Refractive Index and Optical Dispersion of In_2O_3, $InBO_3$ and Gahnite.

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Abstract

Refractive indices of In_2O_3, $In_{2-x}Sn_xO_3$, $InBO_3$ and 2 different gahnite crystals ($ZnAl_2O_4$ and $Zn_{.95}Fe_{.05}Al_2O_4$) were measured at wavelengths of 435.8 to 643.8 nm and were used to calculate n at λ = 589.3 nm (n_D) and at $\lambda = \infty$ (n_∞) using the one-term Sellmeier equation $1/(n^2-1) = -A/\lambda^2 + B$. Total polarizabilities, α_{total}, were calculated from n_∞ and the Lorenz-Lorentz equation. Refractive indices, n_D and dispersion values, A, were, respectively, 2.093 x 10^{-16} m^2 and 133 x 10^{-16} m^2 for In_2O_3; 2.0755 and 138 x 10^{-16} m^2 for $In_{2-x}Sn_xO_3$; 1.7940 and 57 x 10^{-16} m^2 for $ZnAl_2O_4$ and 1.7995 and 56 x 10^{-16} m^2 for $Zn_{.95}Fe_{.05}Al_2O_4$ and n_o = 1.8782 and n_e = 1.7756 and <63> x 10^{-16} m^2 for $InBO_3$. *[Add comments about dispersion here]*

1. Introduction

A set of empirical electronic polarizabilities was recently derived from a large number of minerals, synthetic oxides, hydroxides, oxyhydroxides, oxyfluorides, oxychlorides, hydrates, and fluorides [1] and allowed prediction of mean refractive index (RI) of many minerals and synthetic oxides as well as delineating sets of compounds characterized by steric strain and the presence of corner-shared octahedral groups. However, because predicted polarizabilities and RI values were valid only at infinite wavelength, it was not useful for prediction of normal mineral RI's determined at λ = 589.3 nm. To provide data for the evaluation of polarizabilities and RI's valid at λ = 589.3 nm and as part of an ongoing study of optical properties of minerals, laser materials and synthetic

compounds [1-5], we have established a database of more than 2000 RI values for calculating mean values of polarizabilities using a procedure similar to [1] but using RI measurements made at λ = 589.3 nm. Such a system requires accurate refractive indices, compositions and unit cell volumes. In the early stages of this study it was noted that the polarizabilities of Zn^{2+} in ZnO and In^{3+} in In2O3 were not consistent with the Zn^{2+} and In^{3+} polarizabilities in other Zn- and In-containing compounds. In order to resolve these discrepancies, we have determined the refractive indices and optical dispersion of 2 different gahnite samples (***$ZnAl_2O_4$*** and $Zn_{.95}Fe_{.05}Al_2O_4$), 2 different indium oxide samples (In_2O_3 and $In_{2-x}Sn_xO_3$) and InBO3 and compare the dispersion values of ZnO and In_2O_3, both transparent conductive oxides, with the dispersion of nonconductive oxides.

2. Experimental

Crystal growth of In2O3[Ref 6]

Clear green plate-like crystals of InBO3 were grown from a PbO-Bi2O3 flux.

Two gahnite crystals, $Zn_{.95}Fe_{.05}Al_2O_4$ (Harvard collection No. 111989) from an unspecified location in Brazil and [$ZnAl_2O_4$] from the Alto Mirador Mine in Carauba do Dantes, Rio Grande do Norte, Brazil were used.

The principal method of preparation of small crystal prisms and the procedure for measuring the refractive index and dispersion were described in detail by Medenbach and Shannon [2], along with a comprehensive discussion of the errors involved in the minimum-deviation method. The total error limits are estimated to be less than $\Delta n = \pm 0.0005$ [2].

2. Results and discussion

2.1 Refractive indices

Table 1 lists refractive indices of In_2O_3, $In_{2-x}Sn_xO_3$, $ZnAl_2O_4$, $Zn_{.95}Fe_{.05}Al_2O_4$ and $InBO_3$ as a function of λ. Table 1 also lists the dispersion parameters A and B obtained by fitting to the 1-term Sellmeier expression used by Di Domenico and Wemple [7] and Wemple and Di Domenico and [8] and Wemple [9] :

$$\frac{1}{n^2-1} = -\frac{A}{\lambda^2} + B \qquad (1)$$

where A, the slope of the plot of $(n^2\text{-}1)^{-1}$ vs. $(\lambda^2)^{-1}$, gives a measure of the dispersion and B, the intercept of the plot at $\lambda = \infty$ gives $n_\infty = (1 + 1/B)^{1/2}$. Calculated values of n_∞ and n_D listed in Tables 1 were derived from the dispersion plots. The observed values of the total electronic polarizabilities were determined from the Lorenz-Lorentz equation:

$$\alpha_{obs} = \frac{1}{b} V_m \cdot \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \qquad (2)$$

where the Lorentz factor *b* is defined as b = 4π/3, V_m = molar volume in Å^3, and n_∞ = the refractive index at $\lambda = \infty$ [10,11].

The value of $n_D(In_2O_3) = 2.0930$ agrees reasonably well with the value of 2.080 obtained by Staritzky [12]. The values of n_o = 1.8782 and n_e = 1.7756 agree with the values obtained by Levin et al. [13] for $InBO_3$ (n_o = 1.873 and n_e = 1.773). Gahnite

refractive indices depend on the composition but the values of our two gahnites, 1.7940 (Alto Mirador) and 1.7995 (Harvard, ***111989),*** agree approximately with that of the gahnite $Zn_{.92}Fe_{.07}Mg_{.01}Al_{1.97}Fe_{.03}O_4$ from Jos, Nigeria of 1.7944[14]. ***The differences can be ascribed to varying amounts of Fe?(need microprobe of Alto Mirador)***

2.2 Dispersion values

As a framework for the analysis of dispersion parameters, we use the analysis of Wemple and DiDomenico[8] and Wemple [9]. In this scheme $A = 1/ E_oE_d$ where E_o = the average single oscillator energy and E_d = the oscillator strength which measures the average strength of interband optical transitions. According to and Wemple and DiDomenico [8], E_d is related to physical parameters by the expression:

$$E_d = \beta N_c Z_a N_e \quad (4)$$

where N_c is the cation coordination number, Z_a is the formal valence of the anion, N_e is the effective number of valence electrons/anion, $\beta = 0.26$ for ionic compounds. Using this scheme high dispersion values should result for compounds with:

1. low energy gaps
2. cations having low N_c

Table 2 summarizes the data from the crystals measured here and earlier data [3,15-17].The very high dispersion values of both ZnO and In_2O_3, 160 x 10^{-16} m^2 and 133 x 10^{-16} m^2 respectively are consistent with their low band gaps of 3.4 and 2.8 eV. DiDomenico and Wemple [7] and Wemple [9] concentrated primarily on optical dielectric constants (refractive indices) and their relationships to the above variables but they were not concerned specifically with dispersion, although DiDomenico and Wemple [7] noted that the refractive index dispersion is approximately inversely related to the average single oscillator Sellmeier gap, E_o. In Ref [3] we focussed primarily on the dispersion, A, and the relationship to chemical composition and electron configuration of the atoms involved and found that many of the trends in A could be explained by the above factors. A survey of the dispersion parameters of the compounds in Table 1 of Ref [3] showed high dispersion values, A, associated with the „soft“ d^{10} ion Zn^{2+} and that the dispersion depended on the total concentration of "soft" ions where these ions must be in concentrations > 10-15%. Wemple and DiDomenico [8] and Wemple [9] showed that low values of E_o are associated with the d^{10} cations Cu^+ and Ag^+ and we see here (Table 2) that the d^{10} ions Zn^{2+} and In^{3+} also fit this trend. Among the Zn-containing compounds only ZnO (A= 160 x 10^{-16} m^2) and $ZnWO_4$ (A = 82 x 10^{-16} m^2) have high dispersion. ZnO has both low E_o and E_d (CN = IV) whereas $ZnWO_4$ has low E_o but a higher E_d caused by CN = 6 for both Zn and W. Note that the high dispersion of $ZnWO_4$ results from the combined presence of Zn^{2+} and W^{6+}. The lower dispersions of the other Zn- and In-containing compounds are explained by the presence of large concentration of non-soft ions B3+, Si4+ and P5+.The other Zn-containing compounds ($Zn_{.92}Fe_{.07}Mg_{.01}Al_{1.97}Fe_{.03}O_4$, $ZnAl_2O_4$, $Zn_{.95}Fe_{.05}Al_2O_4$, $Zn_4B_6O_{13}$, and Zn_3BPO_7) and $InBO_3$ for which we have dispersion data have relatively high oscillator energies, Eo = 10-12 eV, and therefore lower dispersion. We believe lack of consistency of the polarizabilities of Zn^{2+} in ZnO and In^{3+} in In2O3 with the Zn^{2+} and In^{3+} polarizabilities in other Zn- and In-containing compounds is related to the very high dispersion and low E_o of the simple oxides.

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List of Tables

Table 1. Experimental refractive indices, total polarizabilities (α_{total})and dispersion parameters of In_2O_3, $In_{2-x}Sn_xO_3$, $ZnAl_2O_4$, $Zn_{.95}Fe_{.05}Al_2O_4$ and $InBO_3$.

Table 2. Dispersion of Zn- and In-containing compounds.

Table 1. Experimental refractive indices, total polarizabilities (α_{total}) and dispersion parameters (A, B, E_o and E_d) of In_2O_3, $In_{2-x}Sn_xO_3$, $ZnAl_2O_4$, $Zn_{.95}Fe_{.05}Al_2O_4$ and $InBO_3$.

wavelength λ, nm	In_2O_3	$In_{2-x}Sn_xO_3$	$ZnAl_2O_4$ Alto Mirador	$Zn_{.95}Fe_{.05}Al_2O_4$ Harvard No.111989	InBO3 n_o	n_e
643.8	2.0778	2.0596	1.7906	1.7959	1.8733	1.7717
576.9	2.0961	2.0801	1.7949	1.8003	1.8795	1.7765
546.0	2.1085	2.0931	1.7977	1.8031	1.8835	1.7799
508.6	2.1271	2.1122	1.8017	1.8074	1.8888	1.7838
480.0	2.1454	2.1310	1.8055	1.8112	1.8938	1.7880
468.0	2.1545	2.1405	1.8075	1.8134	1.8967	1.7904
435.8	2.1875	2.1727	1.8131	1.8180	1.9043	1.7962
A, 10^{-16} m^2	133	138	57	56	<63>	
B	0.3340	0.3421	0.4670	0.4628	<0.4367>	
E_o (eV)	6.34	6.30	11.48	11.52		
E_d (eV)	18.99	18.40	24.64	24.88		
n_∞	1.9985	1.9807	1.7723	1.7778	1.8488	1.7521
n_D (λ=589.3 nm)	2.0930	2.0755	1.7940	1.7995	1.8782	1.7756
α_e, $Å^3$	7.718	7.625	6.602	6.637	<5.366>	

Table 2. Dispersion of Zn- and In-containing compounds

	Dispersion 10^{-16} m^2	Atom % *	E_o	E_d	Reference
ZnO	**160**	**50**	**6.09**	16.51	[3,15]
$ZnAl_2O_4$	57	14	11.48	24.64	This study
$Zn_{.95}Fe_{.05}Al_2O_4$	56	14	11.52	24.88	This study
$Zn_{.92}Fe_{.07}Mg_{.01}Al_{1.97}Fe_{.03}O_4$	56	14	11.50	24.64	[3,14]
$Zn_4B_6O_{13}$	61	17	11.48	22.70	[3,16]
Zn_2SiO_4	81	28	10.48	18.93	[3,17]
Zn_3BPO_7	67	25	11.27	21.29	[18]
$ZnWO_4$	82	33	7.32	26.68	[3,15]
In_2O_3	**133**	**40**	**6.34**	18.99	This study
$In_{2-x}Sn_xO_3$	**138**	**40**	**6.30**	18.40	This study
$InBO_3$	63	20	10.52	24.10	This study

*atom % = total soft ions/total cations + anions

Table 2A. Dispersion of Zn- and In-containing compounds

Compound	**Dispersion**	**Atom % ***	**Eo**	**Reference**
	10-16 m2			
ZnO	**160**	**50**	**6.09**	56 JAPIAU 36 1674
$\boldsymbol{ZnAl_2O_4}$	57	14	11.48	This study
$\mathbf{Zn_{.95}Fe_{.05}Al_2O_4}$	56	14	11.52	This study
$Zn_{.92}Fe_{.07}Mg_{.01}Al_{1.97}Fe_{.03}O_4$	56	14	11.50	97 JOBPDE 14 3299
Zn4B6O13	61	17	11.48	82 ZEKRDZ 161 157
Zn2SiO4	81	28	10.48	23 ZEKRDZ 58 460
Zn3BPO7	67	25	11.27	02 CMATEX 14 2044
ZnWO4	82	33	7.32	65 JAPIAU 36 1674
In2O3	**133**	**40**	**6.34**	This study
$\mathbf{In_{2-x}Sn_xO_3}$	**138**	**40**	**6.30**	This study
InBO3	63	20	10.52	This study

atom % = total soft ions/total cations + anions