Structural dependence of the optical birefringence of crystals with calcite and aragonite type structures.

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Analysis of the available structural and optical data on calcite and aragonite type materials suggests a relationship between their birefringence, anion size and cation electronegativity.

The structural dependence of the birefringence of calcite and the carbonates and nitrates isostructural with calcite, has been the subject of a number of investigations over the past fifty years. The latest and most comprehensive study is that given by Lo (1973).

It was on the subjects of calcite and aragonite that Bragg, in his now classical (1924) paper, first succeeded in correlating birefringence with crystal structure, using the point-dipole theory as developed by Lorentz (1909) and Ewald (1921). In his approach, however, Bragg considered optical anisotropy to arise from different dipole–dipole coupling along different crystallographic directions. and neglected the possibility of intrinsic anisotropy in the constituent atoms, particularly oxygen. The converse was done by Bhagavantum (1942), while Lawless & Devries (1964) took into consideration both sources of anisotropy, but evaluated only nearest-neighbour interactions in their analysis. In his study, Lo (1973) computed, in a manner not subjected to the above criticisms, the cation and anion polarizabilities for all the carbonates and nitrate isostructural with calcite. Lo, in assessing the results of his analysis, considered there to be no established trend between birefringence and cation/anion polarizations or with the cation species. He summarized his conclusions as 'within the validity of the

point-dipole approximation the present investigation indicates that the polarizability of polyatomic anions in crystals is just as dependent on the nature of the constituent atoms as on the crystalline environment in which they are found.'

In all the above mentioned studies it is evident that, without exception, the authors assumed that the dimension of the planar anion, CO_3^{2-}, NO_3^-, is invariant and independent of the associated cation species. The reason for this assumption is perhaps obvious, namely that in very few cases have any of these structures been determined with adequate precision to evaluate the C–O or N–O bond lengths. However, the field of a dipole decays as a function of the inverse cube of the distance, and this brings in two considerations. Firstly, it is apparent that the induction effect on an oxygen atom by other atoms will be stronger for atoms in the same planar group than for those in neighbouring groups. Secondly, relatively small changes in C–O or N–O bond lengths could have a marked effect on the resultant polarization of the oxygen atoms in the anion and thus the ultimate birefringence of the crystal.

A survey of the available literature has revealed that for only relatively few of these structures have the oxygen positional parameters been determined. Table 1 summarizes the known structural data on the calcite type carbonates

Table 1. *Optical and structural data for the calcite and aragonite type carbonates*

Calcite	N_e	N_o	$\Delta N = N_e - N_o$	$\langle N \rangle = \frac{1}{3}(2N_e + N_o)$	$\Delta N/\langle N \rangle$	Lattice constants Å a	c	Anion bond length Å C–O	Cation electro-negativity e.n.
CoCO₃	1·60	1·855	−0·255	1·69	0·150	4·6581	14·958 (a)		1·8
CdCO₃	1·60	1·85	−0·25	1·68	0·150	4·9204	16·298 (a)	1·23 (e)	1·7
FeCO₃	1·633	1·875	−0·242	1·714	0·141	4·6687	15·373 (a)	1·26 (e)	1·8
ZnCO₃	1·621	1·848	−0·227	1·697	0·134	4·6528	15·025 (a)		1·6
NiCO₃	1·692	1·913	−0·221	1·766	0·125	4·5975	14·723 (a)		1·8
MnCO₃	1·597	1·816	−0·219	1·670	0·131	4·7771	15·664 (a)	1·29 (e)	1·5
MgCO₃	1·509	1·700	−0·191	1·573	0·121	4·6330	15·016 (a)		1·2
CaCO₃	1·4864	1·6584	−0·1720	1·5437	0·111	4·9900	17·061 (a)		1·0
CaCO₃						4·9900	17·002 (b)	1·283 ± 2 (b)	1·0
CaCO₃						4·989	17·062 (c)	1·294 ± 4 (c)	1·0
CaCO₃						4·9887	17·0623 (d)		1·0
CaCO₃						4·99008	17·05951 (e)	1·294 (e)	1·0

Aragonite	N_α	N_β	N_γ	ΔN	$\langle N \rangle$	$\Delta N/\langle N \rangle$	Lattice constants Å a	b	c	Average anion bond length, Å C–O	Cation electro-negativity e.n.
PbCO₃	1·8037	2·0763	2·0780	0·2743	1·986	0·1381	5·166	8·468	6·146 (e)	1·23 (e)	1·8
CaCO₃	1·5300	1·6810	1·6854	0·1554	1·632	0·09522	4·959	7·968	5·741 (e)	1·32 (e)	1·0
CaCO₃							4·9614	7·9671	5·7404 (g)	1·282 ± 3 (g)	1·0
CaCO₃							4·9616	7·9705	5·7394 (h)	1·285 ± 4 (h)	1·0
BaCO₃	1·529	1·676	1·677	0·148	1·627	0·0909	5·3126	8·8958	6·4282 (g)	1·287 ± 9 (g)	0·9
SrCO₃	1·5199	1·6666	1·6685	0·1459	1·6148	0·09035	5·090	8·358	5·997 (g)	1·285 ± 8 (g)	1·0

(a) Graf (1961). (b) Chessin, Hamilton & Post (1965). (c) Sass, Vidale & Donohue (1957). (d) Krishna Rao, Nagender Naidu & Satyanara Murthy (1968). (e) Wyckoff (1960). (f) Lo (1973). (g) De Villiers (1961). (h) Dal Negro & Ungaretti (1971).
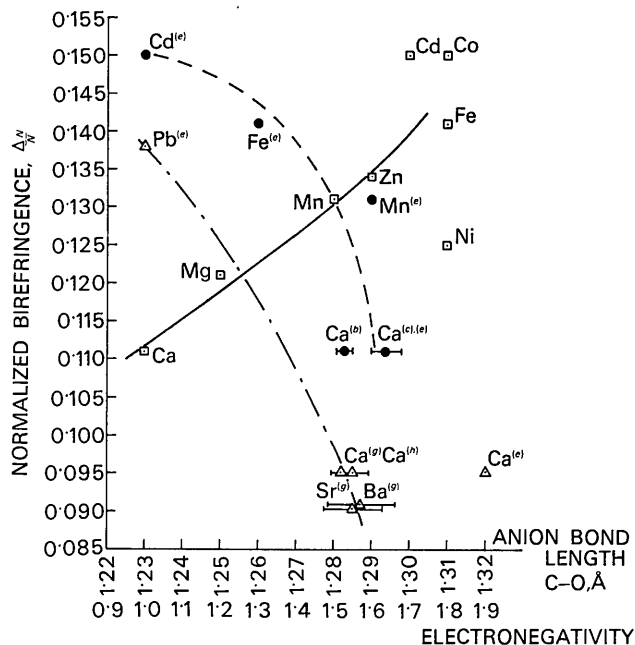
Fig. 1. Birefringence *versus* anion C–O bond length for calcite and aragonite structures, and birefringence *versus* electronegativity of cation in calcite structures. Legend: calcite — — ● — —; aragonite — — △ — —; cation electronegativity —— ⊡ ——.

and, for comparison, the data on the aragonite type structures of lead, barium, strontium and calcium carbonates. The relationship between the measured birefringencies (plotted as the normalized birefringence $\Delta N/\langle N\rangle$ to account for density effects) and C–O bond lengths for these crystals is explored graphically in Fig. 1. The errors on the determination of C–O bond lengths are also plotted in Fig. 1 for those carbonates where they are given in the structural determinations. No attempt, however, has been made to assess such errors where they have not been quoted, but it is expected that they will probably be large in the cases of the cadmium, iron and manganese carbonate determinations. Nevertheless, the trend apparent between the measured birefringencies and oxygen separations is very interesting, and there would have to be a fortuitous distribution of errors to make the C–O bond length appear structurally invariant. This trend would also appear to be confirmed by the data on the aragonite structures, which are also plotted in Fig. 1.

Consideration of Table 1 and Fig. 1 also suggests that the birefringence and oxygen bond length are influenced by the electronegativity of the cation species. For example, the electronegativity of oxygen is quoted as 3·2 compared with 1·0 for calcium and 1·7 for cadmium (Pauling, 1960), thus the difference in electronegativity is greater and the ionic character is greater for the Ca–O bond than the Cd–O bond. It is proposed that the stronger interaction of the Ca^{2+} with the CO_3^{2-} in the plane of the carbonate ion results in the electrons around the oxygen being distorted

towards the Ca^{2+} ion and this reduces the overlap of the electron atomic orbitals of the C–O bond. This weakening of the bond strength will effectively increase slightly the separation of the three oxygens in the anion, thus producing a reduction in the dipole–dipole coupling and consequently a decrease in birefringence. This is displayed graphically in Fig. 1, where, with the exception of the transition metals, the birefringence is seen to increase with the electronegativity of the cation species.

In conclusion, therefore, it would appear from interpretation of the available data, that the size of the planar anion in calcite type structures is probably not invariant, but is influenced by the electronegativity of the associated cation species. Furthermore, as a result of variations in dipole interactions in the planar anion, such a dimensional change could be a controlling factor on the birefringence of the structure. In view of the quality of experimental data on which they are based, these conclusions must be regarded as tentative and require substantiation by a comprehensive structural survey. It is strongly recommended that all future investigations be conducted on well characterized synthetic crystals, for one problem in the interpretation of the existing optical and structural data is that much of it was acquired from the study of minerals, which were often of uncertain composition. If, however, this apparent trend is confirmed, then a further refinement of the optical properties of the calcite type and other structures incorporating planar complex anions would seem to be suggested. The interesting corollary is that in such structures a measure of birefringence could give, to a first approximation, the dimensions of the planar anion.

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