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Dielectric Constants of YVO_4, Fe-, Ge-, and V-Containing Garnets, the Polarizabilities of Fe_2O_3, GeO_2, and V_2O_5, and the Oxide Additivity Rule

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The dielectric constants and dissipation factors of $Y_3Fe_5O_{12}$, YVO_4, $NaCa_2Mg_2V_3O_{12}$, and a variety of Ge garnets were determined at 1 MHz using a two-terminal method and empirically determined edge corrections. The results are:

$Y_3Fe_5O_{12}$	$\kappa' = 15.70$	$\tan\delta = 0.0009$
$Ca_3Ga_2Ge_3O_{12}$	$\kappa' = 9.73$	$\tan\delta = 0.0007$
$Ca_{.90}Y_{1.88}Mg_{2.27}Ge_3O_{12}$	$\kappa' = 10.35$	$\tan\delta = 0.0006$
$CaY_{1.96}Nd_{.04}Zn_2Ge_3O_{12}$	$\kappa' = 11.32$	$\tan\delta = 0.0006$
$Nd_{2.95}Mg_{1.48}In_{.68}Ga_{1.54}Ge_{1.32}O_{12}$	$\kappa' = 11.86$	$\tan\delta = 0.0009$
$NaCa_2Mg_2V_3O_{12}$	$\kappa' = 10.32$	$\tan\delta = 0.0007$
YVO_4	$\kappa_a' = 9.68$	$\tan\delta_a = 0.0010$
	$\kappa_c' = 16.59$	$\tan\delta_c = 0.0278$

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The dielectric polarizabilities of Fe_2O_3, GeO_2, and V_2O_5 derived from the dielectric constants of the above compounds are 10.5, 5.5, and 15.8 Å^3, respectively. The agreement between measured dielectric polarizabilities as determined from the Clausius–Mosotti equation and those calculated from the sum of oxide polarizabilities according to $\alpha_D(\text{mineral}) = \Sigma\alpha_D(\text{oxides})$ for the above garnets is ~0.5%.

Introduction

The dielectric polarizability, α_D, is related to the measured dielectric constant, κ', by the Clausius–Mosotti equation,

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

where V_m is the molar volume in Å^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 (*1, 2*). The Clausius–Mosotti equation is strictly valid only for compounds where the molecule or ion has cubic symmetry (*1–9*), but has been shown to be approximately valid for a number of noncubic crystals (*2, 8, 10–14*).

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

$$\alpha_D(M_2M'X_4) = 2\alpha_D(MX) + \alpha_D(M'X_2). \qquad (2)$$

Previous applications of the additivity rule to minerals were reviewed by Shannon and Subramanian (*14*).

The purpose of this paper is to accurately determine the 1-MHz dielectric constants of YVO_4, $Y_3Fe_5O_{12}$, $NaCa_2Mg_2V_3O_{12}$, and four Ge-containing garnets, to derive the polarizability of Fe_2O_3, GeO_2, and V_2O_5, and to evaluate the validity of the oxide additivity rule in these materials.

Experimental

The $Ca_3Ga_2Ge_3O_{12}$ crystals were grown by Damen *et al.* using the Czochralski method reported earlier (*15*). The YVO_4 crystals were also grown by the Czochralski method. Crystals of $CaY_2Mg_2Ge_3O_{12}:Cr$ and $CaY_2Zn_2Ge_3O_{12}:Nd$ were grown by a top-seeded solution method for use as laser crystals (*16, 17*). Crystals of $Nd_{2.97}Mg_{1.35}In_{0.73}Ga_{1.60}Ge_{1.35}O_{12}$ were grown by the Czochralski method according to Mateika *et al.* (*18*). Chemical analysis was previously performed at the top and bottom of the boule from which this crystal was taken by X-ray fluorescence; estimated errors were ±0.02 formula units for all elements except Mg for which an error of ±0.05 formula units is estimated. The yttrium iron garnet crystals were grown by the flux method using a flux of unknown composition. $NaCa_2Mg_2V_3O_{12}$ crystals were grown by the Kyropoulos method using a sodium vanadate flux.

X-ray diffraction patterns were obtained on a Guinier-type focusing camera using Cu$K\alpha_1$ radiation and a Si SRM 640 internal standard. Cell dimensions were obtained by least-squares refinement.

Electron microprobe analyses were made using a JEOL 733 electron microprobe. Data reduction methods are described by Armstrong (*19, 20*) who states that the mean relative errors of the analyses are generally 1% or lower for typical silicate minerals except for the lowest atomic number elements. For samples with higher average atomic numbers than found in common silicate minerals, these data reduction methods yield larger errors due in part to uncertainties in the absorption and fluorescence correction factors used for some of the less common elements. Such errors may be particularly noticeable for certain combinations of light elements such as Mg in heavy matrices. The uncertainties in our analyses appear to conform to these guidelines.

Microprobe analyses of points on individual crystals did not reveal any significant chemical heterogeneities. Analysis of YVO_4, $NaCa_2Mg_2V_3O_{12}$, $Ca_3Ga_2Ge_3O_{12}$, the Nd–Mg–In–Ga–Ge garnet, and the Nd doped Ca–Y–Zn and Cr-doped Ca–Y Mg garnets yielded:

$Y_{0.98}V_{1.01}O_4$,
$Na_{1.05}Ca_{2.00}Mg_{1.99}V_{2.99}O_{12}$,
$Nd_{2.95}La_{0.01}Y_{0.01}Mg_{1.48}In_{0.68}Ga_{1.54}Ge_{1.32}Si_{0.02}O_{12}$,
$Ca_{2.95}Na_{0.04}Ga_{2.03}Ge_{2.96}V_{0.02}O_{12}$,
$Ca_{1.01}Y_{2.02}Nd_{0.04}Zn_{2.01}Ge_{2.94}O_{12}$,
$Ca_{0.90}Y_{1.88}Mg_{2.27}Ge_3O_{12}$.

The crystal reported to be $CaY_2Mg_2Ge_3O_{12}:Cr$ by Christensen and Jenssen (*16*) apparently has a somewhat different composition. Similarly, the composition of the Nd–Mg–In–Ga–Ge garnet determined here by electron microprobe differs slightly from that found by X-ray fluorescence analysis.

Electron microprobe analysis indicated the YVO_4 crystals to contain 0.02 wt% Na_2O, which results in <0.001 Na by formula weight but which might significantly affect dielectric loss. Optical absorption spectroscopy showed low levels (~0.03 wt%) of Nd, Pr, and Sm and the absence of a V^{4+}–V^{5+} charge transfer band.

Rectangular- or triangular-shaped samples were cut from the bulk crystals using a low-speed diamond wheel saw. Sample thickness and area varied from 0.04 to 0.12 cm and from 0.13 to 0.85 cm^2, respectively. Sputtered gold electrodes were applied over the entire parallel surfaces of the sample using a Denton Vacuum Desk II sputtering unit. Sample preparation is described in detail in Subramanian *et al.* (*21*).

Dielectric constant measurements were performed over the frequency range 30 KHz–3 MHz with a parallel plate capacitance technique using a Hewlett–Packard 4275A LCR bridge and fixture 16034B (test tweezers) (*22*) according to the procedure described by Subramanian *et al.* (*21*). Edge corrections were made using the expression

$$C_e = (0.019 \ln P/t - 0.043)P, \qquad (3)$$

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 and Discussion

Table I summarizes unit cell dimensions and dielectric data for the crystals studied here. The dielectric constants determined showed deviations of less than 0.2% over the range of frequencies 30 KHz to 3 MHz. The relatively low values of $\tan \delta = 0.0006$–0.0009 for the garnets suggest good sample quality. The high loss factor in YVO_4 ($\tan \delta_c = 0.0278$) does not seem to be a result of reduced V^{5+}, but may result from Na^+ mobility and therefore be responsible for the differences in κ_c' between our sample and that reported by Armbruster (*23*).

Table II lists mean dielectric constants and molar volumes of the oxides used to test the oxide additivity rule. Table III lists the total polarizabilities of the ternary oxides and the polarizabilities of Fe_2O_3, GeO_2, and V_2O_5 derived by subtracting the components of polarizabilities due to the binary oxides as was done for FeO (*13*), Ga_2O_3 and La_2O_3 (*31*), and ZrO_2 (*36*). The experimentally microprobe-determined compositions were used to calculate the total polarizability of the Ge garnets. Values for $\alpha_D(Fe_2O_3)$ of 10.5 Å^3, $\alpha_D(GeO_2)$ of 5.5 Å^3, and $\alpha_D(V_2O_5)$ of 15.8 Å^3 were extracted from $\alpha_D(Fe_2O_3, GeO_2, \text{or } V_2O_5) = \alpha_D(\text{complex oxide}) - \alpha_D(\text{simple oxide})$. The dielectric data of $LuVO_4$, obtained from infrared reflectivity measurements (*23*), were not used in the derivation of $\alpha_D(V_2O_5)$ because of inherently lower accuracies obtained from classical dispersion analyses relative to 1-MHz ca-

TABLE I

CELL DIMENSIONS, MOLAR VOLUMES, DIELECTRIC CONSTANTS, AND TOTAL POLARIZABILITIES OF VARIOUS GARNET SINGLE CRYSTALS

A. Garnet	a(Å)	V_m(Å^3)	κ'	tan δ	α_D(Å^3)	Frequency
$Ca_3Ga_2Ge_3O_{12}$	12.252[a]	229.89	9.73	0.0007	40.84	1 MHz
$Ca_{.90}Y_{1.88}Mg_{2.27}Ge_3O_{12}$	12.3071	233.01	10.35	0.0006	42.11	1 MHz
$CaY_{1.96}Nd_{0.04}Zn_2Ge_3O_{12}$	12.3856	237.50	11.32	0.0006	43.93	1 MHz
$Nd_{2.95}Mg_{1.48}In_{0.68}Ga_{1.54}Ge_{1.32}O_{12}$	12.651	253.1	11.86	0.0009	47.34	1 MHz
$Y_3Fe_5O_{12}$	12.376[b]	236.95	15.70	0.0009	46.98	1 MHz
$NaCa_2Mg_2V_3O_{12}$	12.455[c]	241.51	10.32	0.0007	43.62	1 MHz

B. Other	a(Å)	c(Å)	V_m(Å^3)	κ'_a,tan δ	κ'_c,tan δ	α_D (Å^3)	Frequency	Ref.
YVO_4	7.1192	6.2898	79.70[d]	9.676 ± 0.03 0.0010	16.59 ± 0.06 0.0278	14.94	1 MHz	This work
				9.7	14.4	14.72	IR	(*23*)
$LuVO_4$	7.0243	6.2316	76.86[e]	9.0	14.8	14.09	IR	(*23*)
$ZnFe_2O_4$	8.433		74.96[f]	14.7		14.68	IR	(*24*)
$MnFe_2O_4$	8.499		76.73[f]	14.8		15.04	IR	(*24*)

[a] Ref. (*15*).
[b] Ref. (*25*).
[c] Ref. (*26*).
[d] JCPDS: 17-341 (1965).
[e] JCPDS: 17-880 (1965).
[f] Ref. (*27*).

pacitance measurements (*37, 38*). Similarly, dielectric constants of $MnFe_2O_4$ and $ZnFe_2O_4$, obtained from reflectivity measurements of ceramic samples (*24*), were not weighted heavily in the determination of $\alpha_D(Fe_2O_3)$.

Table IV compares the total molecular dielectric polarizabilities determined from the measured dielectric constants using the Clausius–Mosotti relationship (Eq. (1)) and from the oxide additivity rule using what we believe are the most accurate dielectric

TABLE II

DIELECTRIC CONSTANTS AND MOLAR POLARIZABILITIES OF SIMPLE OXIDES

Compound	$\langle\kappa'\rangle$	V_m(Å^3)	a(Å^3)	Ref.
Na_2O			5.59	(*11*)
MgO	9.830	18.69	3.331	(*28*)
ZnO	8.49	23.55	4.01	(*29*)
MnO	18.70	22.00	4.49	(*30*)
CaO	11.95	27.83	5.22	(*21*)
Ga_2O_3			8.80	(*31*)
In_2O_3	8.9	64.72	11.20	(*32*)
	9.0	64.72	11.24	(*33*)
Y_2O_3	11.4	74.50	13.81	(*34*)
Lu_2O_3	12.5	70.10	13.27	(*35*)
Nd_2O_3	14.3	85.01	16.56	(*35*)

TABLE III

DIELECTRIC POLARIZABILITY DATA FOR Fe_2O_3, GeO_2, AND V_2O_5

Compound	α_D(total)(Å^3)	$\alpha_D{}^a$(Å^3)
$Ca_3Ga_2Ge_3O_{12}$	40.84	5.46
$Ca_{0.90}Y_{1.88}Mg_{2.27}Ge_3O_{12}$	42.11	5.62
$CaY_{1.96}Nd_{0.04}Zn_2Ge_3O_{12}$	43.93	5.61
$Nd_{2.95}Mg_{1.48}In_{0.68}Ga_{1.54}Ge_{1.32}O_{12}$	47.34	5.44
		$\langle\alpha_D(GeO_2)\rangle = 5.5$
$Y_3Fe_5O_{12}$	46.98	10.51
$ZnFe_2O_4$	14.68	10.67
$MnFe_2O_4$	15.04	10.55
		$\langle\alpha_D(Fe_2O_3)\rangle = 10.5$
$NaCa_2Mg_2V_3O_{12}$	43.62	15.81
YVO_4 (this work)	14.94	16.08
(Ref. *(23)*)	14.72	15.64
		$\langle\alpha_D(V_2O_5)\rangle = 15.8$

[a] Obtained from $\alpha_{tot} = \Sigma\ (\alpha_{oxides})$.

constants of Na_2O, MgO, ZnO, MnO, CaO, Ga_2O_3, In_2O_3, Y_2O_3, Lu_2O_3, and Nd_2O_3 listed in Table II. The agreement between the observed dielectric polarizabilities and those calculated from the sum of the oxide polarizabilities according to the oxide additivity rule (Eq. (2)) is excellent and is comparable to the typical 1% variation observed previously for a series of aluminates, gallates, and silicates *(12–14, 31, 36)*.

This group of compounds, along with several other groups of oxides including Y and RE aluminates, chrysoberyl, spinel, olivine-type silicates, phenacite, and zircon, form a class of "well-behaved" oxides whose dielectric polarizabilities follow the oxide additivity rule to ±0.5–1.5%. This group forms a basis for comparison with compounds which show larger deviations (>5%) because of ionic or electronic conductivity,

TABLE IV

COMPARISON OF OBSERVED AND PREDICTED SINGLE CRYSTAL DIELECTRIC POLARIZABILITIES OF VARIOUS GARNETS

Composition	$\langle\kappa\rangle$	Predicted α_T	Measured α_T(exp)	Δ(%)
$Ca_3Ga_2Ge_3O_{12}$	9.73	40.96	40.84	−0.3
$Ca_{0.90}Y_{1.88}Mg_{2.27}Ge_3O_{12}$	10.35	41.74	42.11	+0.9
$CaY_{1.96}Nd_{0.04}Zn_2Ge_3O_{12}$	11.32	43.61	43.93	+0.7
$Nd_{2.95}Mg_{1.48}In_{0.68}Ga_{1.54}Ge_{1.32}O_{12}$	11.86	47.42	47.34	−0.2
$Y_3Fe_5O_{12}$	15.70	46.96	46.98	0.0
$NaCa_2Mg_2V_3O_{12}$	10.32	43.75	43.62	0.0
YVO_4 (this work)	11.98	14.80	14.94	+0.9
(Ref. *(23)*)	11.27	14.80	14.72	0.5

the presence of H_2O or CO_2, or structural peculiarities (*11*).

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