

Electronic and Ionic Polarizabilities in Some Rutile Type Crystals

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In several earlier papers (1-3), we suggested that certain transition metal oxides with a high dielectric constant as well as large refractive indices such as TiO_2 (rutile), WO_3 , and $\text{H-Nb}_2\text{O}_5$ use crystallographic shear (CS) planes to accommodate nonstoichiometry. In view of the correlation between a high dielectric constant and CS planes, the relaxation due to polarizabilities seems to be one of the factors which predisposes such a material to this type of stoichiometric change. To reveal this correlation in greater depth, we have calculated electronic and ionic polarizabilities of rutile, because the most reliable experimental data are available for this crystal compared to WO_3 and $\text{H-Nb}_2\text{O}_5$. We found that rutile has an extremely large value for the electronic polarizability of the anion (2, 3); this polarizability appears to be one of the most important factors in formation of CS planes. To compare the electronic polarizability of the anion in TiO_2 with that of other rutile-type crystals, we have determined polarizabilities of TiO_2 ,¹ SnO_2 , PbO_2 , MgF_2 , and ZnF_2 , the dielectric properties of which have been obtained experimentally.

¹ In our previous calculations of polarizabilities in rutile (2, 3), we used Lorentz factors evaluated by Parker (5). Here we have recalculated Lorentz factors with the lattice parameters reported by Wyckoff (6).

In calculating polarizabilities, we have employed Ruffa's theory (4) and Parker's theory (5) with the lattice parameters quoted from Wyckoff (6) and the free-ion polarizabilities of cations evaluated by Pauling (7). These theoretical procedures require specification of the Lorentz factors and the Madelung potential acting on each ion site. We have obtained Madelung potentials by the procedure of van Gool and Piken (8), and have calculated Lorentz factors by direct summation, because of excellent convergences.

The polarizabilities calculated in this way have been tabulated in Table I, in which the static dielectric constants and the refractive indices employed in the calculations are also indicated, together with references. As there are two sets of experimental data for the static dielectric constant in SnO_2 (9, 10), we have calculated the polarizabilities in SnO_2 using both of them. As for PbO_2 , Meisner (11) reported that the refractive index in the **a** direction (n_a) is 2.3, while that in the **c** direction (n_c) is less than n_a . According to him, the static dielectric constant in the **a** direction, $(\epsilon_0)_a$, and that in the **c** direction, $(\epsilon_0)_c$, are represented by $(\epsilon_0)_a = 20.7 + 5.29$ and $(\epsilon_0)_c = 41.5 + n_c^2$. Therefore, we have adopted the following refractive index values in the **c** direction: $n_c = 2.3 = (5.29)^{1/2}$, $(5.0)^{1/2}$, $(4.0)^{1/2}$, $(3.0)^{1/2}$ and

TABLE I

		TiO ₂	SnO ₂	SnO ₂	PbO ₂	PbO ₂
Static dielectric constant	(ϵ_0) _a	89.8 ^(2,3)	14.0 ⁽⁹⁾	23.4 ⁽¹⁰⁾	25.99 ⁽¹¹⁾	25.99
	(ϵ_0) _c	180.0	9.0	24.0	46.79	46.5
Refractive index	n_a	2.616 ^(2,3)	1.9968 ⁽¹⁸⁾	1.9968	(5.29) ^{1/2(11)}	(5.29) ^{1/2}
	n_c	2.903	2.0929	2.0929	(5.29) ^{1/2}	(5.0) ^{1/2}
Electronic polarisability of the cation		0.587	1.520	1.520	1.448	1.448
Electronic polarisability of the anion	a axis	1.950	1.233	1.233	1.980	1.980
	c axis	2.227	1.221	1.221	1.868	1.794
Ionic polarisability of the cation	a axis	0.865	1.066	1.233	0.967	0.967
	c axis	1.036	1.005	1.708	1.784	1.883
Ionic Polarisability of the anion	a axis	0.453	0.425	0.486	0.453	0.453
	c axis	0.684	0.723	1.039	1.109	1.160

(2.0)^{1/2}, and we have calculated the polarizabilities in PbO₂ associated with these refractive indices. Since three evaluations of dielectric constants in MgF₂ (12–14) have been reported, we have calculated polarizabilities in MgF₂ using all of them.

Among the crystals investigated, it is only TiO₂ which can contain CS planes in the nonstoichiometric state. In a comparison of polarizabilities in Table I, TiO₂ is found to have a large electronic polarizability of the anion, whereas the other polarizabilities in TiO₂ are, in general, lower than those in other crystals. It is therefore clearly the high electronic polarizability of the oxygen more than any other single factor which is responsible for the high dielectric constant of TiO₂. Therefore, such a comparison suggests a correlation between the electronic polarizability of the anion and the occurrence of CS planes. On the other hand, PbO₂ has also a large value for the electronic polarizability of the anion. As seen in Table I, we have changed the value for n_c from (5.29)^{1/2} to (2.0)^{1/2} and calculated the electronic polarizability of the anion associated with the change in the

value of n_c . We thus obtained values in the range of $1.94 \times 10^{-3} \text{ nm}^3$ to $1.46 \times 10^{-3} \text{ nm}^3$ for the average electronic polarizability of the O²⁻ ion, [$\epsilon(\epsilon_0)_c + 2 \epsilon(\epsilon_0)_a$]/3, while the average value in TiO₂ is $2.04 \times 10^{-3} \text{ nm}^3$. Therefore, the minimum difference in the average value between TiO₂ and PbO₂ is only $0.1 \times 10^{-3} \text{ nm}^3$. However, according to another calculation of ours (15), even a small change in the electronic polarizability of the anion such as $0.15 \times 10^{-3} \text{ nm}^3$ results in a very large change in the static dielectric constant (about 200) in the rutile structure. Therefore, even as small a difference in the electronic polarizability as that between TiO₂ and PbO₂ has a significant influence upon dielectric properties. To establish definitely the correlation between the electronic polarizability of the anion and formation of CS planes, we have to quantify the relaxation effect due to polarizabilities in formation of CS planes; this effort is under way.

Last of all, it is of some interest to compare our results with others. Shanker *et al.* (16) obtained electronic polarizabilities in rutile type crystals using a relationship that

TABLE I—Continued

PbO ₂	PbO ₂	PbO ₂	MgF ₂	MgF ₂	MgF ₂	MgF ₂	ZnF ₂
25.99	25.99	25.99	5.4 ⁽¹³⁾	5.501 ⁽¹⁴⁾	5.4 ⁽¹³⁾	5.501 ⁽¹⁴⁾	7.5 ⁽¹³⁾
45.5	44.55	43.55	4.6	4.826	4.6	4.826	7.2
(5.29) ^{1/2}	(5.29) ^{1/2}	(5.29) ^{1/2}	1.378 ⁽¹²⁾	1.378	(1.9) ^{1/2(13)}	(1.9) ^{1/2}	(2.1) ^{1/2(13)}
(4.0) ^{1/2}	(3.0) ^{1/2}	(2.0) ^{1/2}	1.390	1.390	(1.9) ^{1/2}	(1.9) ^{1/2}	(2.6) ^{1/2}
1.448	1.448	1.448	0.149	0.149	0.149	0.149	0.455
1.980	1.980	1.980	0.753	0.753	0.754	0.754	0.828
1.482	1.050	0.408	0.846	0.846	0.822	0.822	1.177
0.967	0.967	0.967	2.124	2.145	2.123	2.144	2.237
2.313	2.964	4.063	1.835	1.916	1.877	1.957	1.913
0.453	0.453	0.453	0.847	0.853	0.846	0.853	0.859
1.375	1.674	2.120	1.036	1.079	1.056	1.100	1.143

they had derived earlier, but they did not take into account the optical dielectric constant determined experimentally nor the effective electric fields acting on ions, which involve the Lorentz factors. In comparing our results with theirs, there are significant differences in the values for electronic polarizabilities of TiO₂, SnO₂, and PbO₂, though agreements in polarizabilities of MgF₂ and ZnF₂ is good. However, considering the difference in the theoretical treatments, this agreement is rather unexpected. Calage *et al.* (17) obtained experimentally a value of about $1.60 \times 10^{-3} \text{ nm}^3$ for the electronic polarizability of the O²⁻ ion in SnO₂. Though our calculated value for this polarizability is somewhat lower, ours is closer to the experimental value than to the value evaluated by Shanker *et al.* ($2.10 \times 10^{-3} \text{ nm}^3$).

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