Variation of refractive index with ionization potential in some isostructural crystals.

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Summary. A closer understanding of the causes for the variation of refractive index with change of composition has been sought in terms of certain properties of ions. The study is confined to isostructural ionic crystals. It is assumed that polarization of the anions (usually O^{2-} or F^-) makes the principal contribution to the total refractive index effect, and that variation of refractive index is determined mainly by variable anion polarization. Polarization of the anion is controlled largely by the field in which it finds itself which, in turn, depends on the effective force of attraction of the cation: ionization potentials are used for the purpose of comparing such forces. For compounds involving pairs of 8- and 18-electron cations (Mg^{2+} and Zn^{2+}; Al^{3+} and Ga^{3+}; Si^{4+} and Ge^{4+}; Ca^{2+} and Cd^{2+}) or pairs of transition cations (Zr^{4+} and Hf^{4+}; Nb^{5+} and Ta^{5+}; Mo^{6+} and W^{6+}) refractive indices are higher in the crystal that contains the cation of the element with the higher ionization potential. For larger suites of cations of various types (for example, Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, radii from 0·65 to 0·80 Å.) the predicted relationship between ionization potential and refractive index holds precisely for the compounds $A^{2+}SiF_6.6H_2O$ ($A^{2+} = Mg^{2+}$, &c.), but only in part for other compounds; this may be due to the effect of the crystal field on certain $3d$ transition cations.

MANY authors have discussed variation of refractive index with composition: Barth (1930), Hess (1949), Kennedy (1947), Hori (1954 and 1956), Jaffe (1956), and Larsen (1921 and 1934) are a few examples in mineralogy. The present paper is also concerned with the general problem of variation of refractive index with composition: its main purpose will be to seek a closer understanding of the physical causes of the variation of refractive index in ionic crystals.

The refractive index of a crystal depends mainly on its structure (Hori, 1954 and 1956, for example) and certain intrinsic properties of its component atoms or ions (Fajans and Kreidl, 1948, who refer to several earlier publications of Fajans and co-workers). If we consider isostructural ionic crystals only and confine ourselves to examining *variation* of refractive indices in suites of such crystals (the olivines, for example), it is necessary to consider only the properties of the ions in question. Under these conditions and for the purpose of this study the refractive index itself rather than the molar refraction will be used.

In ionic isostructural crystals, variation of refractive index should reflect the average state of polarization of the constituent cations and anions; the greater the degree of polarization (deformation), the greater the interaction with the passage of light waves and the higher the refractive index. The familiar generalization that anions are much more easily polarized (deformed) than cations may be assumed to be valid provided large and singly charged cations (Na^+, K^+, Rb^+, Cs^+, NH_4^+, Tl^+, and Ag^+) are omitted. Accordingly, in crystals other than those involving large singly charged cations, polarization of the anion should make the major contribution to the total refractive index because polarization of the anion will be far greater than that of the cation. The degree of polarization of the anion depends on the field in which it finds itself and this is controlled largely by the effective positive force of attraction of the cation. This force of attraction (polarizing power) depends on the charge and size of the cation and the efficiency with which its electrons shield (screen) the nuclear charge. A further contributing property may be the response of certain $3d$ transition metal cations to the field of the crystal—so-called crystal-field splitting.

The ionization potential[1] may be used to indicate the effective force of attraction of the cation (see, for example, Ahrens (1953) and Ahrens and Morris (1956)); the greater the energy needed to remove an electron the greater the polarizing power of the resultant cation. In suites of isostructural ionic crystals, those that contain cations of metals with the highest ionization potentials should have the highest refractive indices because the constituent anions should be deformed to the greatest extent. This prediction may be tested by examining groups of isostructural crystals, but because of a number of variables the comparisons should be made as rigorous as possible and in each of the discussions which follow, the anion will be the same, cationic charge will be constant, and the radii of the cations will be similar. Cationic charge distribution is another factor: whereas the charge distribution on 8- and 18-electron cations is probably spherical, that on the transition cations may be different and accordingly transition cations are omitted from the first comparisons.

For our purpose, an ionic compound is taken to mean one in which the ionic radius ratio rules are obeyed: this is not meant to imply that the bonds are regarded as purely ionic.

Refractive indices are usually either from Winchell (1931) or Winchell (1951).

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[1] The energy required to remove an electron from an atom or ion.

Isostructural ionic compounds involving 8- and 18-electron cations:
Al^{3+} *and* Ga^{3+}; Si^{4+} *and* Ge^{4+}; Ca^{2+} *and* Cd^{2+}; Mg^{2+} *and* Zn^{2+}.

The α refractive indices of the Ga and Ge substituted felspars (Gold-smith, 1950) are: $KAlSi_3O_8$, α 1·518; $KGaSi_3O_8$, α 1·533; $KAlGe_3O_8$, α 1·595; $KGaGe_3O_8$, α 1·615. Elevation of refractive indices by replacement of Al^{3+} and Si^{4+} by Ga^{3+} and Ge^{4+} respectively accords with prediction. The third ionization potentials of Al and Ga are 28·5 and 30·7 volts respectively, and the fourth ionization potentials of Si and Ge are 45·1 and 45·7 volts respectively. In each pair, the force of attraction of the 18-electron cation is evidently greater than that of the 8-electron cation and should cause greater polarization of the anion. The example is quite a good one as radii are similar; $Si^{4+} = 0·42$ Å, $Ge^{4+} = 0·47$ Å.; $Al^{3+} = 0·51$ Å., and $Ga^{3+} = 0·57$ Å.

CaF_2 and CdF_2. The radii of the two cations, Ca^{2+} and Cd^{2+}, are very similar, namely 1·01 and 0·97 Å. Their second ionization potentials (11·9 and 16·9 volts respectively) differ quite considerably (5 volts) and large refractive index differences are anticipated. Unfortunately structurally ionic compounds of cadmium are rare and few comparisons are possible. The pair, CaF_2–CdF_2, each having the 8:4 fluorite structure, is one good example. Goldschmidt (1926) observed that CaF_2 and CdF_2 were completely miscible and that refractive index varied regularly with composition; for CaF_2, $n = 1·43$ and for CdF_2, $n = 1·56$. The difference is quite large and accords with theory. The refractive index difference would probably be much larger if the anion were easily polarized.[1]

In the isostructural pair CaO and CdO (both NaCl-type), the respective refractive indices (average for various wavelengths) are 1·84 and 2·49; the difference is very large.

Mg and Zn compounds. The structures of many zinc compounds are not ionic but where comparisons can be made, the refractive indices of the zinc compounds are greater than those of magnesium. This accords with theory; for Zn, $I_2 = 17·9$ volts and for Mg, $I_2 = 15·0$ volts ($Zn^{2+} = 0·69$ Å. and $Mg^{2+} = 0·65$ Å.). Further discussion on the Mg–Zn relationship is deferred to a later section which compares variation of refractive indices in isostructural compounds involving a variety of medium-sized cations.

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[1] F^- is the least polarizable of all anions and this appears to account for the fact that the refractive indices of fluorides are often conspicuously low; compare fluor- and hydroxy-apatites, for example.

Isostructural ionic compounds involving some transition element cations.

Refractive index comparisons between compounds of the pairs of Group IV, V, and VI elements, Zr–Hf, Nb–Ta, and Mo–W, respectively, are particularly satisfactory because for each pair the respective cationic radii are virtually the same and electron configurations are very similar.

In the pair Zr and Hf (radius of $Zr^{4+} = Hf^{4+} = 0.79$ Å.), the fourth ionization potentials are ∼34 and ∼31 volts, respectively. The refractive indices of Zr and Hf compounds are therefore predicted to be very similar, with those of Zr slightly greater than those of Hf. In the isometric compounds $(NH_4)_3ZrF_7$ and $(NH_4)_3HfF_7$, the respective refractive indices are 1·433 and 1·426, which accords with theory. Zirconium and hafnium form tetragonal oxyhalides; $ZrOCl_2.8H_2O$ is uniaxial positive ($\omega = 1.552$, $\epsilon = 1.563$) whereas $HfOCl_2.8H_2O$ is uniaxial negative ($\omega = 1.557$, $\epsilon = 1.543$). In this example the comparison is not so clear: the refractive indices are closely similar as we expect and if either the average or $\sqrt[3]{\omega^2\epsilon}$ is compared, the value for the Zr compound is slightly greater, which is in accordance with theory.

For the pair Nb^{5+} and Ta^{5+} (radius = 0·69 Å.) the fifth ionization potentials are ∼50 and ∼45 volts respectively. A difference of about 5 volts for quintuply charged cations is comparatively small, and accordingly we predict that the refractive indices of isostructural compounds of niobium and tantalum will be similar but that those of niobium will be slightly greater. The refractive indices of stibiocolumbite and stibiotantalite support this prediction:

$SbNbO_4$	.	.	. α 2·42	β 2·44	γ 2·46	
$SbTaO_4$	.	.	. α 2·345	β 2·383	γ 2·452.	

In tantalite and columbite $(Fe,Mn)(Nb,Ta)_2O_6$ Fe–Mn substitution is a complication. The refractive indices of columbite are, however, greater than those of tantalite.

In the pair Mo^{6+}–W^{6+} (radius = 0·62 Å.), the sixth ionization potentials are ∼67 volts and ∼60 volts. Refractive indices of the isostructural tetragonal pairs powellite–scheelite and wulfenite–stolzite are as follows:

$CaMoO_4$	.	. ω 1·967	ϵ 1·978	$PbMoO_4$	.	. ω 2·405	ϵ 2·283
$CaWO_4$	.	. ω 1·918	ϵ 1·934	$PbWO_4$	.	. ω 2·27	ϵ 2·19.

The refractive indices of the Mo member in each pair are greater than those of the W member, which is in accordance with theory. We may note also that the refractive indices of the lead minerals are quite distinctly greater than their calcium equivalent ($Pb^{2+} = 1.20$ Å.,

$Ca^{2+} = 1\cdot01$ Å.). This also accords with theory as the second ionization potentials of lead and calcium are $15\cdot0$ and $11\cdot9$ volts respectively; the comparison is, however, not rigorous, as the difference in radius is quite considerable ($0\cdot2$ Å.) and a large divalent cation such as Pb^{2+} is itself perhaps quite strongly polarized in the anion field, thereby causing a further elevation of refractive index.

Medium-sized divalent cations of various types.

The largest number of cations of a similar size is the medium-sized group Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}; their radii range from $0\cdot65$ Å. (Mg^{2+}) to $0\cdot80$ Å. (Mn^{2+} and perhaps Cu^{2+}). It would be desirable to include Pd^{2+} and Pt^{2+} also, but refractive index data on their compounds are not often available. Though the exclusion of other divalent cations from the above series is somewhat arbitrary, we may recall that the fluorides of the cations of this group invariably have the $6:3$ rutile structure, whereas that of BeF_2 ($Be^{2+} = 0\cdot34$ Å.) is $4:2$ (cristobalite) and the fluoride structures of many larger cations (Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}, Cd^{2+}, and Hg^{2+}) are $8:4$ (fluorite).

The second ionization potentials in volts of the metals under consideration are Mg $15\cdot0$, Mn $15\cdot6$, Fe $16\cdot5$, Co $17\cdot4$, Ni $18\cdot2$, Cu $20\cdot2$, and Zn $18\cdot0$. In two types of compounds it is possible to make a comparison involving each of the seven cations. Consider the trigonal hydrated divalent-quadrivalent hexafluorides, $A^{2+}SiF_6.6H_2O$, where A^{2+} may be Mg, Mn, Fe, Co, Ni, Cu, or Zn. The Mg, Mn, Fe, Co, Ni, and Zn compounds are uniaxial positive whereas the Cu compound is uniaxial negative.

The second ionization potential is related to refractive index in fig. 1. A well-developed regularity is clear and in general the relationship is in accordance with theory outlined so far. The change of sign in the copper compound might reflect some unique property associated with Cu^{2+} and in the example below (see fig. 2) the copper compound again shows a peculiarity. It may be recalled that although coordination about Cu^{2+} can often be regarded as octahedral, four neighbours are usually closer than the other two. The Mg–Fe relationship above holds generally for mafic minerals such as olivine and pyroxene and the higher refractive indices of the Fe-rich component are probably due to greater deformation of O^{2-} in the field of Fe^{2+}.

A large number of compounds of the type $A_2^+ B^{2+}(SO_4)_2.6H_2O$ are known in which A^+ is a large singly charged cation (K^+, Rb^+, Cs^+, Tl^+, or NH_4^+) and B^{2+} is a medium-sized divalent cation. The relationship
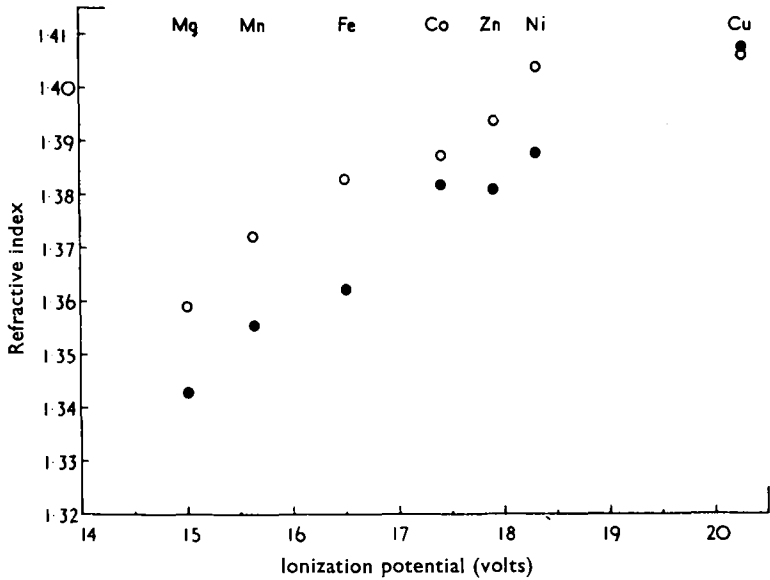
FIG. 1. Variation of refractive indices with second ionization potential of metal in tetragonal crystals of the type $A^2 \cdot SiF_6.6H_2O$. $\bullet = \omega$, $\bigcirc = \epsilon$.
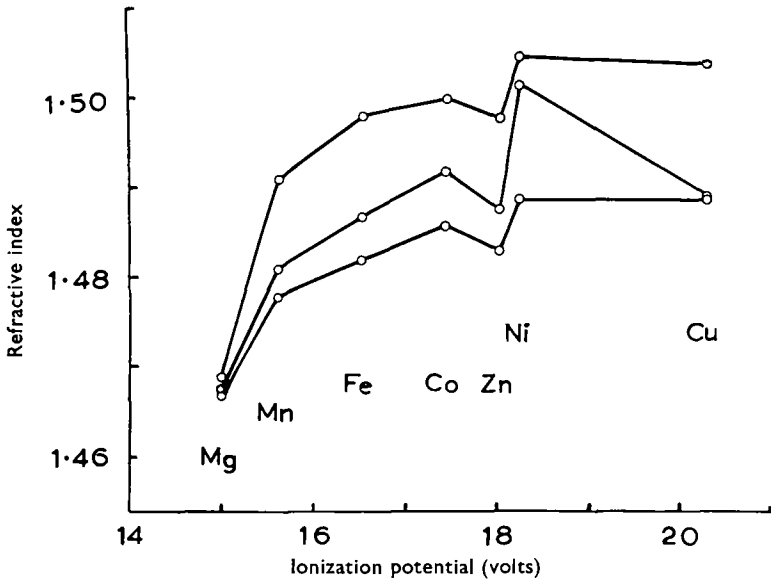

FIG. 2. Variation of refractive indices with second ionization potential of metal in monoclinic sulphates of the type $Rb_2B^{2+}(SO_4)_2.6H_2O$.

between second ionization potential and refractive index shown in fig. 2 refers to the rubidium compounds but holds fairly well for the others as well. The general trend of fig. 1 is again clear in fig. 2, but the regularities are not so well developed and distinct discontinuities appear at zinc. Also, unlike the fluosilicates, the refractive indices of copper rubidium sulphate tend to be less than those of nickel, particularly the β index. In the K, Cs, NH_4, Tl salts, as well as the isomorphous selenates (the Cs selenate excepted), the drop in β index is smaller when passing from the nickel compound to the copper compound.

We may note one difference between the Tutton salts and the fluosilicates that may be important: in the Tutton salts each cation is surrounded by six H_2O's which form an octahedron distorted from the regular shape by being elongated along an axis passing through two opposite water molecules, but having very nearly tetragonal symmetry (Hoffman, 1931; Abragam and Pryce, 1951); magnetic experiments indicate a crystal electric field of tetragonal symmetry. In cobalt fluosilicate (Abragam and Pryce, 1951) and perhaps also in the other fluosilicates, the octahedral group of H_2O molecules is more nearly regular than in the Tutton salts; distortion is in the form of compression along a trigonal axis and the cation is located in a crystal electric field of trigonal symmetry. A refractive index drop at zinc, as above, may be observed also in some other compounds such as the carbonates and simple sulphates, and in fact the relationship $Mg^{2+} < Zn^{2+} < Fe^{2+}$, Co^{2+}, Ni^{2+}, and Cu^{2+} is quite common; thus the refractive index of the compound with an 8-electron cation is lowest, that containing the 18-electron cation comes next, whereas compounds containing $3d$ transition element cations may have the highest refractive indices. Such a relationship holds quite often also for compounds of medium-sized R^{3+} cations: Al^{3+} (8-electron) $< Ga^{3+}$ (18-electron) $< Cr^{3+}$, Fe^{3+}, Co^{3+}, and Rh^{3+} (all transition). In the alums, for example, the relationship is Fe^{3+} (highest) $> Ga^{3+} > Al^{3+}$, and the same relationship holds also for orthoclase where synthetic Fe^{3+} orthoclase has α and γ 1·601 and 1·609, respectively (Gaubert, 1926; see also Coombs, 1954), compared with lower values for Ga and still lower for Al orthoclase (see above). These relationships accord only in part with the magnitudes of the ionization potentials and lack of complete correlation, when a variety of cation types are considered, may be due to the effect of the crystal-field on the transition element cations.

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