



Refractive index and optical dispersion of In_2O_3 , InBO_3 and gahnite

O. Medenbach^{a,2}, Theeranun Siritanon^{b,1}, M.A. Subramanian^{b,3}, R.D. Shannon^{c,*}, R.X. Fischer^{d,4}, George R. Rossman^{e,5}

^a Institut für Mineralogie, Fakultät für Geowissenschaften, Ruhr-Universität Bochum, Universitätsstraße 150, D-44780 Bochum, Germany

^b Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003, USA

^c Geological Sciences/CIRES, University of Colorado, Boulder, CO 80309, USA

^d Fachbereich Geowissenschaften, Universität Bremen, Klagenfurter Straße, D-28359 Bremen, Germany

^e Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125-2500, USA

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ABSTRACT

Refractive indices of In_2O_3 , $\text{In}_{2-x}\text{Sn}_x\text{O}_3$, InBO_3 and 2 different gahnite crystals ($\text{Zn}_{0.95}\text{Fe}_{0.05}\text{Al}_2\text{O}_4$ and $\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Mn}_{0.03}\text{Fe}_{0.03}\text{Al}_{1.99}\text{Fe}_{0.01}\text{O}_4$) were measured at wavelengths of 435.8–643.8 nm and were used to calculate $n(n_D)$ at $\lambda = 589.3$ nm and (n_∞) at $\lambda = \infty$ with 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 , are, respectively, 2.093 and $133 \times 10^{-16} \text{ m}^2$ for In_2O_3 ; 2.0755 and $138 \times 10^{-16} \text{ m}^2$ for $\text{In}_{2-x}\text{Sn}_x\text{O}_3$; 1.7995 and $56 \times 10^{-16} \text{ m}^2$ for $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{Al}_2\text{O}_4$; 1.7940 and $57 \times 10^{-16} \text{ m}^2$ for $\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Mn}_{0.03}\text{Fe}_{0.03}\text{Al}_{1.99}\text{Fe}_{0.01}\text{O}_4$ and $n_o = 1.8782$ and $n_e = 1.7756$ and $\langle 63 \rangle \times 10^{-16} \text{ m}^2$ for InBO_3 . The lack of consistency of the polarizabilities of Zn^{2+} in ZnO and In^{3+} in In_2O_3 with the Zn^{2+} and In^{3+} polarizabilities in other Zn- and In-containing compounds is correlated with structural strain and very high dispersion of ZnO and In_2O_3 .

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1. Introduction

A set of empirical electronic polarizabilities was already derived by us from a large number of minerals, synthetic oxides, hydroxides, oxyhydroxides, oxyfluorides, oxychlorides, hydrates, and fluorides [1] and allowed prediction of the static 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 $\lambda = 589.3$ nm. To provide data for the evaluation of polarizabilities and RI's valid at $\lambda = 589.3$ nm and as part of an ongoing study of optical properties of minerals, laser

materials and synthetic compounds [1–5], we are establishing a database currently containing more than 2000 RI values for calculating mean values of polarizabilities using a procedure similar to [1] but with RI measurements made at $\lambda = 589.3$ 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 In_2O_3 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 ($\text{Zn}_{0.95}\text{Fe}_{0.05}\text{Al}_2\text{O}_4$ and $\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Mn}_{0.03}\text{Fe}_{0.03}\text{Al}_{1.99}\text{Fe}_{0.01}\text{O}_4$), 2 different indium oxide samples (In_2O_3 and $\text{In}_{2-x}\text{Sn}_x\text{O}_3$), and InBO_3 and compare the dispersion values of ZnO and In_2O_3 , both transparent conductive oxides, with the dispersion of nonconductive oxides.

2. Experimental

2.1. Samples

Square tablets of In_2O_3 crystals were grown by a flux method using a B_2O_3 and PbO flux as described in Ref. [6]. A mixture of 4.0 g of In_2O_3 , 4.0 g B_2O_3 , and 50.0 g of PbO was heated in air at 1200 °C for 4 h in a platinum crucible. The mixture was cooled to 500 °C at 10 °C/h and then allowed to cool to room temperature by turning off the furnace. Crystals were isolated by dissolving the flux in hot

* Corresponding author. Tel.: +1 303 417 9961.

E-mail addresses: Olaf.Medenbach@ruhr-uni-bochum.de (O. Medenbach), theeranun_s@hotmail.com (T. Siritanon), mas.subramanian@oregonstate.edu (M.A. Subramanian), bob@theshannons.net (R.D. Shannon), rfischer@uni-bremen.de (R.X. Fischer), grr@gps.caltech.edu (G.R. Rossman).

¹ Present address: School of Chemistry, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand.

² Tel.: +49 0 234 3223519; fax: +49 0 234 3214433.

³ Tel.: +1 541 737 8235; fax: +1 541 737 2062.

⁴ Tel.: +49 421 218 65160; fax: +49 421 218 65189.

⁵ Tel.: +1 626 395 6471; fax: +1 626 568 0935.

20% v/v HNO₃ aqueous solution. Crystals of In_{2-x}Sn_xO₃ were grown by the same method with 11 mg of SnO₂ added in the mixture. The crystals are shiny and dark-black when whole, but bluish-green and transparent in the interior when thinned, with an inhomogeneous distribution of color. Clear, light yellow-green plate-like crystals of InBO₃ were grown from a PbO–Bi₂O₃ flux.

Two gahnite crystals were studied. gahnite1 is a greenish-blue crystal approximately 3 mm in width from the Alto Mirador Mine in Caruba do Dantes, Rio Grande do Norte, Brazil (GRR-2623). gahnite2 is a small slice of a large greenish-blue crystal from an unspecified locality in Brazil (Harvard collection No. 111989).

2.2. Chemical analysis

Chemical analyses were conducted with a JEOL JXA-8200 electron microprobe. InBO₃ and In₂O₃ were both analyzed by a slow wavelength scan over the full range of five wavelength dispersive spectrometers. No elements beyond the stoichiometric components were detected in these scans, including the components of the fluxes from which they were grown. The Sn-doped In₂O₃ was additionally analyzed by a long, quantitative analysis on the microprobe which failed to detect Sn with a Sn detection limit of 50 ppm-wt. at a 99% confidence level. Gahnite1 was analyzed with a full quantitative analysis. The formula, based on the average of five point analyses, is (Zn_{0.91}Mg_{0.04}Mn_{0.03}Fe_{0.03})[Al_{1.99}Fe_{0.01}]O₄ where 0.01 Fe³⁺ was arbitrarily added to the Al site and the remainder of iron as Fe²⁺ was added to the Zn site.

The composition of gahnite2 was determined by electron microprobe analysis at Harvard University. Its composition is Zn_{0.95}Fe_{0.05}Al₂O₄. The presence of Fe²⁺ in both the gahnites was confirmed through observation of the tetrahedral Fe²⁺ absorption bands in a near-infrared transmission spectrum through doubly polished wafers of the crystals.

2.3. Optical methods

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 [7], along with a comprehensive discussion of the errors involved in the minimum-deviation method. The total error limits are estimated to be less than $\Delta n = \pm 0.0005$.

3. Results and discussion

3.1. Refractive indices

Table 1 lists refractive indices of In₂O₃, In_{2-x}Sn_xO₃, Zn_{0.95}Fe_{0.05}Al₂O₄, Zn_{0.91}Mg_{0.04}Mn_{0.03}Fe_{0.03}Al_{1.99}Fe_{0.01}O₄ and InBO₃ 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 DiDomenico and Wemple [8], Wemple and DiDomenico [9], and Wemple [10]:

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

where *A*, the slope of the plot of $(n^2 - 1)^{-1}$ 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 Table 1 were derived from the dispersion plots. The observed values of the total electronic polarizabilities were determined from the Lorentz–Lorentz equation:

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

where the Lorentz factor *b* is defined as $b = 4\pi/3$, V_m = molar volume in Å³, and n_∞ = the refractive index at $\lambda = \infty$ [11,12].

The value of $n_D(\text{In}_2\text{O}_3) = 2.0930$ agrees reasonably well with the value of 2.080 obtained by Staritzky [13]. The values of $n_o = 1.8782$ and $n_e = 1.7756$ agree with the values obtained by Levin et al. [14] for InBO₃ ($n_o = 1.873$ 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_{0.92}Fe_{0.07}Mg_{0.01}Al_{1.97}Fe_{0.03}O₄ from Jos, Nigeria of 1.7944 [7]. The small differences among them can be ascribed to varying amounts of Fe and other minor components.

3.2. Dispersion values

As a framework for the analysis of dispersion parameters, we use the analysis of Wemple and DiDomenico [9] and Wemple [10]. In this scheme, $A = 1/E_o E_d$ 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 Wemple and DiDomenico [9], E_d is related to physical parameters by the expression:

$$E_d = \beta N_c Z_a N_e \quad (3)$$

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 band 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 In₂O₃, $160 \times 10^{-16} \text{ m}^2$, and $133 \times 10^{-16} \text{ m}^2$ respectively are consistent with their low band gaps of 3.4 and 2.8 eV. DiDomenico and Wemple [8] and Wemple [10] 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 [8] noted that the refractive index dispersion is approximately inversely related to the average single oscillator Sellmeier gap, E_o . In Ref. [3] we focused 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 Zn²⁺ and that the dispersion depended on the total concentration of “soft” ions where these ions must be in concentrations >10–15%. Wemple and DiDomenico [9] and Wemple [10] 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 Zn²⁺ and In³⁺ also fit this trend. Among the Zn-containing compounds only ZnO ($A = 160 \times 10^{-16} \text{ m}^2$) and ZnWO₄ ($A = 82 \times 10^{-16} \text{ m}^2$) have high dispersion. ZnO has both low E_o and E_d (CN = IV) whereas ZnWO₄ has low E_o but a higher E_d caused by CN = VI for both Zn and W. Note that the high dispersion of ZnWO₄ results from the combined presence of Zn²⁺ and W⁶⁺. 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_{0.92}Fe_{0.07}Mg_{0.01}Al_{1.97}Fe_{0.03}O₄, gahnite1, gahnite2, Zn₄B₆O₁₃, and Zn₃BPO₇) and InBO₃ for which we have dispersion data have relatively high oscillator energies, $E_o = 10$ –12 eV, and therefore lower dispersion. We believe that lack of consistency of the polarizabilities of Zn²⁺ in ZnO and In³⁺ in In₂O₃

Table 1
Experimental refractive indices, total polarizabilities (α_e) and dispersion parameters (A , B , E_o and E_d) of In_2O_3 , $\text{In}_{2-x}\text{Sn}_x\text{O}_3$, $\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Mn}_{0.03}\text{Fe}_{0.03}\text{Al}_{1.99}\text{Fe}_{0.01}\text{O}_4$, $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{Al}_2\text{O}_4$ and InBO_3 . n_D = refractive index at $\lambda = 589.3$ nm; n_∞ = refractive index at $\lambda = \infty$; n_o = ordinary refractive index with polarization perpendicular to the optic axis; n_e = extraordinary refractive index with polarization perpendicular to the optic axis.

Wavelength, λ (nm)	In_2O_3	$\text{In}_{2-x}\text{Sn}_x\text{O}_3$	Gahnite1 Alto Mirador	Gahnite2 Harvard No. 111989	InBO_3	
					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 ($\lambda = 589.3$ 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	Atom % ^a	E_o (eV)	E_d (eV)	Reference
ZnO	160	50	6.09	16.51	[3,15]
$\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Mn}_{0.03}\text{Fe}_{0.03}\text{Al}_{1.99}\text{Fe}_{0.01}\text{O}_4$	57	14	11.48	24.64	This study
$\text{Zn}_{0.95}\text{Fe}_{0.05}\text{Al}_2\text{O}_4$	56	14	11.52	24.88	This study
$\text{Zn}_{0.92}\text{Fe}_{0.07}\text{Mg}_{0.01}\text{Al}_{1.97}\text{Fe}_{0.03}\text{O}_4$	56	14	11.50	24.64	[3,7]
$\text{Zn}_4\text{B}_6\text{O}_{13}$	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
$\text{In}_{2-x}\text{Sn}_x\text{O}_3$	138	40	6.30	18.40	This study
InBO_3	63	20	10.52	24.10	This study

^a Atom % = total soft ions/total cations + anions.

Table 3
Zn and In polarizabilities, cation bond valence, and structural strain indices for Zn- and In-containing compounds. Cation polarizabilities other than Zn taken from Ref. [1].

	$\alpha(\infty)$ (Å^3)	V_o (Å^3)	BV, Zn,In	R1	α_o^a (Å^3)	$\alpha_{(\text{Zn,In})}$ (Å^3)
ZnO	2.646	23.55	1.91	0.093	1.311	1.335
$\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Mn}_{0.03}\text{Fe}_{0.03}\text{Al}_{1.99}\text{Fe}_{0.01}\text{O}_4$	6.602	16.54	(2.05)		1.174	1.051
$\text{Zn}_{0.95}\text{Fe}_{0.05}\text{Al}_2\text{O}_4$	6.637	16.58	(2.05)		1.175	1.091
$\text{Zn}_{0.92}\text{Fe}_{0.07}\text{Mg}_{0.01}\text{Al}_{1.97}\text{Fe}_{0.03}\text{O}_4$	6.602	16.60	(2.05)		1.176	0.994
$\text{Zn}_4\text{B}_6\text{O}_{13}$	19.834	16.08	1.98	0.031	1.162	1.166
Zn_2SiO_4	7.874	21.75	(2.03)	0.064	1.282	1.206
Zn_3BPO_7	12.634	19.12	(1.95)	0.103	1.233	1.244
In_2O_3	7.718	21.57	(2.82)	0.143	1.279	1.944
$\text{In}_{2-x}\text{Sn}_x\text{O}_3$	7.625	21.57		0.143	1.279	
InBO_3	5.366	17.27	3.00	0.037	1.192	1.781

^a $\log \alpha(\text{O}) = \log \alpha_o(\text{O}) - N_o/V^{2/3} = 1.988 - 1.484/V^{2/3}$ from Ref. [1].

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.

3.3. Structural strain

Deviations of observed and calculated polarizabilities were earlier shown to occur in sterically strained structures including the La_2NiO_4 , melilite, pyrope garnet and zoisite structures [1]. The deviations were associated with underbonded or overbonded cations showing differences between calculated and ideal bond valences (BV) [1,19]. Here we choose to evaluate a related parameter, structural strain index, R1 [20,21] also referred to as GII = Global instability index [22,23] or G [24] where $R1 = \{\sum_j [\sum_i$

$(s_{ij} - V_i)^2/N\}^{1/2}$, and $s_{ij} = \exp[(R_o - R_{ij})/B]$, [25] and $\sum_i (s_{ij} - V_i)$ is the difference between the sum of the valence bonds around a cation or anion and the formal valence of the i th cation or anion, N = the number of atoms in the asymmetric unit, R_{ij} is the bond length, R_o is a constant characteristic of the cation–anion pair and $B = 0.37$. R1 is usually less than 0.1; values between 0.1 and 0.2 indicate a sterically strained structure. In Table 3 we have evaluated bond valence sums for Zn and In and R1 for ZnO, $\text{Zn}_4\text{B}_6\text{O}_{13}$, Zn_2SiO_4 , Zn_3BPO_7 , In_2O_3 and InBO_3 . It is clear that Zn and In in ZnO and In_2O_3 , respectively, are underbonded and that there is some structural strain as indicated by $R1 = 0.09$ for ZnO and 0.14 for In_2O_3 . In contrast $\text{Zn}_4\text{B}_6\text{O}_{13}$, Zn_2SiO_4 and InBO_3 have smaller R1 values. Fig. 1 shows the relationship between R1 and $\alpha(\text{Zn})$ and $\alpha(\text{In})$.

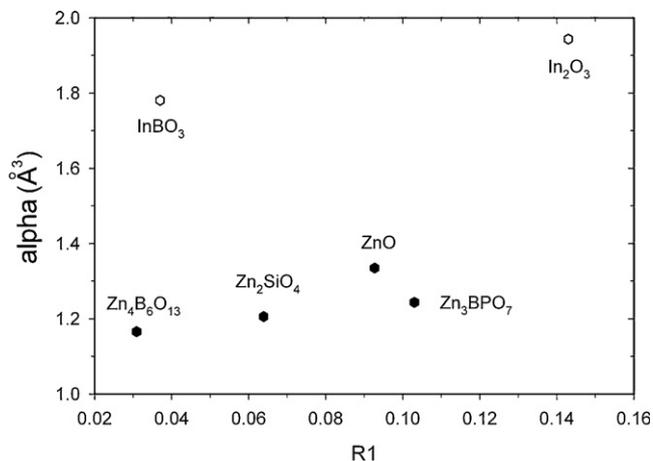


Fig. 1. α vs. R1 of Zn and In compounds.

If we calculate the oxygen polarizability according to:

$$\log \alpha(O^{2-}) = \log \alpha^o(O^{2-}) - N_o/V_o^{2/3} \quad (4)$$

where $\alpha(O^{2-})$ = oxygen polarizability, $\alpha^o(O^{2-})$ = empirical free-oxygen polarizability = 1.988 \AA^3 , V_o = oxide molar volume in each oxide with $N_o = 1.484$ [1] in conjunction with the additivity rule:

$$\alpha_T(M_2 M' X_4) = 2\alpha_e(M^{2+}) + \alpha_e(M'^{4+}) + 4\alpha_e(X^{2-}) \quad (5)$$

where cation polarizabilities other than Zn and In were taken from Ref. [1], we obtain the values of $\alpha(\text{Zn,In})$ given in Table 3. It is clear that if we use $\alpha(\text{Zn}) = 1.33 \text{ \AA}^3$ in ZnO, the other Zn compounds will not give good agreement between observed and calculated total α . Similarly, if we use $\alpha(\text{In}) = 1.944 \text{ \AA}^3$, we will not obtain good agreement for InBO_3 . In Ref. [1], we used $\alpha(\text{Zn}) = 1.297 \text{ \AA}^3$ and $\alpha(\text{In}) = 1.95 \text{ \AA}^3$. From Fig. 1 values of $\alpha(\text{Zn}) = 1.2 \text{ \AA}^3$ and $\alpha(\text{In}) = 1.8 \text{ \AA}^3$ derived from compounds with a minimum of structural strain would have given better fits. We conclude that a primary cause of lack of consistency of the polarizabilities of Zn^{2+} in ZnO and In^{3+} in In_2O_3 with the Zn^{2+} and In^{3+} polarizabilities in other Zn- and In-containing compounds in Ref. [1] is correlated with structural strain and very high dispersion of ZnO and In_2O_3 .

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