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Dielectric constants of diaspore and B-, Be-, and P-containing minerals, the polarizabilities of B_2O_3 and P_2O_5, and the oxide additivity rule

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ABSTRACT

The 1-MHz dielectric constants and loss factors of the minerals diaspore, euclase, hambergite, sinhalite, danburite, datolite, beryllonite, and montebrasite and of the synthetic oxides $La_2Be_2O_5$, AlP_3O_9, and NdP_5O_{14} were determined. The dielectric polarizabilities of B_2O_3 and P_2O_5 derived from the dielectric constants of these compounds are 6.15 and 12.44 Å^3, respectively. The dielectric constants of the above minerals and oxides, along with the dielectric polarizabilities of Li_2O, Na_2O, BeO, MgO, CaO, Al_2O_3, Nd_2O_3, La_2O_3, SiO_2, diaspore, and the derived values of the polarizabilities of B_2O_3 and P_2O_5, were used to calculate dielectric polarizabilities from the Clausius-Mosotti equation and to test the oxide additivity rule. The oxide additivity rule is valid to ±0.5% for all except beryllonite. These compounds with deviations from additivity of 0.5–1.5%, along with previously studied aluminate and gallate garnets, chrysoberyl, spinel, phenacite, zircon, and olivine-type silicates, form a class of well-behaved oxides that can be used as a basis for comparison of compounds that show larger deviations (>5%) caused by ionic or electronic conductivity, the presence of H_2O or CO_2, or structural peculiarities.

INTRODUCTION

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

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

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, was measured in the range 1 KHz to 10 MHz (Roberts, 1950, 1951). 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 has been shown to be approximately valid for a number of noncubic crystals (Roberts, 1949, 1951; Lasaga and Cygan, 1982; Shannon et al., 1989, 1990).

The concept of additivity of molecular polarizabilities implies that the molecular polarizability of a complex substance can be divided 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 (1989).

The purpose of this paper is to determine the 1-MHz dielectric constants of diaspore and several Be-, B-, and P-containing oxides and minerals, to derive the polarizabilities of B_2O_3 and P_2O_5, and to evaluate the validity of the oxide additivity rule in these materials.

EXPERIMENTAL

The sources of the crystals were as follows: diaspore—grayish green crystal from Turkey; euclase—clear, colorless crystals, one from San Sebastao de Maranhao, Minas Gerais, and the other from Diamantina, Minas Gerais, Brazil; $La_{1.98}Nd_{0.02}Be_2O_5$—from Allied-Signal Corp.; hambergite—clear, colorless crystal from Antsirabe, Tananarive, Madagascar; sinhalite—greenish yellow crystal from the Ellawalla River, Ratnapura, Sri Lanka; danburite—clear, colorless crystal from Charcus, Mexico; datolite—clear, colorless crystal from Westfield, Massachusetts; $AlPO_4$—clear, colorless crystals grown hydrothermally from a hydrochloric acid–phosphoric acid solution at 170 °C as described by Ozimek and Chai (1978); NdP_5O_{14}—light purple crystals obtained from Ferrox-

TABLE 1. Cell dimensions and molar volumes

	a (Å)	*b* (Å, β°)	*c* (Å)	V_m (Å³)	Reference
$Al_{0.99}Fe_{0.01}OOH$	4.4005(3)	9.4268(6)	2.8458(2)	29.51	This work
$BeAlSiO_4OH$	4.7795(4)	14.332(1) 100.296(6)	4.6323(5)	78.05	This work
$La_2Be_2O_5$	7.5356	7.348 91.55	7.4387	102.94	Harris and Yakel (1968)
Be_2BO_3OH	9.7641(5)	12.2080(8)	4.4335(3)	66.06	This work
$Mg_{0.98}Fe_{0.02}AlBO_4$	9.8806(7)	5.6788(4)	4.3295(4)	60.73	This work
$CaB_2Si_2O_8$	8.0477(5)	8.7628(9)	7.7330(5)	136.33	This work
$CaBSiO_4OH$	9.634(2)	7.610(1) 90.15(1)	4.8334(7)	88.59	This work
$Zn_4B_6O_{13}$	7.4659	7.4659	7.4659	209.08	Smith-Verdier and Garcia-Blanco (1980)
BaB_2O_4	12.547	12.547	12.736	96.46	Eimerl et al. (1987)
$AlPO_4$	4.9423	4.9423	10.9446	77.17	Thong and Schwarzenbach (1979)
AlP_3O_9	13.729	13.729	13.729	161.73	NBS Mon 25
NdP_5O_{14}	8.7672	8.9948 90.481	13.0326	256.93	Allbrand et al. (1974)
$LiAlPO_4OH$	5.1988(4) 112.29(1)	7.1721(7) 97.840(7)	5.0415(5) 67.848(6)	80.54	This work
$NaBePO_4$	8.1354(4)	7.8003(3) 90.000(4)	14.2030(6)	75.11	This work

TABLE 2. Summary of single-crystal dielectric constants

	κ'_{a^*}, tan δ	κ'_{b^*}, tan δ	κ'_{c^*}, tan δ	$\langle\kappa'\rangle$	Frequency	Reference
$Al_{0.99}Fe_{0.01}OOH$	8.335 ± 0.05 0.0009	9.146 ± 0.05 0.0008	7.848 ± 0.05 0.0007	8.443	1 MHz	This work
	7.70	8.38	7.27			Takubo et al. (1953)
	5.7, undefined orientation 0.0264				1 MHz	Olhoeft (1981)
$BeAlSiO_4OH$	6.481 ± 0.02 0.0005	6.663 ± 0.05 0.0006	6.764 ± 0.03 0.0006	6.64	1 MHz	This work
$La_2Be_2O_5$	38.74 ± 0.8 0.0010	25.93 ± 0.02 0.0009	22.65 ± 0.2 0.0012	29.11	1 MHz	This work
Be_2BO_3OH	4.451 ± 0.02 0.0014	4.738 ± 0.05 0.0013	5.28 ± 0.1 0.0011	4.82	1 MHz	This work
$Mg_{0.98}Fe_{0.02}AlBO_4$	7.753 ± 0.01 0.0009	8.339 ± 0.02 0.0008	8.113 ± 0.01 0.0007	8.075	1 MHz	This work
$CaB_2Si_2O_8$	6.720 ± 0.01 0.0007	6.618 ± 0.01 0.0009	6.869 ± 0.01 0.0009	6.735	1 MHz	This work
	6.35	6.34	6.58	6.4	500 Hz	Takubo et al. (1953)
	—	6.34	6.77			Takubo et al. (1953)
	6.9, undefined orientation				1 MHz	Olhoeft (1981)
$CaBSiO_4OH$	6.84 ± 0.2 0.020	8.328 ± 0.02 0.002	6.86 ± 0.1 0.010	7.34	1 MHz	This work
	7.2, undefined orientation 0.006				1 MHz	Olhoeft (1981)
$Zn_4B_6O_{13}$	7.24			7.24	100 KHz	Bohaty et al. (1982)
BaB_2O_4	5.78 <0.001		6.6 <0.001	6.05	1 MHz	Guo and Bhalla (1989)
$AlPO_4$	4.57 ± 0.05 0.001		4.54 ± 0.05 0.001	4.56	1 MHz	Shannon et al. (1990)
AlP_3O_9	5.185 ± 0.05 0.0005			5.185	1 MHz	This work
NdP_5O_{14}	6.567 ± 0.05 0.0009	5.699 ± 0.02 0.0009	6.722 ± 0.06 0.0037	6.33	1 MHz	This work
$LiAlPO_4OH$	6.808 ± 0.005 0.005	8.342 ± 0.007 0.010	8.159 ± 0.15 0.008	7.77	1 MHz	This work
	7.7, undefined orientation 0.0178				1 MHz	Olhoeft (1981)
$NaBePO_4$	6.34 ± 0.06 0.0005	6.44 ± 0.07 0.0005	6.32 ± 0.06 0.0005	6.37	1 MHz	This work

Note: $\kappa'_{a^*} = \kappa'_{11}$, $\kappa'_{b^*} = \kappa'_{22}$, $\kappa'_{c^*} = \kappa'_{33}$ except for $La_2Be_2O_5$, NbP_5O_{14}, euclase, datolite, and montebrasite. See experimental section for details.

TABLE 3. Dielectric constants and molar polarizabilities

Compound	$\langle\kappa'\rangle$	V_m (Å^3)	α_D (Å^3)	Reference
Li_2O	8.06		4.11	Osaka and Shindo (1984)
Na_2O			5.59	Shannon (1991)
BeO	7.16	13.79	2.213	Subramanian et al. (1989)
MgO	9.830	18.69	3.331	Fontanella et al. (1974)
ZnO	8.49	23.55	4.01	Kobiakov (1980)
CaO	11.95	27.83	5.22	Subramanian et al. (1989)
BaO	14.40	41.59	8.11	Jonker and VanSanten (1947)
Al_2O_3	10.126	42.45	7.627	Fontanella et al. (1974)
Nd_2O_3			16.3*	This work
La_2O_3			17.7**	This work
SiO_2	4.559	37.66	4.878	Fontanella et al. (1974)
$Al_{0.99}Fe_{0.01}OOH$	8.443	29.51	5.021	This work
$BeAlSiO_4OH$	6.64	78.05	12.16	This work
$La_2Be_2O_5$	29.11	102.94	22.21	This work
Be_2BO_3OH	4.82	66.06	8.80	This work
$Mg_{0.98}Fe_{0.02}AlBO_4$	8.075	60.73	10.181	This work
$CaB_2Si_2O_8$	6.735	136.33	21.29	This work
$CaBSiO_4OH$	7.34	88.59	14.36	This work
$Zn_4B_6O_{13}$	7.24	209.08	33.71	Bohaty et al. (1982)
BaB_2O_4	6.05	96.46	14.44	Guo and Bhalla (1989)
$AlPO_4$	4.56	77.17	10.0	Shannon (unpublished data)
AlP_3O_9	5.185	161.73	22.49	This work
NdP_5O_{14}	6.33	256.93	39.24	This work
$LiAlPO_4OH$	7.77	80.54	13.32	This work
$NaBePO_4$	6.37	75.11	11.502	This work

* Obtained from $\alpha_D(Nd_2O_3) = [\alpha_D(Nd_3Ga_5O_{12}) - 2.5\alpha_D(Ga_2O_3)]/1.5$; Shannon et al. (1990).
** Obtained from $\alpha_D(La_2O_3) = \alpha_D(La_2Be_2O_5) - 2\alpha_D(BeO)$.

cube, Saugerties, New York; beryllonite—clear, colorless crystal from Stoneham, Maine; and montebrasite—clear, colorless crystal from Minas Gerais, Brazil (USNM 157924).

Crystals of AlP_3O_9 were grown hydrothermally in an Au tube charged with 1.40 g Al_2O_3, 3.50 g 86% H_3PO_4, and 28.0 g polyphosphoric acid (85% P_2O_5). The tube was held 4 h at 900 °C and cooled 1 °C/h to 800 °C. Clear, colorless crystals 8 × 8 × 5 mm were recovered.

Samples were oriented for cutting by polarized light and by back reflection Laue photographs. X-ray diffraction patterns were obtained using a Guinier-type focusing camera using Cu$K\alpha_1$ radiation and Si SRM 640 as an internal standard. Cell dimensions (Table 1) were obtained by least-squares refinement.

Electron microprobe analyses were made using a JEOL 733 electron microprobe. Electron microprobe data reduction methods are described by Armstrong (1982, 1988). Although no systematic effort was made to obtain information on possible chemical zonation, significant color variations were not observed in any of the crystals. Microprobe analyses of points on individual crystals did not reveal any significant chemical heterogeneities.

The composition of diaspore was determined by microprobe analysis to be $Al_{0.99}Fe_{0.05}OOH$. Euclase analysis gave composition $Be_{1.00}Al_{0.99}Si_{1.00}O_4OH$, assuming the theoretical value for Be. The F content of the hambergite was determined by electron microprobe analysis. Assuming Be : B = 2:1, the composition is $Be_2BO_3[F_{0.04}(OH)_{0.96}]$. Microprobe analysis of the danburite and sinhalite crystals led to the compositions $Ca_{1.00}B_{1.99}Al_{0.01}Si_{2.00}O_8$ and $Mg_{0.98}Fe_{0.02}Al_{1.99}BO_4$, respectively, assuming theoretical values for B. Microprobe analysis of beryllonite indicated a composition of $Na_{1.00}Be_{1.00}P_{1.00}O_4$, assuming the theoretical value for Be. A typical analysis of the montebrasite crystals indicated a composition $Li_{1.00}Al_{1.00}P_{1.00}O_4[(OH)_{0.98}F_{0.02}]$. This analysis and the unit-cell volume of 161.08 Å^3 indicate a composition close to that of pure montebrasite (Cerna et al., 1972).

Rectangular- or triangular-shaped samples were cut from the bulk crystals using a low-speed diamond wheel saw. Slabs were cut perpendicular to the reciprocal axes of all crystals, allowing determination of κ'_{11}, κ'_{22}, and κ'_{33} in the cubic, hexagonal, and orthorhombic crystals. To determine κ'_{11} and κ'_{33} of monoclinic crystals, it was necessary to obtain values of κ' in at least three directions in the $(h0l)$ plane. Similarly, to determine κ'_{11}, κ'_{22}, and κ'_{33} of triclinic crystals, it was necessary to measure κ' in directions other than parallel to **a***, **b***, and **c***. A detailed description of the determination of κ'_{11}, κ'_{22}, and κ'_{33} of anisotropic crystals is given by Takubo (1941). Because of insufficient sample size, slabs were not cut in a third orientation parallel to **b*** of the monoclinic crystals or in directions other than perpendicular to the reciprocal axes of montebrasite. Thus, values of κ'_{11}, κ'_{22}, κ'_{33}, and κ'_{13} were not determined for the monoclinic crystals of $La_2Be_2O_5$, NdP_4O_{14}, euclase, or beryllonite, and κ'_{11}, κ'_{22}, κ'_{33}, κ'_{12}, κ'_{13}, and κ'_{23} were not determined for triclinic montebrasite. However, for $La_2Be_2O_5$, NdP_4O_{14}, datolite, and beryllonite, the deviations from orthorhombic symmetry are very slight, so the deviations of κ'_{11}, κ'_{22}, and κ'_{33} from the values κ'_{a*}, κ'_{b*}, and κ'_{c*} indicated in Table 2 are believed to be small. For monoclinic euclase $\kappa_{a*} \cong \kappa_{b*} \cong \kappa_{c*}$, so the mean value of $\langle\kappa'\rangle$ listed in Tables 2 and 3 is probably close to the actual value of $\langle\kappa'\rangle$. For triclinic montebrasite, the deviations are probably larger, and the mean value of $\langle\kappa'\rangle$

TABLE 4. Dielectric polarizability data for B_2O_3 and P_2O_5

Compound	α_D(total), Å^3	$\alpha_D(B_2O_3)$*, Å^3
B_2O_3		
$Mg_{0.98}Fe_{0.02}AlBO_4$	10.181	6.04
$CaB_2Si_2O_8$	21.29	6.31
$Zn_4B_6O_{13}$	33.71	5.89
BaB_2O_4	14.44	6.33
	$\langle\alpha_D(B_2O_3)\rangle = 6.15$	
P_2O_5		
$AlPO_4$	10.0	12.37
AlP_3O_9	22.49	12.45
$LiAlPO_4OH$	13.32	12.49
NdP_5O_{14}	39.24	12.44
$NaBePO_4$	11.502	12.98
	$\langle\alpha_D(P_2O_5)\rangle = 12.44$ omitting $NaBePO_4$	

* Obtained from $\alpha_{tot} = \Sigma\ (\alpha_{oxides})$.

TABLE 5. Comparison of observed and predicted beryllate, borate, and phosphate single-crystal dielectric polarizabilities

Compound	$\langle\kappa'\rangle$	Pred. α_T	Measured α_T(exp)	Δ (%)
$BeAlSiO_4OH$	6.64	12.11	12.16	+0.4
$La_2Be_2O_5$	29.11	22.23	22.21	0.0
$Mg_{0.98}Fe_{0.02}AlBO_4$	8.075	10.24	10.18	−0.6
$CaB_2Si_2O_8$	6.735	21.13	21.29	+0.8
$AlPO_4$	4.56	10.03	10.0	−0.3
AlP_3O_9	5.185	22.47	22.49	+0.1
NdP_5O_{14}	6.33	39.25	39.24	−0.0
$LiAlPO_4OH$	7.77	13.30	13.32	+0.2
$NaBePO_4$	6.37	11.23	11.50	+2.4
				$\langle\Delta\rangle = 0.5\%$

in Tables 2 and 3 can be expected to deviate considerably from the actual mean $\langle\kappa'\rangle$ value.

The datolite crystal contained numerous veils and a few small inclusions, and it was difficult to obtain dielectric specimens free of chipped edges. These imperfections resulted in larger estimated errors than found in other crystals. The crystal of NdP_5O_{14} showed pronounced {010} cleavage, and most specimens cut perpendicular to **b*** contained small delaminated areas at the sample perimeter. These delaminations may be responsible for the unusually high dissipation factors of the samples cut perpendicular to **c***. Sample thickness and area varied from 0.02 to 0.12 cm and 0.05 to 1.5 cm^2, 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 detail by Subramanian et al. (1989).

Dielectric constant measurements were performed over the frequency range 30 KHz to 3 MHz with a parallel plate capacitance technique using a Hewlett-Packard (1984) 4275A LCR bridge and fixture 16034B (Test Tweezers) according to the procedure described by Subramanian et al. (1989). 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

Table 1 summarizes unit-cell dimensions of the crystals studied here and of $Zn_4B_6O_{13}$ and β BaB_2O_4, used for derivation of the polarizability of B_2O_3. Table 2 lists the dielectric constants and dielectric loss (tan δ) values at 1 MHz of the crystals studied here and compares them with previously reported dielectric data. The dielectric constants showed deviations of less than 0.2% over the range of frequencies 30 KHz to 3 MHz. In Table 2 we also compare our data with previously reported dielectric data for diaspore, danburite, datolite, and amblygonite. The values of $\kappa'_a = 7.70$, $\kappa'_b = 8.38$, and $\kappa'_c = 7.27$ for diaspore reported by Takubo et al. (1953) are all ~8% smaller than the values reported by us. Because their values obtained for quartz are also ~8% low, there is apparently a systematic error in the Takubo et al. technique for measuring dielectric constants. The value of 5.7 reported by Olhoeft (1981) for a sample of diaspore from Rosebud, Missouri, is anomalously low. The relatively high value of tan δ = 0.0264 suggests poor sample quality. The value of κ' = 6.9 reported by Olhoeft for a sample of danburite of unknown orientation from New York is consistent with our mean value of 6.735. The values of Takubo et al. for danburite from Toroku, Japan, are lower than our values by ~5%. The value of 7.7 obtained for amblygonite by Olhoeft is in good agreement with our mean value of 7.77, although the dielectric loss of his specimen is significantly higher than that found for our sample of montebrasite.

DISCUSSION

Table 3 lists mean dielectric constants and molar volumes of the crystals studied here and the oxides that are used to test the oxide additivity rule. Arithmetic, rather than geometric, mean values are used. Geometric mean values are smaller by 0.0–0.2% for crystals with little or no anisotropy, whereas they can amount to 2.7% for crystals such as $La_2Be_2O_5$ with significant anisotropy. Table 4 lists the total polarizabilities of the ternary oxides and the polarizabilities of B_2O_3 and P_2O_5 derived by subtracting the components of polarizabilities due to the binary oxides. Composite values for $\alpha_D(B_2O_3)$ of 6.15 Å^3 and $\alpha_D(P_2O_5)$ of 12.44 Å^3 were extracted from $\alpha_D(B_2O_3$ or $P_2O_5) = \alpha_D$(complex oxide) $- \alpha_D$(simple oxide).

Table 5 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 constants of Li_2O, Na_2O, BeO, MgO, CaO, Al_2O_3, Nd_2O_3, La_2O_3, SiO_2, and AlOOH (Table 3). 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 (Shannon and Subramanian, 1989; Subramanian and Shannon, 1989; Shannon et al., 1989, 1990, 1991).

The slightly larger deviation of beryllonite might be caused by the inaccuracy of $\alpha_D(Na_2O)$ estimated from the polarizability of NaF in conjunction with a value of $\alpha_D(O^{2-}) = 2.01$ Å (Shannon, 1991). It might also be caused by the "rattling cation" effect, which 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 such as in the Na1 site of beryllonite. When crystal symmetry restricts the motion of both cation and anion such as is observed in cubic pyrope, larger than normal bond distances and thermal motion may occur (Shannon and Rossman, 1992). In both instances evidence for rattling cations can be seen from decreased apparent bond valences or increased thermal motion. Na1, which occupies a nine-coordinated site in $NaBePO_4$ (Giuseppetti and Tadini, 1973), is characterized by unusually large thermal parameters and by bond valence sums, calculated from the Brown and Altermatt (1985) parameters, which are somewhat low, 0.87 valence units (vu), relative to its theoretical value of 1.0 vu. Na2 and Na3 occupy distorted octahedral sites and have more normal apparent bond valences of 1.06 and 1.15 vu, respectively.

This group of beryllates, borates, and phosphates, 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 that show larger deviations (>5%) because of ionic or electronic conductivity, the presence of H_2O or CO_2, or structural peculiarities (Shannon, 1991). This latter type of deviation is illustrated by several structural groups such as silicate garnets and melilite-type compounds that contain certain members (pyrope, hardystonite, akermanite) that show strong deviations (± ~5%) from the additivity rule.

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