

Dielectric constants of yttrium and rare-earth garnets, the polarizability of gallium oxide, and the oxide additivity rule

R. D. Shannon and M. A. Subramanian^{a)}

Central Research and Development Department, E. I. Du Pont de Nemours and Co.,
Experimental Station, Wilmington, Delaware 19880-0356

T. H. Allik

Science Applications International Corporation, 1710 Goodridge Drive, P. O. Box 1303,
McLean, Virginia 22102

H. Kimura

National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305, Japan

M. R. Kokta

Union Carbide Corp., 750 So. 32nd Street, P. O. Box 6381, Washougal, Washington 98671

M. H. Randles

Litton Airtron, P. O. Box 410168, Charlotte, North Carolina 28421-0168

G. R. Rossman

Division of Geological and Planetary Sciences, California Institute of Technology,
Pasadena, California 91125

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The dielectric constants (κ') and dielectric loss values of 10 rare-earth gallium garnets and 1 rare-earth aluminum garnet were measured at 1 MHz using a two-terminal method with empirically determined edge corrections. The results are: $\kappa'(\text{Dy}_3\text{Al}_5\text{O}_{12}) = 11.07 \pm 0.05$; $\kappa'(\text{Ho}_3\text{Ga}_5\text{O}_{12}) = 12.38 \pm 0.05$; $\kappa'(\text{Dy}_3\text{Ga}_5\text{O}_{12}) = 12.36 \pm 0.06$; $\kappa'(\text{Tb}_3\text{Ga}_5\text{O}_{12}) = 12.40 \pm 0.03$; $\kappa'(\text{Gd}_3\text{Ga}_5\text{O}_{12}) = 12.18 \pm 0.10$; $\kappa'(\text{Eu}_3\text{Ga}_5\text{O}_{12}) = 12.46 \pm 0.05$; $\kappa'(\text{Sm}_3\text{Ga}_5\text{O}_{12}) = 12.55 \pm 0.03$; $\kappa'(\text{Nd}_3\text{Ga}_5\text{O}_{12}) = 12.59 \pm 0.12$; $\kappa'(\text{Y}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}) = 12.94 \pm 0.03$; $\kappa'(\text{Sm}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}) = 13.67 \pm 0.04$; and $\kappa'(\text{La}_{2.66}\text{Lu}_{2.66}\text{Ga}_{2.66}\text{O}_{12}) = 14.40 \pm 0.03$. The dielectric polarizability of Ga_2O_3 derived from the dielectric constants of these and other Ga compounds is $8.80 \pm 0.14 \text{ \AA}^3$. The agreement between measured dielectric polarizabilities as determined from the Clausius-Mosotti equation and those calculated from the sum of oxide polarizabilities according to $\alpha_D(\text{mineral}) = \sum \alpha_D(\text{oxides})$ for six aluminum garnets and twelve gallium garnets is $\sim 1\%$.

INTRODUCTION

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

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

has been discussed.¹⁻⁷ We recently evaluated the validity of the oxide additivity rule in several Y and rare-earth aluminate garnets, in the minerals chrysoberyl (BeAl_2O_4), spinel (MgAl_2O_4), phenacite (Be_2SiO_4), forsterite (Mg_2SiO_4), and danburite ($\text{CaB}_2\text{Si}_2\text{O}_8$) and found agreement between calculated and observed polarizabilities of 0.5%–1.5%.^{8,9}

Evaluation of the oxide additivity rule requires knowledge of the polarizabilities of simple oxides. If single crystals of the simple oxides are not available for dielectric constant measurements, it is sometimes possible to derive simple oxide polarizabilities from complex oxides if the polarizability of one of the components is well known. For example, the polarizability of ZrO_2 was derived from the polarizabilities of ZrSiO_4 and Y-stabilized zirconia.¹⁰

The purpose of this paper is to accurately determine the dielectric constant of a variety of rare-earth gallium garnets, to derive the dielectric polarizability of Ga_2O_3 from these

data and data from other Ga-containing compounds reported in the literature, and to evaluate the validity of the oxide additivity rule in these materials.

EXPERIMENT

All garnet crystals with the exception of the flux grown $\text{Eu}_3\text{Ga}_5\text{O}_{12}$ were grown by the Czochralski technique. Crystal growth of $\text{Dy}_3\text{Al}_5\text{O}_{12}$ is described by Kimura.¹¹ Rectangular-shaped samples having areas ranging from 0.15 to 0.90 cm^2 and thicknesses 0.05–0.10 cm, prepared according to the technique described earlier,¹² were used to measure the dielectric constant.

The electron microprobe analysis of dysprosium gallium garnet was conducted on a JEOL 733 electron microprobe using Ga_2O_3 and $\text{Dy}_3\text{Al}_5\text{O}_{12}$ as standards. Data were corrected by the ZAF method using the program CITZAF.¹³ The results, $\text{Dy}_{3.04}\text{Ga}_{4.95}\text{O}_{12}$, are in close agreement with those previously published.¹⁴ X-ray diffraction patterns were obtained on a Guinier-type focusing camera using $\text{CuK}\alpha_1$ radiation and Si SRM 640 internal standard. Cell dimensions of $\text{Ho}_3\text{Al}_5\text{O}_{12}$, $\text{Y}_{1.5}\text{Er}_{1.5}\text{Al}_5\text{O}_{12}$, and $\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}:\text{Nd,Cr}$ were obtained from the literature.

The composition of $\text{La}_{2.655}\text{Nd}_{0.027}\text{Lu}_{2.656}\text{Ga}_{2.655}\text{O}_{12}$

^{a)} Contribution No. 5264.

was determined by the inductively coupled plasma (ICP) technique. This composition differs from the previously published results of $\text{La}_{2.26}\text{Nd}_{0.04}\text{Lu}_{2.63}\text{Ga}_{3.07}\text{O}_{12}$.¹⁵ In the earlier characterization of this material as a potential laser host, the sample was analyzed by x-ray fluorescence (XRF). The purpose of the analysis was to obtain a concentration for Nd^{3+} absorption and fluorescence transitions due to mixed occupancy of the crystallographic sites. The refinement of the host composition by ICP is more accurate because the XRF analysis used films for calibration instead of solid (> 3 mm) standards. These thin films yielded fluorescence intensities (c/s) that were 1–2 orders of magnitude lower than from the sample, thus, decreasing the accuracy of the analysis. Furthermore, a composition containing less than 3 Ga/ μc is more in line with results obtained for other Ga garnets.¹⁶

Dielectric constant measurements were performed over the frequency range 30 kHz–3 MHz with a parallel plate capacitance technique using Hewlett–Packard 4274A and 4275A LCR bridges and fixture 16034B (Test Tweezers).¹⁷ Details of the experimental procedure were published previously.¹²

Edge capacitance was calculated from an expression determined empirically from data on standard fused silica, CaF_2 , and SrF_2 (Ref. 12):

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

where P and t are sample perimeter and thickness in cm. The parameters in this expression are similar to those found by Field.¹⁸

The accuracy of the dielectric constant measurements using the above technique was determined from a series of measurements on standard fused silica^{19,20} and on samples of CaF_2 and SrF_2 , previously used in two-fluid technique measurements.^{21,22} The accuracy and precision in the measurement of κ' for samples having areas of 0.05–1.0 cm^2 is 0.5%–1.5% with the largest errors probably being associated with irregularities in sample geometry. The error in dielectric loss ($\tan \delta$) is 5%–20% at levels of 0.002 and is 50%–100% at levels of 0.0004–0.0005.¹²

RESULTS AND DISCUSSION

Tables I and II summarize the unit cell dimensions and single crystal dielectric data for LiGaO_2 , CoGa_2O_4 , and a variety of yttrium and rare-earth aluminum and gallium garnets. Most of these samples showed deviations of less than 0.2% in κ' over the frequency range 30 kHz–3 MHz. The exceptions are $\text{Y}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$ and $\text{Gd}_{3.03}\text{Ga}_{4.97}\text{O}_{12}$ with decreases of 0.4% and 0.6%, respectively, from 30 kHz to 3 MHz. In addition, we have listed what we believe are the most accurate dielectric constants and molar volumes of Li_2O , CoO , Al_2O_3 , Y_2O_3 , Sc_2O_3 , Lu_2O_3 , Er_2O_3 , Ho_2O_3 , Dy_2O_3 , Tb_2O_3 , Gd_2O_3 , Eu_2O_3 , Nd_2O_3 , and La_2O_3 for

TABLE I. Cell dimensions.

Compound	a (Å)	V_m^a	Ref.
Li_2O	4.6114	24.51	30
CoO	4.2581	19.30	30
LiGaO_2^b		43.09	31
CoGa_2O_4	8.326	72.14	32
$\text{Y}_3\text{Al}_5\text{O}_{12}$	12.009	216.5	33
$\text{Lu}_3\text{Al}_5\text{O}_{12}$	11.912	211.3	34
$\text{Er}_3\text{Al}_5\text{O}_{12}$	11.981	215.0	34
$\text{Ho}_3\text{Al}_5\text{O}_{12}$	12.0146 ± 1	216.8	This work
$\text{Dy}_3\text{Al}_5\text{O}_{12}$	12.038	218.0	JCPDS FILE 22-1093
$\text{Tb}_3\text{Al}_5\text{O}_{12}$	12.074	220.0	34
$\text{Y}_{1.5}\text{Er}_{1.5}\text{Al}_5\text{O}_{12}$	11.9976 ± 1	215.5	This work
$\text{Y}_3\text{Sc}_2\text{Al}_3\text{O}_{12}:\text{Nd}^c$	12.271	230.9	8
$\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}:\text{Nd,Cr}^d$	12.4054 ± 1	238.6	This work
$\text{Ho}_{3.06}\text{Ga}_{4.94}\text{O}_{12}^e$	12.296	232.4	14
$\text{Dy}_{3.05}\text{Ga}_{4.95}\text{O}_{12}^e$	12.3209 ± 1	233.8	This work
$\text{Tb}_{3.04}\text{Ga}_{4.96}\text{O}_{12}^e$	12.349	235.4	14
$\text{Gd}_{3.03}\text{Ga}_{4.97}\text{O}_{12}^e$	12.383	237.3	36
$\text{Eu}_{3.02}\text{Ga}_{4.98}\text{O}_{12}^e$	12.408	238.8	14
$\text{Sm}_{3.02}\text{Ga}_{4.98}\text{O}_{12}^e$	12.438	240.5	14
$\text{Nd}_{3.01}\text{Ga}_{4.99}\text{O}_{12}^e$	12.509	244.7	14
$\text{Y}_3\text{Sc}_2\text{Ga}_4\text{O}_{12}$	12.251	229.8	37
$\text{Sm}_3\text{Sc}_2\text{Ga}_5\text{O}_{12}$	12.640	252.4	37
$\text{La}_{2.96}\text{Lu}_{2.66}\text{Ga}_{2.66}\text{O}_{12}:\text{Nd}$	12.930	270.2	15

^a V_m = molar volume, Å³.

^b $a = 5.402$ Å, $b = 6.372$ Å, $c = 5.007$ Å (Ref. 31).

^c $\text{Y}_{2.93}\text{Nd}_{0.07}\text{Sc}_2\text{Al}_3\text{O}_{12}$.

^d $\text{Gd}_{2.95}\text{Nd}_{0.05}\text{Sc}_{1.98}\text{Cr}_{0.02}\text{Al}_3\text{O}_{12}$.

^e Nonstoichiometric compositions taken from Ref. 14.

TABLE II. Summary of dielectric constants and total polarizabilities.^a

Compound	$\langle \kappa' \rangle$	$\tan \delta$	Frequency	α_D (Å)	Reference
Li ₂ O	8.06		IR ^b	4.11	38
CoO	12.9		1 MHz	3.68	39
	12.9		IR ^b	3.68	40
Al ₂ O ₃	10.126		1 kHz	7.63	41
Sc ₂ O ₃	13		1 MHz	11.39	42
Y ₂ O ₃	11.4		100 kHz	13.81	43
Lu ₂ O ₃	12.5		IR ^b	13.27	44
Er ₂ O ₃	13.0		IR ^b	14.00	44
Ho ₂ O ₃	13.1		IR ^b	14.2	44
Dy ₂ O ₃	13.1		IR ^b	14.51	44
Tb ₂ O ₃	13.3		IR ^b	14.81	44
Gd ₂ O ₃	13.6		IR ^b	15.24	44
Eu ₂ O ₃	13.9		IR ^b	15.50	44
Nd ₂ O ₃	14.3		IR ^b	16.56	44
La ₂ O ₃			1 MHz	17.7 ^c	
LiGaO ₂	7.27 ^d			6.96	45
	7.27 ^d			6.96	46
CoGa ₂ O ₄	9.20 ± 0.1		0.1 GHz	12.63	32
Y ₃ Al ₅ O ₁₂	10.60 ± 0.05	0.0009	1 MHz	39.38	This work
Y ₃ Al ₅ O ₁₂	10.97 ± 0.05		1 kHz	39.73	23
Lu ₃ Al ₅ O ₁₂	10.87 ± 0.05		1 kHz	38.68	23
Er ₃ Al ₅ O ₁₂	10.90 ± 0.05		1 kHz	39.39	23
Ho ₃ Al ₅ O ₁₂	10.93 ± 0.03	0.0008	1 MHz	39.70	This work
Ho ₃ Al ₅ O ₁₂	11.02 ± 0.05		1 kHz	39.83	23
Dy ₃ Al ₅ O ₁₂	11.07 ± 0.05		1 MHz	40.10	This work
Dy ₃ Al ₅ O ₁₂	11.08 ± 0.06		1 kHz	40.11	23
Tb ₃ Al ₅ O ₁₂	11.13 ± 0.06		1 kHz	40.52	23
Y _{1.5} Er _{1.5} Al ₅ O ₁₂	10.76 ± 0.03	0.0007	1 MHz	39.42	This work
Y ₃ Sc ₂ Al ₃ O ₁₂ :Nd ^e	12.20 ± 0.03	0.0008	1 MHz	43.48	This work
Gd ₃ Sc ₂ Al ₃ O ₁₂ :Nd,Cr ^f	12.71 ± 0.06	0.0007	1 MHz	45.35	This work
Ho _{3.06} Ga _{4.94} O ₁₂	12.38 ± 0.05	0.0005	1 MHz	43.90	This work
Dy _{3.05} Ga _{4.95} O ₁₂	12.36 ± 0.06	0.0007	1 MHz	44.15	This work
Tb _{3.04} Ga _{4.96} O ₁₂	12.40 ± 0.03	0.0005	1 MHz	44.49	This work
Gd _{3.00} Ga _{5.00} O ₁₂	12.11 ± 0.02		1 kHz	44.61	24
Gd _{3.03} Ga _{4.97} O ₁₂	12.24 ± 0.01		1 kHz	44.72	24
Gd _{3.03} Ga _{4.97} O ₁₂	12.18 ± 0.10	0.0011	1 MHz	44.66	This work
Eu _{3.02} Ga _{4.98} O ₁₂	12.46 ± 0.05	0.0008	1 MHz	45.18	This work
Sm _{3.02} Ga _{4.98} O ₁₂	12.55 ± 0.03	0.0008	1 MHz	45.59	This work
Nd _{3.01} Ga _{4.99} O ₁₂	12.59 ± 0.12	0.0010	1 MHz	46.40	This work
Y ₃ Sc ₂ Ga ₃ O ₁₂	12.94 ± 0.03	0.0011	1 MHz	45.42	This work
Sm ₃ Sc ₂ Ga ₃ O ₁₂	13.67 ± 0.04	0.0010	1 MHz	48.72	This work
La _{2.66} Lu _{2.66} Ga _{2.66} O ₁₂ :Nd	14.40 ± 0.03	0.0008	1 MHz	52.62	This work

^aUsing the Clausius–Mosotti relationship: $\alpha_D = (3/4\pi)(V_m)[(\kappa' - 1)/(\kappa' + 2)]$, where V_m = molar volume.

^bDielectric constant derived from infrared reflectivity data.

^cObtained from $\alpha_D(\text{La}_2\text{O}_3) = \alpha_D(\text{La}_2\text{Be}_2\text{O}_5) - \alpha_D(\text{BeO})$.

^dMean value obtained from κ_{11}^S , κ_{22}^S , and κ_{33}^S .

^eY_{2.93}Nd_{0.07}Sc₂Al₃O₁₂.

^fGd_{2.95}Nd_{0.05}Sc_{1.98}Cr_{0.02}Al₃O₁₂.

evaluation of the additivity of polarizabilities. The dielectric constants of a series of M₃Al₅O₁₂ garnets with M = Y, Lu, Er, Ho, Dy, and Tb were recently reported.²³ Excellent agreement with our values for Ho₃Al₅O₁₂ and Dy₃Al₅O₁₂ in Table II is observed. The dielectric constant of Gd₃Ga₅O₁₂ (GGG) was from Lal and Jhans.²⁴

The congruent melting compositions from which gal-

lium garnet crystals are grown are generally nonstoichiometric and result in crystals where two or more ions share the same site.¹⁶ The nonstoichiometric Ga garnet compositions listed in Tables I–IV are from Brandle and Barns.¹⁴ The best estimate of the composition of GGG is Gd_{3.05}Ga_{4.95}O₁₂ from cell dimension changes chemical analysis and melt composition variations.^{25–27} No information is available on

TABLE III. Dielectric polarizability data for Ga₂O₃.

Compound	α_D (total) (\AA^3)	α_D (Ga ₂ O ₃) ^a (\AA^3)	V_0 (\AA^3)
CoGa ₂ O ₄	12.63	8.95	18.0
Ho _{3.06} Ga _{4.94} O ₁₂	43.90	8.94	19.4
Dy _{3.05} Ga _{4.95} O ₁₂	44.14	8.95	19.5
Tb _{3.04} Ga _{4.96} O ₁₂	44.49	8.86	19.6
Tb _{3.04} Ga _{4.96} O ₁₂	44.63	8.92	19.6
Gd ₃ Ga ₅ O ₁₂	44.61	8.70	19.8
Gd _{3.03} Ga _{4.97} O ₁₂	44.71	8.65	19.8
Gd _{3.03} Ga _{4.97} O ₁₂	44.66	8.68	19.8
Eu _{3.02} Ga _{4.98} O ₁₂	45.18	8.74	19.9
Nd _{3.01} Ga _{4.99} O ₁₂	46.40	8.60	20.4
$\langle \alpha_D(\text{Ga}_2\text{O}_3) \rangle = 8.80 \pm 0.14 \text{\AA}^3$			

^aObtained from $\alpha_{\text{tot}} = \sum(\alpha_{\text{oxides}})$.

TABLE IV. Comparison of observed and predicted single crystal dielectric polarizabilities.

Compound	$\langle \kappa' \rangle$	Predicted ^a		Measured ^b α_T (exp)	$\Delta\%$
		α_T (oxide rule)			
LiGaO ₂	7.27	6.47		6.96	+ 7.0
CoGa ₂ O ₄	9.2	12.48		12.63	+ 1.2
Y ₃ Al ₅ O ₁₂	10.60	39.79		39.38	- 1.0
Y ₃ Al ₅ O ₁₂	10.97			39.73	- 0.1
Lu ₃ Al ₅ O ₁₂	10.87	38.97		38.68	- 0.7
Er ₃ Al ₅ O ₁₂	10.90	40.07		39.39	- 1.7
Ho ₃ Al ₅ O ₁₂	10.93	39.56		39.70	+ 0.4
Ho ₃ Al ₅ O ₁₂	11.02			39.83	+ 0.7
Dy ₃ Al ₅ O ₁₂	11.07	40.84		40.10	- 1.8
Dy ₃ Al ₅ O ₁₂	11.08			40.11	- 1.8
Tb ₃ Al ₅ O ₁₂	11.13	41.28		40.52	- 1.9
Y _{1.5} Er _{1.5} Al ₅ O ₁₂	10.76	39.93		39.41	- 1.3
Y ₃ Sc ₂ Al ₃ O ₁₂ :Nd	12.20	43.64		43.48	- 0.4
Gd ₃ Sc ₂ Al ₃ O ₁₂ :Nd,Cr	12.71	45.73		45.35	- 0.8
Ho _{3.06} Ga _{4.94} O ₁₂	12.38	43.55		43.90	+ 0.8
Dy _{3.05} Ga _{4.95} O ₁₂	12.36	43.91		44.15	+ 0.5
Tb _{3.04} Ga _{4.96} O ₁₂	12.40	44.33		44.49	+ 0.3
	12.57	44.33		44.03	+ 0.7
Gd _{3.00} Ga _{5.00} O ₁₂	12.11	44.96		44.61	- 0.8
Gd _{3.03} Ga _{4.97} O ₁₂	12.18	44.83		44.66	- 0.4
	12.24	44.83		44.72	- 0.2
Eu _{3.02} Ga _{4.98} O ₁₂	12.46	45.32		45.18	- 0.3
Sm _{3.02} Ga _{4.98} O ₁₂	12.55	45.6		45.59	0.0
Nd _{3.01} Ga _{4.99} O ₁₂	12.59	46.88		46.4	- 1.0
Y ₃ Sc ₂ Ga ₃ O ₁₂	12.94	45.30		45.42	+ 0.3
Y _{2.96} Sc _{1.90} Ga _{3.14} O ₁₂ ^c		45.08			+ 0.8
Sm ₃ Sc ₂ Ga ₃ O ₁₂	13.67	48.1		48.72	+ 1.2
Sm _{2.96} Sc _{1.90} Ga _{3.14} O ₁₂		47.87			+ 1.7
La _{2.66} Lu _{2.66} Ga _{2.66} O ₁₂	14.40	53.3		52.70	+ 1.2
Aluminates				$\langle \Delta_0 \rangle = 1.1\%$	
Gallates (omitting data from LiGaO ₂):				$\langle \Delta \rangle = 0.7\%$	

^a $\alpha_D(\text{Ga}_2\text{O}_3) = 8.80 \text{\AA}^3$.

^bUsing the Clausius-Mosotti relationship; polarizabilities in \AA^3 .

^cAssuming nonstoichiometry of the type found in Gd_{2.957}Sc_{1.905}Ga_{3.138}O₁₂ (Ref. 16).

the composition of Y₃Sc₂Ga₃O₁₂ and Sm₃Sc₂Ga₃O₁₂, but they are probably similar to the composition of Gd_{2.957}Sc_{1.905}Ga_{3.138}O₁₂ found for gadolinium scandium gallium garnet.²⁸

Table III lists the total polarizabilities of the ternary oxides and the polarizabilities of Ga₂O₃ derived by subtracting the component of polarizability due to the binary oxides. Omitting the values for LiGaO₂ which deviate significantly from calculated values, the mean value of $\alpha_D(\text{Ga}_2\text{O}_3)$ is $8.80 \pm 0.14 \text{\AA}^3$. The value of $\alpha_D(\text{Ga}_2\text{O}_3)$ derived from LiGaO₂ is considerably larger than the other values.

Table IV compares the total molecular dielectric polarizabilities determined from the measured dielectric constants using the Clausius-Mosotti relationship:

$$\alpha_D = \frac{3}{4\pi} (V_m) \frac{\kappa' - 1}{\kappa' + 1},$$

where V_m = molar volume, κ' = dielectric constant at 10^5 - 10^{10} Hz, and from the oxide additivity rule. With the exception of LiGaO₂, the agreement is better than $\pm 1.0\%$ and compares well with agreement of approximately $\pm 1.0\%$ for Be₂SiO₄, Mg₂SiO₄, BeAl₂O₄, and MgAl₂O₄.^{8,9}

The poor agreement for LiGaO₂ probably arises from its ionic conductivity.²⁹ Although significant conductivity is only observed at temperatures above 400 °C, the residual mobility of the Li ions at lower temperatures could conceivably contribute to the overall polarizability of LiGaO₂ at room temperature.

The aluminum and gallium garnets provide another example of structures where the compound dielectric polarizabilities do not depend on the coordination numbers of the cations. The additivity rule seems to be valid despite the fact that the simple oxides Al₂O₃ and Ga₂O₃ contain Al³⁺ and Ga³⁺ in octahedral coordination whereas the garnets contain Al³⁺ or Ga³⁺ in both tetrahedral and octahedral coordination. Similar behavior was noted for BeAl₂O₄ and MgAl₂O₄.⁹

In conclusion, the oxide additivity rule seems valid for a variety of structures including the fluorite, zircon, phenacite, forsterite, spinel, chrysoberyl, aluminum garnet, and gallium garnet structures.

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