



## Refractive index and optical dispersion of $\text{In}_2\text{O}_3$ , $\text{InBO}_3$ and gahnite

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### ABSTRACT

Refractive indices of  $\text{In}_2\text{O}_3$ ,  $\text{In}_{2-x}\text{Sn}_x\text{O}_3$ ,  $\text{InBO}_3$  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  $(n_\infty)$  at  $\lambda = \infty$  with the one-term Sellmeier equation  $1/(n^2 - 1) = -A/\lambda^2 + B$ . Total polarizabilities,  $\alpha_{\text{total}}$ , were calculated from  $n_\infty$  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  $\text{In}_2\text{O}_3$ ; 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  $\text{InBO}_3$ . The lack of consistency of the polarizabilities of  $\text{Zn}^{2+}$  in  $\text{ZnO}$  and  $\text{In}^{3+}$  in  $\text{In}_2\text{O}_3$  with the  $\text{Zn}^{2+}$  and  $\text{In}^{3+}$  polarizabilities in other Zn- and In-containing compounds is correlated with structural strain and very high dispersion of  $\text{ZnO}$  and  $\text{In}_2\text{O}_3$ .

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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  $\text{Zn}^{2+}$  in  $\text{ZnO}$  and  $\text{In}^{3+}$  in  $\text{In}_2\text{O}_3$  were not consistent with the  $\text{Zn}^{2+}$  and  $\text{In}^{3+}$  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 ( $\text{In}_2\text{O}_3$  and  $\text{In}_{2-x}\text{Sn}_x\text{O}_3$ ), and  $\text{InBO}_3$  and compare the dispersion values of  $\text{ZnO}$  and  $\text{In}_2\text{O}_3$ , both transparent conductive oxides, with the dispersion of nonconductive oxides.

## 2. Experimental

### 2.1. Samples

Square tablets of  $\text{In}_2\text{O}_3$  crystals were grown by a flux method using a  $\text{B}_2\text{O}_3$  and  $\text{PbO}$  flux as described in Ref. [6]. A mixture of 4.0 g of  $\text{In}_2\text{O}_3$ , 4.0 g  $\text{B}_2\text{O}_3$ , and 50.0 g of  $\text{PbO}$  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

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20% v/v HNO<sub>3</sub> aqueous solution. Crystals of In<sub>2–x</sub>Sn<sub>x</sub>O<sub>3</sub> were grown by the same method with 11 mg of SnO<sub>2</sub> 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 InBO<sub>3</sub> were grown from a PbO–Bi<sub>2</sub>O<sub>3</sub> 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. InBO<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> 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 In<sub>2</sub>O<sub>3</sub> 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<sub>0.91</sub>Mg<sub>0.04</sub>Mn<sub>0.03</sub>Fe<sub>0.03</sub>)[Al<sub>1.99</sub>Fe<sub>0.01</sub>]O<sub>4</sub> where 0.01 Fe<sup>3+</sup> was arbitrarily added to the Al site and the remainder of iron as Fe<sup>2+</sup> was added to the Zn site.

The composition of gahnite2 was determined by electron microprobe analysis at Harvard University. Its composition is Zn<sub>0.95</sub>Fe<sub>0.05</sub>Al<sub>2</sub>O<sub>4</sub>. The presence of Fe<sup>2+</sup> in both the gahnites was confirmed through observation of the tetrahedral Fe<sup>2+</sup> 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 In<sub>2</sub>O<sub>3</sub>, In<sub>2–x</sub>Sn<sub>x</sub>O<sub>3</sub>, Zn<sub>0.95</sub>Fe<sub>0.05</sub>Al<sub>2</sub>O<sub>4</sub>, Zn<sub>0.91</sub>Mg<sub>0.04</sub>Mn<sub>0.03</sub>Fe<sub>0.03</sub>Al<sub>1.99</sub>Fe<sub>0.01</sub>O<sub>4</sub> and InBO<sub>3</sub> as a function of  $\lambda$ . 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  $n_\infty$  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 Å<sup>3</sup>, and  $n_\infty$  = 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 InBO<sub>3</sub> ( $n_o = 1.873$  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<sub>0.92</sub>Fe<sub>0.07</sub>Mg<sub>0.01</sub>Al<sub>1.97</sub>Fe<sub>0.03</sub>O<sub>4</sub> 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 In<sub>2</sub>O<sub>3</sub>,  $160 \times 10^{-16} \text{ m}^2$ , 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 Zn<sup>2+</sup> 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<sup>+</sup> and Ag<sup>+</sup> and we see here (Table 2) that the  $d^{10}$  ions Zn<sup>2+</sup> and In<sup>3+</sup> also fit this trend. Among the Zn-containing compounds only ZnO ( $A = 160 \times 10^{-16} \text{ m}^2$ ) and ZnWO<sub>4</sub> ( $A = 82 \times 10^{-16} \text{ m}^2$ ) have high dispersion. ZnO has both low  $E_o$  and  $E_d$  (CN = IV) whereas ZnWO<sub>4</sub> has low  $E_o$  but a higher  $E_d$  caused by CN = VI for both Zn and W. Note that the high dispersion of ZnWO<sub>4</sub> results from the combined presence of Zn<sup>2+</sup> and W<sup>6+</sup>. The lower dispersions of the other Zn- and In-containing compounds are explained by the presence of large concentration of non-soft ions B<sup>3+</sup>, Si<sup>4+</sup> and P<sup>5+</sup>. The other Zn-containing compounds (Zn<sub>0.92</sub>Fe<sub>0.07</sub>Mg<sub>0.01</sub>Al<sub>1.97</sub>Fe<sub>0.03</sub>O<sub>4</sub>, gahnite1, gahnite2, Zn<sub>4</sub>B<sub>6</sub>O<sub>13</sub>, and Zn<sub>3</sub>BPO<sub>7</sub>) and InBO<sub>3</sub> 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 Zn<sup>2+</sup> in ZnO and In<sup>3+</sup> in In<sub>2</sub>O<sub>3</sub>

**Table 1**  
Experimental refractive indices, total polarizabilities ( $\alpha_e$ ) and dispersion parameters ( $A$ ,  $B$ ,  $E_o$  and  $E_d$ ) of  $\text{In}_2\text{O}_3$ ,  $\text{In}_{2-x}\text{Sn}_x\text{O}_3$ ,  $\text{Zn}_{0.91}\text{Mg}_{0.04}\text{Mn}_{0.03}\text{Fe}_{0.03}\text{Al}_{1.99}\text{Fe}_{0.01}\text{O}_4$ ,  $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{Al}_2\text{O}_4$  and  $\text{InBO}_3$ .  $n_D$  = refractive index at  $\lambda = 589.3$  nm;  $n_\infty$  = 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, $\lambda$ (nm)	$\text{In}_2\text{O}_3$	$\text{In}_{2-x}\text{Sn}_x\text{O}_3$	Gahnite1 Alto Mirador	Gahnite2 Harvard No. 111989	$\text{InBO}_3$	
					$n_o$	$n_e$
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
$A$ , $10^{-16} \text{ m}^2$	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		
$n_\infty$	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
$\alpha_e$ , $\text{Å}^3$	7.718	7.625	6.602	6.637	(5.366)	

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

	Dispersion	Atom % <sup>a</sup>	$E_o$ (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]
$\text{Zn}_2\text{SiO}_4$	81	28	10.48	18.93	[3,17]
$\text{Zn}_3\text{BPO}_7$	67	25	11.27	21.29	[18]
$\text{ZnWO}_4$	82	33	7.32	26.68	[3,15]
$\text{In}_2\text{O}_3$	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
$\text{InBO}_3$	63	20	10.52	24.10	This study

<sup>a</sup> 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].

	$\alpha(\infty)$ ( $\text{Å}^3$ )	$V_o$ ( $\text{Å}^3$ )	BV, Zn,In	R1	$\alpha_o^a$ ( $\text{Å}^3$ )	$\alpha_{(\text{Zn,In})}$ ( $\text{Å}^3$ )
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
$\text{Zn}_2\text{SiO}_4$	7.874	21.75	(2.03)	0.064	1.282	1.206
$\text{Zn}_3\text{BPO}_7$	12.634	19.12	(1.95)	0.103	1.233	1.244
$\text{In}_2\text{O}_3$	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	
$\text{InBO}_3$	5.366	17.27	3.00	0.037	1.192	1.781

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

with the  $\text{Zn}^{2+}$  and  $\text{In}^{3+}$  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  $\text{La}_2\text{NiO}_4$ , 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,  $\text{Zn}_4\text{B}_6\text{O}_{13}$ ,  $\text{Zn}_2\text{SiO}_4$ ,  $\text{Zn}_3\text{BPO}_7$ ,  $\text{In}_2\text{O}_3$  and  $\text{InBO}_3$ . It is clear that Zn and In in ZnO and  $\text{In}_2\text{O}_3$ , respectively, are underbonded and that there is some structural strain as indicated by  $R1 = 0.09$  for ZnO and 0.14 for  $\text{In}_2\text{O}_3$ . In contrast  $\text{Zn}_4\text{B}_6\text{O}_{13}$ ,  $\text{Zn}_2\text{SiO}_4$  and  $\text{InBO}_3$  have smaller R1 values. Fig. 1 shows the relationship between R1 and  $\alpha(\text{Zn})$  and  $\alpha(\text{In})$ .

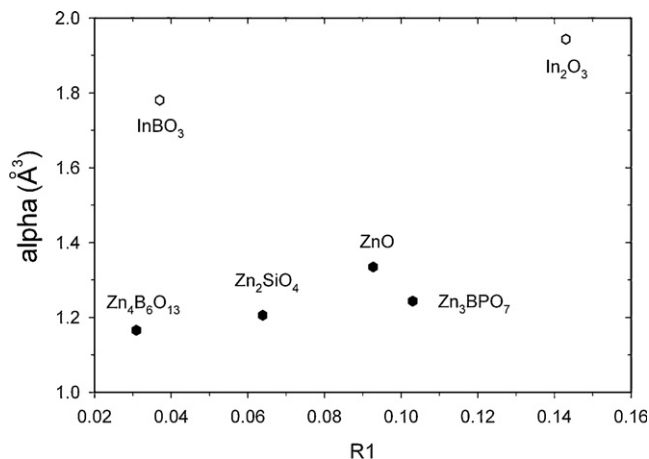


Fig. 1.  $\alpha$  vs. R1 of Zn and In compounds.

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 =  $1.988 \text{ \AA}^3$ ,  $V_o$  = 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  $\alpha$ . Similarly, if we use  $\alpha(\text{In}) = 1.944 \text{ \AA}^3$ , we will not obtain good agreement for InBO<sub>3</sub>. 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<sup>2+</sup> in ZnO and In<sup>3+</sup> in In<sub>2</sub>O<sub>3</sub> with the Zn<sup>2+</sup> and In<sup>3+</sup> polarizabilities in other Zn- and In-containing compounds in Ref. [1] is correlated with structural strain and very high dispersion of ZnO and In<sub>2</sub>O<sub>3</sub>.

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