

# On the Relations between the Dielectric Constants and Chemical Constitutions, Crystal Structures of Carbonate and Sulphate Minerals.

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*With 6 figures*

## Abstract

This study was carried on with the object of elucidating the fundamental mechanism underlying the dielectric constants of carbonate and sulphate minerals from the stand-points of polarization theory. The Polarization of these minerals are considered to be composed of the two components such as electronic and atomic polarizations. The main part of the electronic polarization is almost due to that of acid radicle and shows nearly same value in each group, but different value according to the crystal orientation. The residual part of the electronic polarization is due to the polarizability of cation and increase its value proportionally according to the magnitude of it. The intensity of atomic polarization depends on the polarizability of each ion, that is to say, the distortionability of ion itself and the existence of distortionable space in crystal lattice. These facts were confirmed with the minerals of aragonite-group, calcite-group and barite-group.

## Preface

It is evident that the dielectric constants of minerals change their values according to chemical constitutions and crystal structures. In the case of isomorphous substance the variation of the dielectric constants depends chiefly upon the chemical constitutions.<sup>(1)</sup> So if we have a standard curve showing the relationship between the dielectric constants and the chemical constitutions of isomorphous minerals, it is possible to determine the chemical constitution of a mineral belonging to that isomorphous series by means of the determination of the dielectric constant.

When the change of crystal structure or the dehydration of combined water is observed with a mineral subjected to heating, these phenomena are followed by the rapid change of the dielectric constant. Therefore we can also determine the transition or dehydration temperature by the heating curve of the dielectric constant of the mineral.

This study was carried on with the object of elucidating the fundamental

mechanism underlying the abovementioned variation phenomena of the dielectric constant.

### Dielectric Constant and Polarization

As is well known as "polarization", the normal internal state of substance is subjected to the electric displacement or electric doublets by the electromagnetic induction. When the displacement is restricted to the electronic, it is called "electronic polarization" and when restricted to the atomic displacement, "atomic polarization". Some substances which have permanent dipolemoments, however, undergo the "orientation polarization" beside the two kinds of the polarizations above mentioned. Therefore the polarizations of substances are distinguished as electronic, atomic and orientation polarization (generally referred to as  $P_e$ ,  $P_a$  and  $P_o$ ).

The electronic polarization is due to the displacement of electron, namely of the valency electron by the electromagnetic oscillation of a frequency higher than that of the visible ray; the relation between the electronic polarization and the dielectric constant is shown in the following Clausius-Mosotti formula;  $P_e$  stands for molar electronic polarization,  $M$  for molecular weight,  $\rho$  for density and  $\epsilon$  for dielectric constant.

$$P_e = \frac{M}{\rho} \frac{\epsilon - 1}{\epsilon + 2} \quad (1)$$

Since the molar electronic polarization is generally equal to the molar refractivity when the polarization is caused by the electro-magnetic wave of a frequency higher than that of the visible ray therefore, the above formula may be transformed into the following equation;  $R$  indicates the molar refractivity and  $n$ , mean refractive index.

$$P_e = R = \frac{M}{\rho} \frac{n^2 - 1}{n^2 + 2} \quad (2)$$

According to this equation, we can obtain the molar electronic polarization by determining the refractive index. Under the electro-magnetic wave of a frequency near that of infra-red, the electronic polarization is accompanied with the atomic polarization. Therefore, the molar polarization consists of both the electronic and the atomic polarization.

With the polar materials, on the other hand, the orientation polarization is caused especially by the electro-magnetic wave of lower frequency. But this polarization gradually disappears with the increase of the frequency owing to the corresponding increase of the resistance for the orientational displacement of the permanent electrostatic dipole.

As the orientation polarization is, in general, inversely proportional to the absolute temperature, the molar polarization can be expressed in the following equation introduced by F. C. Frank;<sup>3)</sup> where  $N$  shows Avogadro's number  $6.02 \times 10^{23}$ ,  $k$  Boltmann's constant  $1.38 \times 10^{-16}$ ,  $u$  dipole moment,  $\alpha_e$  electronic polarizability,  $\alpha_a$  atomic polarizability and  $T$  absolute temperature.

$$P = P_e + P_a + P_o = \frac{4\pi N}{3} \left( \alpha_e + \alpha_a + \frac{u^2}{3kT} \right) \quad (3)$$

By substituting a and b for  $\frac{4\pi N}{3}(\alpha_e + \alpha_i)$  and  $\frac{4\pi N}{3}\left(\frac{u^2}{k}\right)$  respectively, we have a following simple equation;  $P = a + \frac{b}{T}$ . Accordingly the molar polarization of the polar substance undergoes a change with the rise or fall of the temperature. As is described later, the observed values of  $P_e$  and  $P_a$  likewise change with the rise or fall of the temperature, but the variation degree  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  calculated with calcite and aragonite is merely in the vicinity of the order of  $10^{-4}$ .

Considering the above mentioned facts, all materials may be classified into the following three types by the point of view of polarization phenomena.<sup>(4)</sup>

- (1) Non-polar substances showing the electronic or optical polarization only.
- (2) Polar substances showing the electronic as well as the atomic or infra-red polarization.
- (3) Dipolar substances showing the orientation polarization in addition to the electronic and atomic polarization.

The polarization of the first class is due to the elastic displacement of electrons only. All dielectrics consisted of monoatomic molecule such as sulphur, diamond, inert gases etc. belong to the first class and their dielectric constants satisfy the Maxwell relation  $\epsilon = n^2$ .

Substances included in class(2) have the atomic as well as the electronic polarization and consist of dipolar groups of atoms but have no total dipole moment. The atomic polarizations of these substances are, however, generally so small compared with the electronic polarizations that they may be considered as non-polar substances. All minerals under consideration in our study are ionic crystals, and the atomic polarizations are found in the same degree as that of the electronic polarization. The polarization ratios  $\frac{P_a}{P_e}$  of aragonite, calcite and barite groups, are measured as shown in the following table.

		$\frac{P_e}{P_a}$	Mean value
Aragonite group	Aragonite	1.14	
	Witherite	1.24	
	Strontianite	1.25	
	Cerrusite	2.10	1.43
Calcite group	Calcite	0.94	
	Dolomite	0.99	
	Magnesite	1.09	
	Smithonite	1.35	
	Rhodocrosite	1.42	
	Siderite	1.60	1.23
Barite group	Anhydrite	0.63	
	Celestite	0.84	
	Barite	0.96	
	Anglesite	1.04	0.86

The mean value of  $\frac{P_e}{P_a}$  of aragonite group is largest, that of barite group is

smallest and that of calcite group is intermediate. Of these minerals, the minerals of Pb-salt show largest value, and with others, the values are found decreasing in the order of Ba-salt, Sr-salt and Ca-salt.

There are various kinds of organic and inorganic substances consisted of dipolar molecules in the state of liquid or gas. Those substances thereby have extraordinary large dielectric constant owing to dipole moments and belong to the third class.

### Chemical Constitution and Dielectric Constant

As already stated, the molar polarization calculated by the dielectric constant consists of both the electronic and atomic polarization. Of these, the electronic polarization  $P_e$  can be determined by the refractive index according to the above equation(2), and the atomic polarization by the difference between the total and electronic polarization. The value of each mineral belonging respectively to aragonite, calcite and barite groups is shown in Table 1; where  $\epsilon$  stands for the mean value of respective axial dielectric constant and  $P$  for the total polarization.

Table 1

		$\epsilon$	$M/\delta$	$P$	$P_e$	$P_a$
A) Aragonite group						
Aragonite	$\text{CaCO}_3$	7.48	34.01	22.80	12.15	10.65
Witherite	$\text{BaCO}_3$	6.33	45.90	29.37	16.25	13.12
Strontianite	$\text{SrCO}_3$	5.88	39.87	24.69	13.81	10.88
Cerussite	$\text{PbCO}_3$	22.60	41.05	36.04	20.23	15.81
B) Calcite group						
Magnesite	$\text{MgCO}_3$	5.99	23.57	17.22	10.06	7.16
Calcite	$\text{CaCO}_3$	8.30	36.57	25.61	12.38	13.23
Dolomite	$(\text{Ca}, \text{Mg})\text{CO}_3$	7.18	32.00	21.54	11.27	10.27
Rhodocrosite	$\text{MnCO}_3$	7.65	31.19	21.49	12.60	8.89
Siderite	$\text{FeCO}_3$	7.68	22.65	15.63	9.61	6.02
Smithonite	$\text{ZnCO}_3$	9.35	57.97	20.58	11.82	8.76
C) Barite group						
Barite	$\text{BaSO}_4$	9.33	52.46	38.57	18.90	19.67
Anglesite	$\text{PbSO}_4$	36.47*	47.76	43.03	21.94	21.09
Celestite	$\text{SrSO}_4$	11.50	46.39	36.08	16.42	19.66
Anhydrite	$\text{CaSO}_4$	26.06*	45.63	39.48	15.34	24.15

Some of the figures marked by\* in Table 1 were copied from data given by J. Errea and Brasseur<sup>(5)</sup>, since it was impossible to determine such high dielectric constants by our apparatus and moreover to obtain an adequate specimen necessary for the measurement of the axial directions.

#### (1) Chemical constitution and electronic polarization

With respect to the electronic polarization of minerals, there are two fundamental factors. The one is the total sum of respective polarizabilities of all ions,  $a_1, a_2, \dots, a_n, \dots$  and the other is the crystal structure of minerals. First of all we shall consider here the effects which the polarizabilities of ions have on the dielectric constant. There are mutual relations among polarizability, radius of ion and atomic number<sup>(6)</sup>. It is to be noted that anion has larger volume and larger polarizability than those of cation, and therefore, the former has more important

effect on dielectric constant than the latter has. The lower the atomic valency of anion and the higher the atomic valency of cation is, the smaller the polarizability is; ions which have loosely combined electrons, that is to say, have large ionic radius, generally possess large polarizabilities. Judging from the above facts, the minerals composed of ions with large ionic radius generally show high electronic polarization, in other words, high refractive index. Therefore, the majority of electronic polarization in carbonate and sulphate minerals is mostly due to the acid radicales  $\text{CO}_3^{''}$ ,  $\text{SO}_4^{''}$  which contain the most polarizable atomic ions such as  $\text{O}''$ , or  $\text{S}''$ .

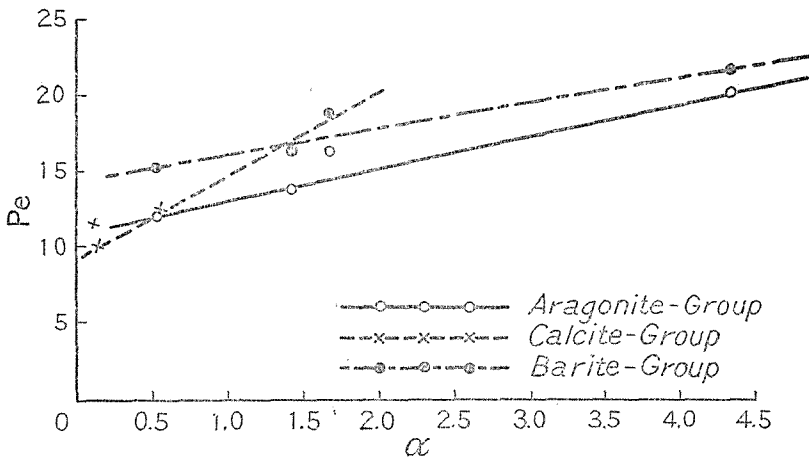


Fig. 1 Electronic Polarization ( $P_e$ )- Polarizability ( $\alpha$ )

As the result of calculation, the polarizations of acid radicles are rarely affected<sub>(7)</sub> by the varieties of cations which combine with them, but the total electronic polarization of minerals belonging to the same group depends upon the polarizability of cation as shown in Fig. 1. The electronic polarizations of each group are nearly proportional to the polarizabilities of cations with the exceptions of Ba-salts. Siderite and rhodocrosite are not entered in Fig. 1 on account of the fact that the polarizabilities of cations  $\text{Fe}''$  and  $\text{Mn}''$  are unknown. The electronic polarizations of anions such as  $\text{SO}_4^{''}$ ,  $\text{CO}_3^{''}$  can be calculated as follows by means of W. L. Bragg method.

Aragonite-group	10.22
Calcite -group	10.06
Barite -group	13.29

The electronic polarization of  $\text{CO}_3^{''}$  of aragonite-group is almost equal to that of calcite-group, and that of  $\text{SO}_4^{''}$  is larger than that of  $\text{CO}_3^{''}$  probably owing to the fact that the polarizability of S is larger than that of C.

As the atoms of these anions are tightly combined and some valency elect-

rons do not take part in the electronic polarization, the above polarization values should be smaller than the values calculated from the polarizabilities of each atomic ion.

## (2) Chemical constitution and atomic polarization

The atomic polarization is caused by the displacements of cations towards anions under the electro-magnetic induction. Accordingly the atomic polarization depends upon the distortionability of ion itself on one hand and upon the distortionable spacing of crystal structure on the other hand. Even if the distortionable space is absent, atomic polarization may possibly take place owing to the distortionability of ion itself, but the existence of distortionable spacing makes it larger. Concerning the distortionability of ion, the following factors must be considered from the standpoint of chemical constitutions ;

- (a) The higher valency ions are more distortionable.
- (b) The intensity of the polarizing powers of cation and anion are inversely proportional to the distortionability.
- (c) The more distortionable the ion is, the larger its polarizability is.

The mutual relations among the atomic polarizations, polarizabilities of cations and ion-radii of cations of minerals belonging to aragonite-group, calcite-group and barite-group are graphically represented in Fig. 2, Fig. 3.

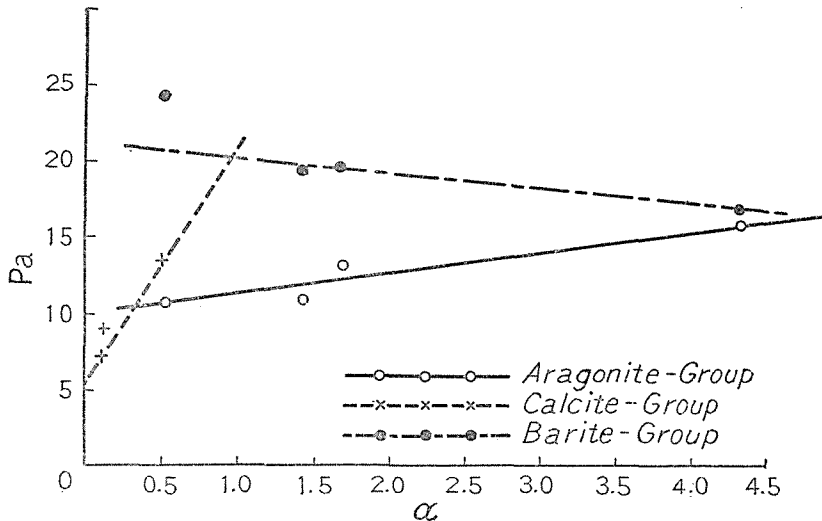


Fig. 2 Atomic Polarization (Pa)- Polarizability ( $\alpha$ )

Very regular relations between the atomic polarizations and polarizabilities of cations can be recognized in these minerals. The deviation of the barite-group may be ascribed to the fact that the crystal structure of this mineral is different from the other minerals. It is noteworthy that both the atomic polarizations and the

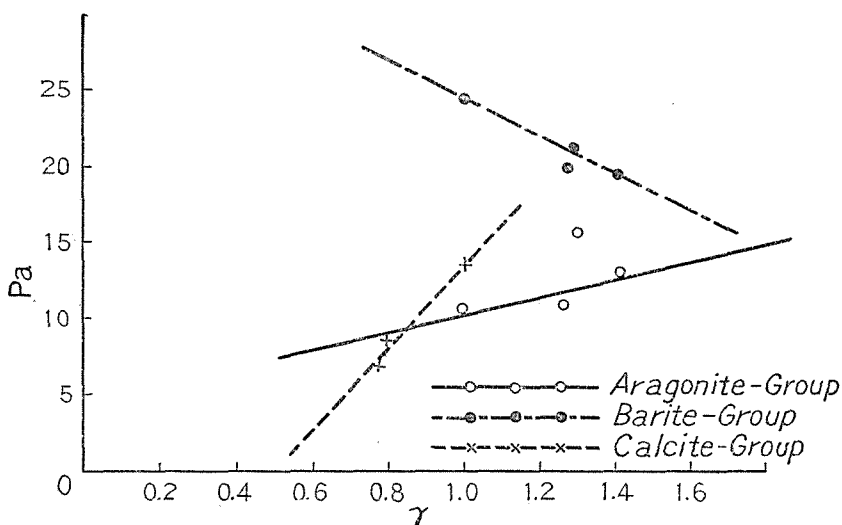


Fig. 3 Atomic Polarization (Pa)- Radius of Cation ( $\gamma$ )

polatizabilities of cations of aragonite-group and calcite-group minerals undergo similar variation but with the barite-group, the variation is the reverse. Similar facts may be found in the relation between the atomic polarization and the ion radius, with the exception of cerrusite of aragonite-group, the radius of Pb-ion being too small for its large polarizability. The decrease of atomic polarization of barite-group with the increase of polarizability of cation very favourably accounts for the effect of distortionable space in crystal structure. As the volume of the unit cell of barite-group is almost constant in spite of the increase of ion radius, the increase of cation radius makes the crystal packing more compact, thus diminishing the distortionable space in crystal lattice. The degrees of crystal packing of minerals of the barite-group are shown by comparing the univalent radii of these minerals<sub>(S)</sub>.

### Crystal Structure and Dielectric Constant

Crystal structure plays an important role in determining the dielectric constant. As shown in the table below, the dielectric constants of calcite and aragonite are not equal notwithstanding their identical constitutions.

	$\epsilon$	P	Pe	Pa
Calcite	8.30	25.60	12.38	13.25
Aragonite	7.48	22.80	12.15	10.65

The double refracting minerals show different polarizations according to the directions of the electric field towards the crystal axis. The results of measurements made with aragonite-group calcite-group and barite-group are shown in Table 2.

The electronic polarizations of calcite and aragonite are so alike that the

difference between the dielectric constants of the two minerals mainly depends that of atomic polarization. As already described, the atomic polarization is due to the distortionability, that is, to the crystal structure. The difference between the crystal structures of both minerals lies in the fact that the  $\text{CO}_3^{''}$  in calcite is situated at a position rotated by  $30^\circ$  from that in aragonite<sub>(9)</sub>. Therefore the distortionable space for  $\text{Ca}^{''}$  in calcite is larger than that of aragonite. To compare the distortionable space of both minerals is practically impossible. However, it is to be noted here that the volumetric ratio of unit cell of both minerals coincide remarkably with the ratio of atomic polarization.

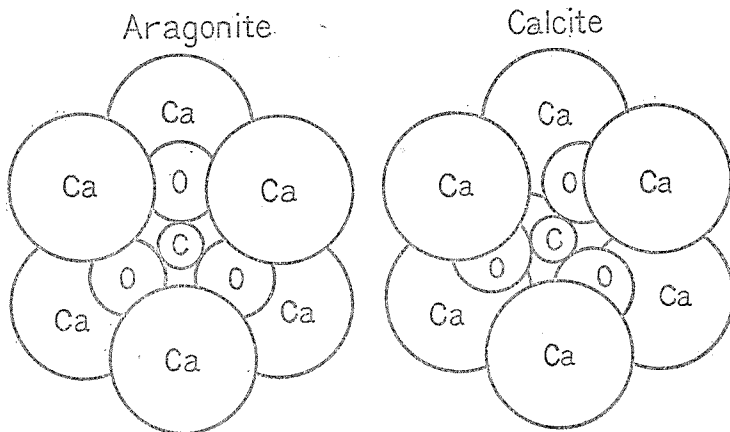


Fig. 4

$$\frac{\text{volume of unit cell of calcite}}{\text{volume of unit cell of aragonite}} = \frac{265.59}{224.36} = 1.20$$

$$\frac{\text{atomic polarization of calcite}}{\text{atomic polarization of aragonite}} = \frac{13.23}{10.65} = 1.24$$

#### (1) Crystal structure and electronic polarization

It is evident from Table 2 that the electronic polarizations of these minerals are influenced mainly by the electronic polarizations of acid radicals. Therefore the difference owing to crystal orientation depends on the directionality of the acid radicals. With the calcite,  $\text{CO}_3^{''}$  group lies on a plane perpendicular to the threefold vertical axis and their electronic polarizations are different according to the directions of electric fields.

When the electric field is parallel to the plane of the  $\text{CO}_3^{''}$  group as shown in Fig. 5 (A), the electronic polarizations of oxygen atoms are increased by the neighbouring oxygen atoms as well as by the effect of electric field, and when the electric field is perpendicular to the plane of the  $\text{CO}_3^{''}$  group as shown in Fig. 5 (B), the electronic polarizations of oxygen atoms are decreased by the mutual effects of the neighbouring oxygen atoms from the electronic polarizations induced by electric field. That is the reason why the electronic polarization is high in the former case and is low in the latter case. There is a relation between the dielectric constant and refractive index ( $n$ ) which is expressed by



Table 2

Mineral	$\epsilon$	$\epsilon$			n			P		
		//a	//b	//c	//a	//b	//c	//a	//b	//c
A) Aragonite-Group										
Aragonite	7.48	9.66	7.42	6.56	1.636	1.682	1.532	25.26	23.19	21.81
Witherite	6.33	7.80	7.50	6.35	1.677	1.676	1.529	31.85	41.41	29.41
Strontianite	5.88	7.69	7.56	6.58	1.667	1.667	1.520	27.53	27.36	25.93
Cerrousite	2.60	25.40	23.20	19.20	2.078	2.076	1.804	36.56	36.16	25.24
B) Calcite-Group										
	$\epsilon$	ic		//c	ic		//c	ic		//c
Magnesite	5.99	6.53	5.10		1.717	1.515		17.87	15.92	
Calcite	8.30	8.53	7.85		1.658	1.486		25.84	25.17	
Dolomite	7.18	7.53	6.11		1.682	1.503		21.70	20.16	
Rhodocrosite	7.65	8.22	7.06		1.815	1.597		22.03	20.90	
Siderite	7.68	7.90	6.90		1.872	1.632		15.79	15.02	
Smithonite	9.35	9.40	9.30		1.872	1.618		20.61	20.54	
C) Barite-Group										
	$\epsilon$	//a	//b	//c	//a	//b	//c	//a	//b	//c
Barite	9.33	6.97	10.07	7.70	1.636	1.637	1.648	34.91	39.44	36.29
Anglesite	36.47	27.50	54.60	27.30	1.877	1.882	1.894	42.90	45.22	42.87
Celestite	11.50	7.70	18.50	8.30	1.622	1.624	1.631	32.04	39.60	32.68
Anhydrite	20.60	9.30	44.00	8.50	1.571	1.576	1.614	33.52	42.65	32.59

A	Pe			Pa			Pe(Anion)			Pe(ation)		
	//a	//b	//c	//a	//b	//c	//a	//b	//c	//a	//b	//c
	12.94	12.88	10.54	12.32	10.30	11.27	10.92	10.92	8.52	2.02	11.96	2.02
	17.29	17.27	14.16	14.56	14.14	15.25						
	14.84	14.84	12.12	12.69	12.52	13.81	11.49	11.49	8.78	3.35	3.35	3.34
	21.56	21.53	17.61	15.00	14.63	17.63	11.27	11.27	7.41	10.29	10.26	10.20
B	ic		//c	ic		//c	ic		//c	ic		//c
	10.85	8.31		7.02	7.61	10.39	7.86		0.46	0.45		
	13.30	10.37		12.54	14.80	11.32	8.38		1.98	1.98		
	12.12	9.46		9.58	10.70	10.89	8.23		1.23	1.23		
	13.52	10.62		8.51	10.28	11.19	8.29		2.33	2.33		
	10.31	8.08		5.48	6.94	11.19	8.28		-0.88	-0.20		
	12.73	9.80		7.88	10.74	11.02	8.09		1.81	1.71		
C	//a	//b	//c	//a	//b	//c	//a	//b	//c	//a	//b	//c
	18.81	18.83	19.09	16.10	20.61	17.20	13.36	13.36	13.68	5.48	5.47	5.41
	21.82	21.91	22.12	21.08	23.31	20.75						
	16.34	16.38	16.53	15.70	23.22	16.35	13.06	13.06	13.25	3.28	3.32	3.28
	14.99	15.01	15.90	18.53	17.64	16.69						

Maxwell's law as  $\epsilon = n^2$ , so the axial electronic polarizations can be calculated from the respective indexes determined by each axial oriented section. The

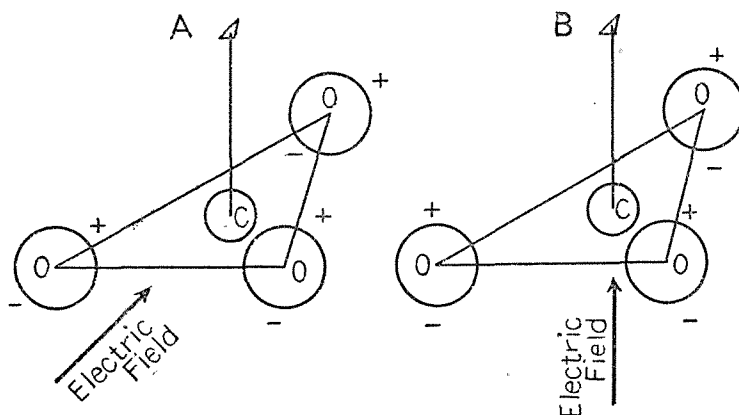


Fig. 5

calculated results of calcite-group, aragonite-group and barite-group minerals are shown in Table 2.

(2) Crystal structure and atomic polarization

The atomic polarizations of calcite-group and aragonite-group which were determined by the sections parallel to vertical axis, on the contrary, is higher than that determined by the sections perpendicular to vertical axis. The electronic polarizations of each mineral which belongs to the barite-group increase their values slightly in the directions of a, b and c successively but atomic polarization is highest in the direction of b axis. The relations of atomic polarizations determined by the direction of vertical axis and lattice constants to vertical axis or polarizabilities of cations and anions are shown in Table 3 and in Fig. 6.

Table 3

	$C_0 \text{ \AA}$	$C_\alpha$	$A_\alpha$	$C_0(C_\alpha + A_\alpha)$	Pa
Aragonite	5.72 \AA	0.531	8.51	51.77	11.27
Strontianite	6.08	1.420	8.78	62.02	13.81
Witherite	6.54	1.690	8.30*	65.20	15.25
Cerussite	6.10	4.340	7.41	71.18	17.63

- $C_\alpha$  Polarizability of cation
- $A_\alpha$  Polarizability of anion to the direction of vertical axis
- $C_0$  Lattice constant along the vertical axis
- \* Polarizability of anion in witherite is unknown so this is a mean value of three other minerals

Judging from the above results, the ratio of atomic polarizations parallel to vertical axis of each minerals of aragonite-group nearly correspond to the ratio calculated by multiplying the lattice constant of c-axis by the polarizabilities of cation and anion.

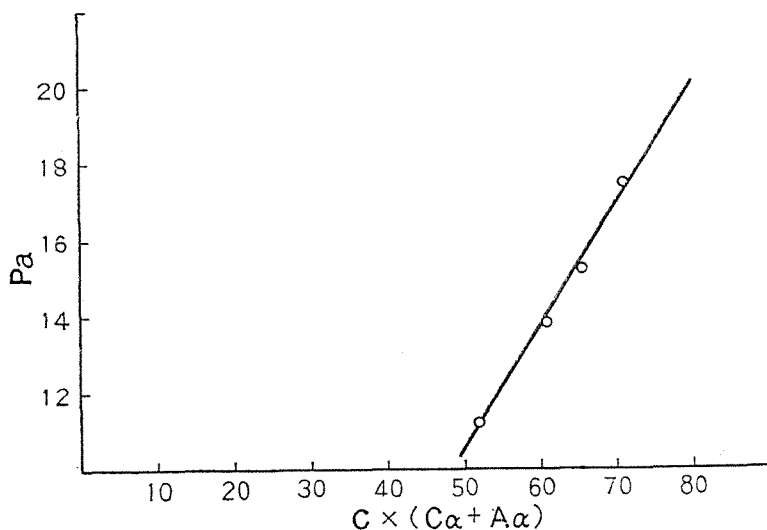


Fig. 6

### Summary

- 1) The dielectric constants of carbonate and sulphate minerals are composed of the two components, electronic and atomic polarizations, and have no orientation polarization.
- 2) The differences of electronic polarizations according to the crystal orientation are almost due to the directional magnitudes of the electronic polarizations of acid radicle and have almost no relation to those of cations.
- 3) The electronic polarizations of the isomorphous minerals belonging to aragonite-group, calcite-group and barite-group are proportional to the degrees of polarizabilities of cations.
- 4) The anion group  $\text{CO}_3''$  in carbonate crystal are arranged in the horizontal planes vertical to c-axis, so the electronic polarization in the direction perpendicular to c-axis is generally greater than that in the direction parallel to c-axis. The electronic polarizations of barite-group increase the values slightly in the directions of a, b and c axis.
- 5) The major part of electronic polarizations of carbonate and sulphate minerals are mostly due to the anion group  $\text{CO}_3''$ ,  $\text{SO}_4''$  which contain most polarizable atomic ion.
- 6) The minerals constructed with ionic bonds show nearly the same or smaller quantity of atomic polarization compared with electronic polarization.
- 7) The intensity of atomic polarization depends on the polarizability of each ion, the distortionability of ion itself and the existence of distortionable space in crystal lattice.
- 8) The volumetric ratio of unit cell of calcite to aragonite remarkably coincides with that of the atomic polarization of these minerals.

- 9) The atomic polarization of carbonate minerals is higher in the direction parallel to vertical axis than that in the direction perpendicular to vertical axis. In the case of barite-group, atomic polarization is highest in the direction of b axis.
- 10) The ratio of atomic polarizations parallel to the c-axis of aragonite-group minerals nearly corresponds to the ratio calculated by multiplying the lattice constant  $C_0$  by the polarizabilities of cation and anion.

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