81	37.88	35.87	-5.6	
	Ca _{2.90} Mg _{0.09} Fe _{0.02} Al _{1.91} Fe _{0.09} Si ₃ O ₁₂	8.5	37.91	35.4	-7.1	
Val Malenco, Italy	Andradite					
	Ca _{3.00} Fe _{1.99} Mg _{0.02} Al _{0.01} Si _{2.98} O ₁₂	10.59	40.79	39.90	-2.2	
Ala, Italy	Ca _{2.99} Fe _{2.00} Mg _{0.02} Al _{0.01} Si _{2.98} O ₁₂	10.53	40.80	39.83	-2.4	

* Using the Clausius-Mosotti relationship.

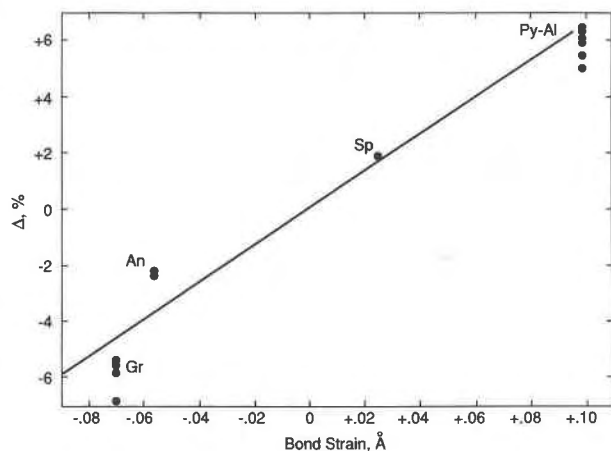


Fig. 1. Deviations from the oxide additivity rule vs. bond strain. Bond strain values from Novak and Gibbs (1971) refer to differences between unshared octahedral edge distances and shared octahedral edge distances.

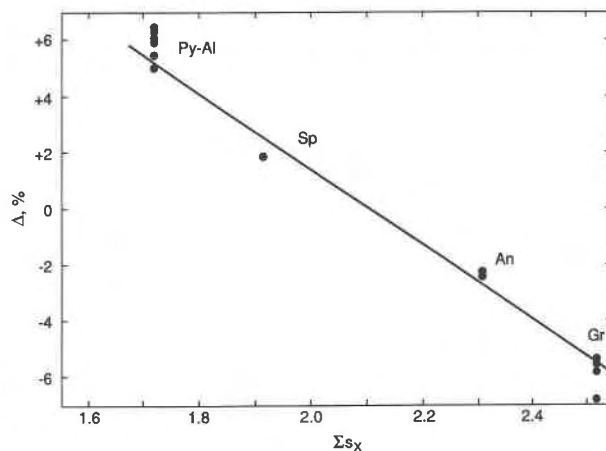


Fig. 2. Deviation from the oxide additivity rule vs. approximate bond valence. Bond valence sums calculated from (1) distances in pyrope, spessartine, andradite, and grossular in Novak and Gibbs (1971) and (2) bond valence parameters in Brown and Altermatt (1985).

of Mg^{2+} and Fe^{2+} in pyrope and Ca^{2+} in grossular to be larger and smaller, respectively, than expected for these cations in eight-coordination.

Apparently, there are special factors operative in the $X_3Y_2Z_3O_{12}$ garnet structure that cause these deviations. One factor that might contribute to these deviations is the unusual amount of edge sharing in the garnet structure, which leads to structural constraints (Zemann, 1962; Novak and Gibbs, 1971). These constraints cause changes in what are normally nearly invariant bond distances. This is apparently the case where $d\langle Si-O \rangle = 1.63 \text{ \AA}$ for $r\{X\} < 1.0 \text{ \AA}$ (pyrope, almandine, and spessartine) and 1.65 \AA for $r\{X\} > 1.10 \text{ \AA}$ (grossular). Similarly, $d\langle Al-O \rangle = 1.886 \text{ \AA}$ for $r\{X\} < 1.10 \text{ \AA}$ but 1.924 \AA for $r\{X\} > 1.10 \text{ \AA}$. However, it should be noted that there is a continuous variation in $d\langle Al-O \rangle$ in the series pyrope-almandine-spessartine-grossular (Novak and Gibbs, 1971).

An unusual feature of grossular and andradite is that the octahedral edges shared with the dodecahedral edges are longer than the unshared edges, in contrast to the rule that shared edges are generally shorter than unshared edges. Although the effect is most obvious at the extreme end of the garnet stability field, i.e., grossular, it is dependent on the differences between unshared and shared octahedral edge distances, referred to as "bond strain" by Novak and Gibbs (1971). In Figure 1, bond strain is plotted vs. deviation from the oxide additivity rule. The deviation from additivity is approximately proportional to the bond strain, suggesting a common origin for the two variables—presumably the structural constraints arising from the extensive edge sharing. Thus, instead of anomalies only at the pyrope and grossular end-members, the additivity deviations are seen to be proportional to the bond strain.

These structural features lead to XO_6 polyhedra whose size is strongly determined by the $Y_2Z_3O_{12}$ framework. The smallest and largest X cations found in the silicate

garnets, Mg^{2+} and Ca^{2+} , are somewhat too small and too large, respectively, to fit in these polyhedra. Along these lines, Zemann (1962) concluded that Mg is slightly too small and Ca slightly too large for the garnet $Al_2Si_3O_{12}$ framework. Subsequently, Novak and Gibbs (1971) placed pyrope and grossular at the extreme limits of the garnet stability field, so unusual behavior in thermodynamic and dielectric properties for these two garnets is perhaps not surprising.

The structural misfit of Mg and Ca can also be seen from their respective bond valences, 1.72 and 2.52 valence units (vu) (O'Keeffe, 1989), when compared to their ideal value of 2.00 vu. The bond valences of Mn and Ca in spessartine and andradite, 1.92 and 2.31 vu, respectively, lie intermediate to those of Mg and Ca in pyrope and grossular. Figure 2 shows that deviations from the additivity rule closely parallel the X bond valences, with the largest positive deviations corresponding to the cations with the lowest bond valences such as Mg and Mn and the largest negative deviations corresponding to the cations with the highest bond valences such as Ca in grossular and andradite. This suggests that Mg is behaving like the "rattling cation" proposed by Orgel (1958) and Dunitz and Orgel (1960). This effect was described by Dunitz and Orgel (1960) as a progressive "loosening of the central cation at the center of its surrounding octahedron to off-center displacements characteristic of ferroelectric and antiferroelectric substances" as the size of the central cation in an octahedron decreases. The polyhedron can adjust its configuration to adapt to the small cation by movement of the cation, the anions, or both, resulting in polyhedral distortion. However, when crystal symmetry restricts the motion of both cation and anion such as in cubic pyrope, larger than normal bond distances and thermal motion may occur. Consistent with this interpretation of Mg as a rattling cation in the garnet

TABLE 5. Isotropic temperature factors for pyrope, grossular, and andradite garnets

Ref.	Pyrope			Grossular			Andradite				
	(1)	(2)	(3)	(2)	(3)	(1)	(2)	(5)	(6)	(6)	(6)
Ion											
Mg,Ca	0.67(8)	0.79(3)	0.93(20)	0.61(1)	0.39(10)	0.26(2)	0.38(1)	0.66(2)	0.523(6)	0.546(7)	0.597(6)
Al,Fe	0.18(5)	0.40(2)	0.40(6)	0.66(2)	0.40(6)	0.20(3)	0.49(2)	0.57(2)	0.346(2)	0.360(4)	0.411(3)
Si	0.13(4)	0.19(2)	0.29(11)	0.56(2)	0.30(11)	0.23(2)	0.48(3)	0.54(3)	0.29(1)	0.20(1)	0.23(1)
O	0.38(5)	0.50(2)	0.47(11)	0.76(2)	0.37(9)	0.22(2)	0.58(2)	0.60(3)	0.54(2)	0.60(2)	0.69(2)
B(Mg,Ca)	5.1	4.2	3.2	1.1	1.3	1.1	0.8	1.2	1.8	2.7	2.6
B(Si)											
B(Mg,Ca)	1.8	1.6	2.0	0.8	1.0	1.2	0.6	1.1	1.0	0.9	0.9
B(O)											

Note: (1) Gibbs and Smith (1965), (2) Novak and Gibbs (1971), (3) Meagher (1975), (4) Prandl (1966), (5) Hazen and Finger (1989), (6) Lager et al. (1989).

structure is the low apparent bond valence noted by O'Keeffe (1989) and the unusually large Mg thermal ellipsoid commented on by Gibbs and Smith (1965) and verified by Novak and Gibbs (1971), Meagher (1975), and Hazen and Finger (1989). Table 5 shows that typical ratios of B(Mg):B(Si) are equal to 3–4. The negative deviation of grossular and the smaller entropy contribution of Ca in grossular can similarly be interpreted as a “compressed cation” effect. It is more difficult to interpret the thermal parameters of Ca in grossular: B(Ca):B(Si) = 1.1–1.3 and B(Ca):B(O) = 0.8–1.2, both of which are much lower than in pyrope (Table 5). However, they should also be lower than in andradite. Unfortunately, the thermal parameters of Ca in andradite show a large spread—B(Ca):B(Si) = 0.8–2.7 and B(Ca):B(O) = 0.6–1.1—so it is not possible to conclude unequivocally that the grossular thermal parameters are unusually small. The concept of distended and compressed Mg and Ca sites in pyrope and grossular, respectively, was also proposed by Hawthorne (1981) from an analysis of garnet bond lengths.

In addition to these general garnet structural considerations, there are other possible factors that might help rationalize the additivity deviations observed in pyrope and grossular. In phenacite, chrysoberyl, and spinel, the additivity rule does not seem to depend significantly on the coordination of Al or Mg, i.e., the polarizabilities of Al and Mg do not depend on their CN and therefore on changes in their bond lengths or partial molar volumes. The change in CN is apparently exactly compensated by cell volume changes (Havinga and Bosman, 1965; Shannon and Subramanian, 1989; Shannon et al., 1990). However, in the garnet structures, it seems conceivable that the extensive edge sharing and consequent structural constraints do not allow the bond length of ions as small as Mg to compensate fully for the coordination change from six to eight. Indeed, the garnet structure is one of the few structures that allows stabilization of eight-coordinated Mg. Thus the increase in polarizability associated with the increase in CN of Mg from six to eight, not entirely compensated by an increase in molar volume, might result in an apparent higher polarizability of pyrope garnet, as is observed.

SUMMARY

Dielectric constants of pyrope-almandine, spessartine, andradite, and grossular were determined at 1 MHz. Deviations of total dielectric polarizabilities from the oxide additivity rule depend on the size of X : +5 to +6% for pyrope-almandine, +1.9% for spessartine, –2.3% for andradite, and –5.5 to –7.0% for grossular. These deviations can be interpreted on the basis of structural constraints in $X_3Y_2Z_3O_{12}$ garnets imposed by extensive edge sharing. This edge sharing results in bond strain that leads to XO_8 polyhedra that cannot adjust completely to the normal X -O bond distance. This results in deviations from normal bond distances and bond valences most evident at the extremes of the size of X : Mg and Ca. At the lower limit, pyrope has an unusually high polarizability consistent with low bond valences, high Mg thermal vibration ellipsoids, and excess entropy. At the other extreme, grossular has an unusually low dielectric polarizability, which is consistent with high bond valences and smaller than normal entropy contributions. The other garnet members spessartine and andradite show additivity deviations intermediate between those of pyrope and grossular, proportional to intermediate values of bond valences.

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