

Dielectric constants of BaO and melilites and the oxide additivity rule

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Abstract: The constant-stress "free" dielectric constants and dissipation factors of BaO and a series of $X_2YZ_2O_7$ melilites were measured at 1 MHz using a two-terminal method and empirically determined edge corrections. The results are:

BaO	$\kappa = 31.1$	
Ca ₂ MgSi ₂ O ₇	$\kappa_a^T = 11.83$	$\kappa_c^T = 7.97$
Ca ₂ CoSi ₂ O ₇	$\kappa_a^T = 12.44$	$\kappa_c^T = 9.00$
Ca ₂ ZnSi ₂ O ₇	$\kappa_a^T = 12.03$	$\kappa_c^T = 8.21$
Sr ₂ CoSi ₂ O ₇	$\kappa_a^T = 8.93$	$\kappa_c^T = 6.87$
Ba ₂ MgGe ₂ O ₇ :Nd,Ce	$\kappa_a^T = 8.75$	$\kappa_c^T = 7.51$

The discrepancies between measured dielectric polarizabilities as determined from the Clausius-Mosotti equation and those calculated from the sum of oxide polarizabilities according to $\alpha_D(X_2YZ_2O_7) = 2 \alpha_D(XO) + \alpha_D(YO) + 2 \alpha_D(ZO_2)$ are + 13.6 to + 16.0% for Ca-containing melilites, + 6.1% for Sr₂CoSi₂O₇ and + 1.0% for Ba_{1.92}Nd_{0.04}Ce_{0.04}MgGe₂O₇. The deviations from additivity in the Ca- and Sr-melilites are believed to result from structural misfit between the alkaline earth X ion and the YZ₂O₇ layers which leads to rattling X ions.

Key-words: melilites, dielectric constants, dielectric polarizabilities, oxide additivity rule, Clausius-Mosotti equation.

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:

$$\alpha_D(X_2YZ_2O_7) = 2 \alpha_D(XO) + \alpha_D(YO) + 2 \alpha_D(ZO_2) \quad (1)$$

has been discussed earlier (Roberts, 1949, 1950, 1951; Lasaga & Cygan, 1982). We recently eval-

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uated the validity of the oxide additivity rule in several Y and rare-earth aluminate garnets, in the minerals chrysoberyl, spinel, phenacite, forsterite, and danburite, zircon, olivine-type silicates and a group of beryllates, borates and phosphates, and found agreement between calculated and observed polarizabilities of 0.5 - 1.5% (Shannon, 1991; Shannon & Subramanian, 1989; Shannon *et al.*, 1989, 1990, 1991a and b, 1992a and b; Subramanian & Shannon, 1989). However, geometrically constrained structures such as the silicate garnets of the type $X_3Al_2Si_3O_{12}$ lead to large deviations from additivity when the X-O bond distances as in pyrope ($X = Mg$) are unusually large relative to distances calculated from ionic radii, and bond valence sums, called apparent valences by O'Keeffe (1989), are significantly lower than their ideal values (Shannon & Rossman, 1992). Similar behavior was noted in $CaYAlO_4$ having the K_2NiF_4 -type structure (Shannon *et al.*, 1992c). It is of interest to see whether other compounds, such as $Ca_2MgSi_2O_7$ with the melilite structure, having constrained structures exhibit the same behavior.

The melilite structure, typified by akermanite, $Ca_2MgSi_2O_7$, is characterized by MgO_4 tetrahedra linked to Si_2O_7 groups to form five-membered rings which in turn make up $MgSi_2O_7$

sheets parallel to (001) of the tetragonal structure. The sheets are linked by eight-coordinated Ca ions. Substitutions in the $X_2YSi_2O_7$ melilites where $X = Cd, Ca, Sr, Pb$, or Ba and $Y = Be, Mg, Cu, Co, Zn, Fe, Mn$, and Cd are described by Seifert (1986), although monovalent and trivalent cation substitutions are also known to give melilites of composition $(Ca, Na, K)_2(Mg, Fe^{2+}, Fe^{3+}, Al, Si)_3O_7$ (Deer *et al.*, 1962) and $Ca_2GaGaZ_2O_7$ where $Z = Si$ or Ge (Belokoneva & Belov, 1981; Kimata, 1985). Compositions of the type $Y_2SiBe_2O_7$ (Bartram, 1969) and $RE_2GeBe_2O_7$ (Ochi *et al.*, 1982) have also been reported.

As noted by Bartram (1969) and Seifert (1986), the melilite structure is versatile, containing members as different as $Ca_2BeSi_2O_7$, $Y_2SiBe_2O_7$ and $Ba_2CdSi_2O_7$. Accordingly, the stability field for the group $X^{2+}_2Y^{2+}_2Z_2O_7$, where $Z = Si$ and Ge , is large as indicated in Fig. 1. The smallest X cation that can exist in the $X^{2+}_2YSi_2O_7$ or $X^{2+}_2YGe_2O_7$ melilite structure is Ca. In akermanite, as in hardystonite ($Ca_2ZnSi_2O_7$) and $Ca_2CoSi_2O_7$, Ca has 4 close oxygen neighbors at ~ 2.4 Å and 4 far neighbors at ~ 2.7 Å. As noted by Seifert *et al.* (1987), Ca is just large enough to fit in the large antiprismatic site formed between the two $MgSi_2O_7$ lay-

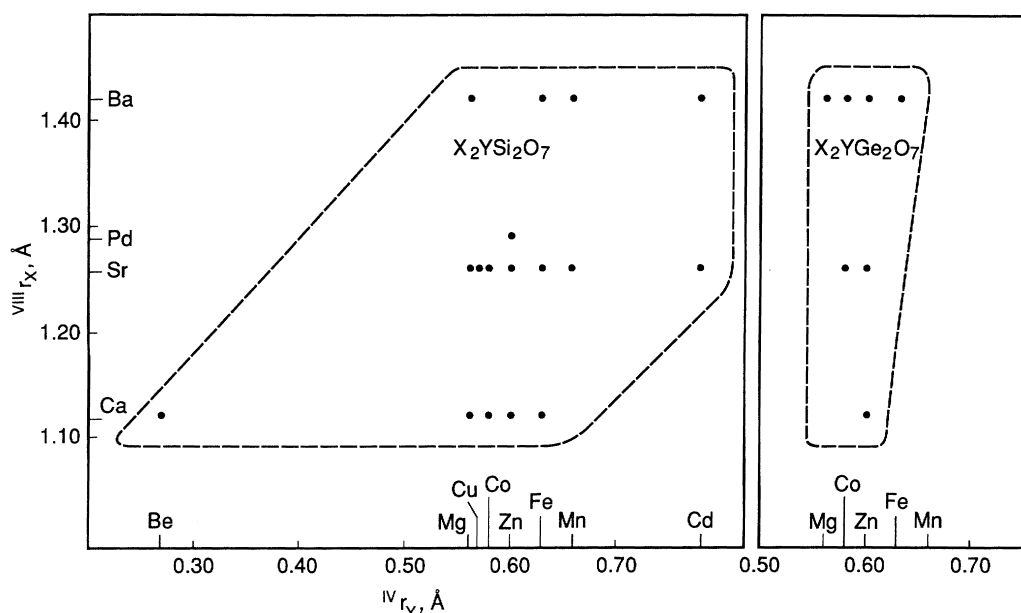


Fig. 1. Stability field of $X_2YZ_2O_7$ melilites with $Z = Si$ and Ge using the tetrahedral radius of Y^{2+} and the eight-coordinated radius of X^{2+} (Shannon, 1976). Points represent established melilite compositions.

ers. Indeed, as suggested by Seifert *et al.*, the tetrahedral sheet deforms to reduce the structural strain, thereby producing structural incommensurability. As the larger Sr and Ba ions are progressively substituted for Ca, the misfit between layers is gradually decreased and the incommensurate structure disappears (Iishi *et al.*, 1990). It should be noted, however, that Röthlisberger *et al.* (1990) find $\text{Ba}_2\text{MgSi}_2\text{O}_7$ to have the $\text{Ba}_2\text{CuSi}_2\text{O}_7$ -type structure.

As noted by Kimata & Ohashi (1982), the mean Ca-O distances of ~ 2.57 Å in a series of Ca-containing melilites is considerably larger than the typical Ca-O distance of 2.50 Å calculated from ionic radii (Shannon, 1976). This suggests that Ca is behaving like the "rattling" cation proposed by Orgel (1958) and Dunitz & Orgel (1960). In other structures, where abnormally large bond distances and thermal parameters have been found to result in unusually large dielectric constants and dielectric polarizabilities as in pyrope (Shannon & Rossman, 1992), beryllonite (Shannon *et al.*, 1992a), spodumene (Shannon *et al.*, 1992b), and CaYAlO_4 (Shannon *et al.*, 1992c), this behavior has been attributed to the "rattling" cation effect.

The purpose of this paper is to report an accurate determination of the 1 MHz dielectric constants of a variety of compounds having the melilite structure, to evaluate the validity of the oxide additivity rule in these materials, and to test the concept of "rattling" cations in Ca-containing melilites. The dielectric constant of BaO was redetermined to allow evaluation of the oxide additivity rule for $\text{Ba}_2\text{MgGe}_2\text{O}_7$.

Experimental procedures

The crystal of BaO, obtained from W. and C. Spicer, Ltd., had been stored for an unknown period of time in petroleum jelly. The exterior of the crystal was covered with a white polycrystalline layer assumed to be a mixture of BaCO_3 and Ba(OH)_2 . The sample used for dielectric constant measurements was obtained by cutting away the white exterior layer to expose a milky interior. A single crystal X-ray diffraction study of an interior fragment of the crystal indicated a cubic unit cell with $a = 5.53$ Å and space group, $Fm\bar{3}m$. The cell edge corresponds to BaO but the space group differs from that published, $F23$. An infrared spectrum obtained in dry N_2 from a slab cut adjacent to the sample used for dielectric constant

measurements indicated a sharp band at 3490 cm^{-1} probably due to hydroxyl content and a broad band at 1410 cm^{-1} similar to the carbonate band in BaCO_3 (Huang & Kerr, 1960). It is not known whether these are surface or bulk species. The milky appearance may be due, in part, to diffusion of OH^- and possible precipitation of minor quantities of Ba(OH)_2 .

The $\text{Ca}_2\text{CoSi}_2\text{O}_7$ and $\text{Sr}_2\text{CoSi}_2\text{O}_7$ crystals were grown in nitrogen using the floating zone technique described by Iishi *et al.* (1989). The color of both Co-akermanites was deep blue. The akermanite and hardystonite crystals were grown by the Czochralski technique described by Liebertz & Stähr (1982). The $\text{Ba}_2\text{MgGe}_2\text{O}_7\text{:Nd,Ce}$ crystal was grown by the top-seeded solution technique from a melt containing 0.04 moles Nd and Ce (Alam *et al.*, 1968). Although not chemically analyzed, the composition of the crystal is assumed to be $\text{Ba}_{1.92}\text{Nd}_{0.04}\text{Ce}_{0.04}\text{MgGe}_2\text{O}_7$.

Samples were oriented for cutting both by polarized light and by Laue back-reflection photographs. An electron microprobe analysis of $\text{Ca}_2\text{CoSi}_2\text{O}_7$, made using a JEOL 733 electron microprobe, gave the composition $\text{Ca}_{1.99}\text{Co}_{0.99}\text{Si}_{2.01}\text{O}_{7.00}$. Data reduction methods are described by Armstrong (1988). Microprobe analyses of points on individual crystals did not reveal any significant chemical heterogeneities. X-ray diffraction patterns of $\text{Sr}_2\text{CoSi}_2\text{O}_7$ and $\text{Ba}_2\text{MgGe}_2\text{O}_7\text{:Nd,Ce}$ were obtained on a Guinier-type focussing camera using $\text{CuK}\alpha_1$ radiation and a Si SRM640 internal standard. Cell dimensions were obtained by least-squares refinement.

Rectangular-shaped samples were cut from the bulk crystals using a low-speed diamond wheel saw. The edges of the (001) slabs of all the melilite-type crystals have a tendency to chip during cutting. This behavior is typical of crystals which show pronounced cleavage such as the melilites, diaspore and $\text{NdP}_5\text{O}_{14}$. The chipping was minimized by immersing the entire crystal in Crystalbond™ (Aremco Products, P.O. Box 429, Ossining, NY) during the cutting operation. Sample thickness and area varied from 0.09 - 0.13 cm and 0.10 to 1.0 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.* (1989). Dielectric constant measurements were performed with a parallel plate capacitance technique using Hewlett-Packard 4275A LCR bridge and fixture 16034B (Test Tweezers) according to

the procedure described by Subramanian *et al.* (1989). Because two-terminal techniques result in a measurable edge capacitance, an empirical correction factor is generally applied to reduce the measured capacitance. Edge corrections were made using the expression:

$$C_e = (0.019 \ln P/t - 0.043) P \quad (2)$$

where t = sample thickness and P = perimeter in cm. The derivation and use of this edge correction factor are described in detail in Subramanian *et al.* (1989). Dielectric constants and dissipation factors were measured at room temperature using the HP 16334A test tweezers and from room temperature to 300°C using a Hewlett-Packard 4275A LCR bridge and a parallel plate electrode device built by M. Subramanian and similar to that described by Scott & Harris (1961). In order to eliminate stray capacitance in the parallel-plate device, the dielectric constant and loss values obtained at room temperature were normalized to

the room-temperature values measured earlier on the test tweezer fixture. Data collected at elevated temperatures were then based on normalized loss and dielectric constant. All dielectric constants and dissipation factors are quoted at 1 MHz. In a piezoelectric crystal, the constant stress or "free" dielectric constant, κ^T , contains a term representing stored mechanical energy. The differences between the constant strain or "clamped" dielectric constant, κ^S , and κ^T are generally small but for crystals with large coupling constants, may be significant (Mason, 1950). We do not know the coupling constants for our crystals. Dielectric constants quoted are "free" rather than "clamped" values.

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.

Table 1. Cell dimensions and molar volumes of BaO and melilite (space group, $\bar{P}4_21m$) single crystals.

	$a, \text{\AA}$	$c, \text{\AA}$	$V_m, \text{\AA}^3$	Reference
BaO	5.5391(1)	5.5391(1)	42.48	Zollweg (1955)
$\text{Ca}_2\text{MgSi}_2\text{O}_7$	7.8332(6)	5.0070(6)	153.63	Hemingway et al. (1986)
$\text{Ca}_2\text{CoSi}_2\text{O}_7$	7.8436(4)	5.0256(3)	154.60	Iishi <i>et al.</i> (1989)
$\text{Ca}_2\text{ZnSi}_2\text{O}_7$	7.8253(4)	5.0153(2)	153.55	Iishi <i>et al.</i> (1990)
$\text{Sr}_2\text{CoSi}_2\text{O}_7$	8.0302(2)	5.1641(2)	166.50	This work
$\text{Ba}_2\text{MgGe}_2\text{O}_7\text{:Nd,Ce}$	8.3760(4)	5.5428(5)	194.43	This work

Table 2. Summary of dielectric constants of single crystal BaO and melilites.

	$\kappa_a, \tan \delta$	$\kappa_c, \tan \delta$	$\langle \kappa \rangle^*$	Frequency	Reference
BaO	31.1 ± 0.5 0.0118		31.1	1 MHz	This work
	$34. \pm 3$		34.		Roberts (1951)
$\text{Ca}_2\text{MgSi}_2\text{O}_7$	$11.83 \pm .10$ 0.0006	$7.97 \pm .10$ 0.004	10.54	1 MHz	This work
$\text{Ca}_2\text{CoSi}_2\text{O}_7$	$12.44 \pm .05$ 0.0008	$9.00 \pm .05$ 0.0005	11.29	1 MHz	This work
$\text{Ca}_2\text{ZnSi}_2\text{O}_7$	$12.03 \pm .05$ < 0.0005	$8.21 \pm .05$ < 0.0005	10.76	1 MHz	This work
$\text{Sr}_2\text{CoSi}_2\text{O}_7$	$8.93 \pm .06$ 0.0006	$6.87 \pm .20$ 0.0012	8.24	1 MHz	This work
$\text{Ba}_2\text{MgGe}_2\text{O}_7\text{:Nd,Ce}$	$8.75 \pm .03$ 0.0010	$7.51 \pm .04$ 0.0024	8.34	1 MHz	This work

* $\langle \kappa \rangle$ = arithmetic mean dielectric constant

Results

Tables 1 and 2 list unit-cell dimensions, dielectric constants and loss tangents of BaO and the melilites studied here. The dielectric constant of BaO was determined by Jonker & Van Santen (1947) to be 14.4 and by Sproull quoted in Roberts (1951) to be 34 ± 3 . The Van Santen value is clearly too low and the Sproull value is

in agreement with our value. The high dissipation factor (0.0118) is probably caused by the hydroxyl content of the milky BaO crystal. The dissipation factors of the melilites are generally less than 0.0010, suggesting good crystal quality. Exceptions are $\tan \delta_c$ of $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and $\tan \delta_c$ of $\text{Ba}_2\text{MgGe}_2\text{O}_7\text{:Nd,Ce}$.

Fig. 2 shows a plot of κ_a and κ_c ($\text{Ca}_2\text{CoSi}_2\text{O}_7$) vs. temperature. Both κ_a and κ_c increase regularly

Table 3. Dielectric constants and molar polarizabilities of MgO, CoO, ZnO, CaO, SrO, BaO, Nd_2O_3 , Ce_2O_3 , SiO_2 and GeO_2 .

Compound	Orientation	κ'	$\langle \kappa' \rangle$	$V_m, \text{\AA}^3$	$\alpha_D^a, \text{\AA}^3$	Reference
MgO		9.830	9.830	18.69	3.331	Fontanella <i>et al.</i> (1974)
CoO		12.9	12.9	19.30	3.67	Rao & Smakula (1965)
ZnO		8.49	8.49	23.55	4.01	Kobiakov (1980)
CaO		11.95	11.95	27.83	5.22	Subramanian <i>et al.</i> (1989)
SrO		14.5	14.5	33.16	6.48	Bartels <i>et al.</i> (1979)
BaO		31.1	31.1	42.48	9.22	This work
Nd_2O_3					16.3	Shannon <i>et al.</i> (1992a)
Ce_2O_3					17.3	This work ^b
SiO_2	E a	4.520	4.559	37.66	4.878	Fontanella <i>et al.</i> (1974)
	E c	4.637				
GeO_2					5.45	Shannon <i>et al.</i> (1991b)

a. The dielectric polarizability, $\alpha_D = 1/b [(V_m)(\kappa' - 1)/(\kappa' + 2)]$ where V_m is the molar volume in $\text{\AA}^3$, 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).

b. Estd. from $\alpha_D(\text{CeF}_3) = 10.54 \text{\AA}^3$, $\alpha_D(\text{F}^-) = 1.63 \text{\AA}^3$ and $\alpha_D(\text{O}^{2-}) = 2.01 \text{\AA}^3$ (Westphal & Sils, 1972; Shannon, 1991)

Table 4. Comparison of observed and predicted single-crystal dielectric polarizabilities of melilites.

Compound	$\langle \kappa \rangle$	Pred. α_T	Measured $\alpha_T(\text{exp})$	$\Delta, \%$	$\langle \text{X-O} \rangle^a$	$\langle \text{X-O} \rangle^c$ exp	$S_x, \text{v.u.}^b$
$\text{Ca}_2\text{MgSi}_2\text{O}_7$	10.54	23.53	27.90	+15.7	2.50	2.576 ^c	1.64
$\text{Ca}_2\text{CoSi}_2\text{O}_7$	11.29	23.87	28.58	+16.0	2.50	2.576 ^d	1.62
$\text{Ca}_2\text{ZnSi}_2\text{O}_7$	10.76	24.21	28.03	+13.6	2.50	2.569 ^e	1.67
$\text{Sr}_2\text{CoSi}_2\text{O}_7$	8.24	26.39	28.1	+ 6.1	2.64	2.662 ^f	1.90
$\text{Ba}_2\text{MgGe}_2\text{O}_7$	8.34	32.64	32.95	+ 1.0	2.80	2.824 ^g	1.94

a. Mean X-O distance estimated from the sum of ionic radii (Shannon, 1976)

b. Apparent valence, calculated from the bond valence parameters of Brown and Altermatt (1985).

c. Kimata & Ii (1981)

d. Kimata (1983a)

e. Louisnathan (1969)

f. Kimata (1983b) [$\text{Sr}_2\text{MgSi}_2\text{O}_7$]

g. Malinetskii *et al.* (1976) [$\text{Ba}_2\text{FeGe}_2\text{O}_7$]

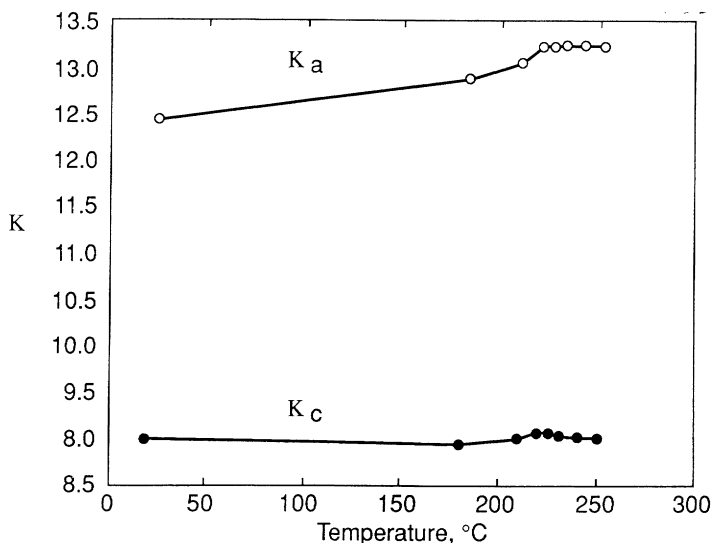


Fig. 2. Dielectric constants κ_a^T and κ_c^T of $\text{Ca}_2\text{CoSi}_2\text{O}_7$ vs. temperature. κ_a^T and κ_c^T are dielectric constants measured parallel to the crystallographic a and c axes, respectively.

or are essentially flat up to $\sim 200^\circ\text{C}$ where an increase of $\sim 1\%$ is observed. This corresponds to the transition from an incommensurate phase to a commensurate phase at 216°C as determined by TGA and discussed by Iishi *et al.* (1991). R  thlisberger *et al.* (1990) found the transition to occur at $210 - 220^\circ\text{C}$.

Discussion

Table 3 lists what we believe are the most accurate dielectric constants of MgO , CoO , ZnO , CaO , SrO , BaO , Nd_2O_3 , Ce_2O_3 , SiO_2 and GeO_2 used to calculate molar polarizabilities of the melilites studied here. Table 4 compares the total molecular dielectric polarizabilities determined from the measured dielectric constants using the Clausius-Mosotti relationship and from the oxide additivity rule using the dielectric data in Table 3.

The discrepancies (Δ) between the observed dielectric polarizabilities of the Ca- and Sr-containing members of the melilite family and those calculated from the sum of the oxide polarizabilities according to the oxide additivity rule (Eqn 1) are significantly greater than the typical 1% variation observed previously for a series of aluminates, gallates and silicates (Shannon, 1991; Shannon & Subramanian, 1989; Shannon *et al.*, 1989, 1990, 1991a and b, 1992a and 1992b; Subramanian & Shannon, 1989). The discrepancy

factor for $\text{Sr}_2\text{CoSi}_2\text{O}_7$ (6.1%) is outside the limits found for typical well-behaved oxides (Shannon, 1991) and the agreement between observed and calculated polarizabilities of $\text{Ca}_2\text{CoSi}_2\text{O}_7$, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, and $\text{Ca}_2\text{MgSi}_2\text{O}_7$ is significantly worse (13.6 to 16.0%). Part of this disagreement results from the use of "free" rather than "clamped" dielectric constants. However, the overall trend of higher Δ from Ca-containing melilites and lower Δ from Sr- and Ba-containing melilites is clear.

The increased polarizabilities of the melilite phases are not caused by the structure incommensurability because only a small change in κ' is observed at the incommensurate-commensurate transition at 216°C in $\text{Ca}_2\text{CoSi}_2\text{O}_7$ (Fig. 2).

The structural misfit between the X ions and YZ_2O_7 layers in the $\text{X}_2\text{YZ}_2\text{O}_7$ melilite structure is believed to cause these deviations. The structural misfit of the Ca ions can also be seen from the X-O interatomic distances and apparent valence of the X ions. Table 4 shows that Ca-O distances in the Ca silicate melilite varieties are significantly larger ($2.565 \text{ \AA}$ to $2.576 \text{ \AA}$) than the $2.50 \text{ \AA}$ expected from ionic radii considerations (Shannon, 1976). This is in contrast to the more normal Sr-O and Ba-O distances found in $\text{Sr}_2\text{CoSi}_2\text{O}_7$ and $\text{Ba}_2\text{FeGe}_2\text{O}_7$ where the differences between the close and far oxygen neighbors has been narrowed considerably.

The apparent Ca^{2+} valences in akermanite,

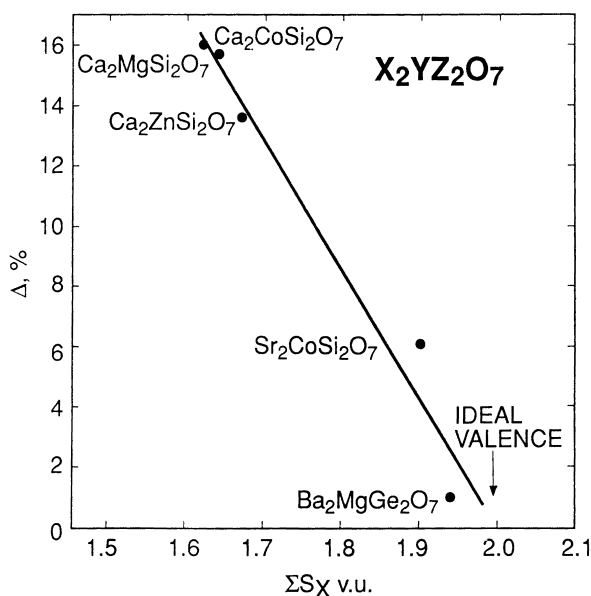


Fig. 3. Deviations from the oxide additivity rule vs. apparent bond valence. Bond valence sums calculated from distances in $\text{Ca}_2\text{MgSi}_2\text{O}_7$ from Kimata & Ii (1981), in $\text{Ca}_2\text{CoSi}_2\text{O}_7$ from Kimata (1983a), in $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ from Louisnathan (1969), $\text{Sr}_2\text{CoSi}_2\text{O}_7$ ($\text{Sr}_2\text{MgSi}_2\text{O}_7$) from Kimata (1983b), and in $\text{Ba}_2\text{MgGe}_2\text{O}_7$ ($\text{Ba}_2\text{FeGe}_2\text{O}_7$) from Malinovskii *et al.* (1976) and bond valence parameters given in Brown & Altermatt (1985).

hardystonite and $\text{Ca}_2\text{CoSi}_2\text{O}_7$ (~ 1.6 valence units (v.u.)) differ widely from those expected (1.85 - 2.2 v.u., O'Keefe, 1989) whereas the apparent valences of Sr^{2+} in $\text{Sr}_2\text{CoSi}_2\text{O}_7$ and Ba^{2+} in $\text{Ba}_2\text{MgGe}_2\text{O}_7$ are much closer to their ideal values. Armbruster *et al.* (1990) have evaluated bond valence sums in a wide variety of melilites. From their compilation, it seems likely that other compositions such as $\text{Ca}_2\text{ZnGe}_2\text{O}_7$, $\text{Sr}_2\text{MnSi}_2\text{O}_7$ and $\text{Sr}_2\text{ZnGe}_2\text{O}_7$ will also show deviant dielectric behavior. Fig. 3 shows that deviations from ideal valences correlate well with the deviations from the oxide additivity rule. This correlation indicates that the oxide additivity rule deviations are caused by the relative looseness of fit of the X ions in their antiprismatic sites with the deviations increasing in the order Ba-Sr-Ca. This suggests that Ca is behaving like the "rattling" cation proposed by Orgel (1958). The effect was described by Dunitz & 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

and/or anions resulting in polyhedral distortion. However, when crystal symmetry restricts the motion of the cation and/or anion such as in melilite, pyrope garnet and CaYAlO_4 , larger than normal bond distances and/or thermal motion may occur. As the cation size becomes smaller and smaller, instabilities begin to set in. In certain structures such as those containing Ti^{4+} and Nb^{5+} , this instability can give rise to ferroelectricity. In melilites, this instability gives rise to incommensurate structures.

Normally, increases of interatomic distances when accompanied by a coordination number change do not cause deviations from the additivity rule. For example, the additivity rule is obeyed reasonably well even with octahedral Mg in MgO and with tetrahedral Mg in MgAl_2O_4 (Shannon & Subramanian, 1989; Shannon & Rossman, 1991) and with octahedral Al in Al_2O_3 and mixed octahedral/tetrahedral Al in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (Shannon *et al.*, 1990). Evidently changes in κ associated with coordination changes are compensated by changes in molar volume. However, when increased distances are not accompanied by a change in coordination number, such as in the melilite, pyrope garnet and CaYAlO_4 , the results appear as an apparent increase in total polariza-

bility. An appealing physical interpretation of this phenomenon is that the polarizability of Mg or Ca is increased when the bond distances are larger than normal, i.e. the "rattling ion" concept.

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