A critical assessment of the Photocurrent Spectroscopy (PCS) Technique for the semi-quantitative characterization of passive film and corrosion layers composition is carried out. We take into account more than three decades of PCS usage as “in-situ” analytical technique and related results as well as the criticism of the underlying semi-empirical correlation relating the measured optical bandgap (E_g) to the passive film composition. The discrepancies between the experimental data, gathered by PCS measurements, and E_g estimates originating from recently developed Density Functional Theory based modeling of solid state properties are stressed with particular emphasis on the case of anodic passive film grown on technologically important alloys (Fe-Cr and stainless steels). The extension of this correlation to mixed oxides and its use for relating the oxide composition to the bandgap values is critically reviewed by comparing the predicted E_g of mixed oxides with the experimental values. Suggestions on how to account for different bandgap values of oxide polymorphs and how to correlate the E_g values to the composition of mixed s,p,d-metal oxides are presented and discussed on the basis of experimental results reported in the literature. On the basis of this assessment, the ability of PCS in providing quantitative information on the composition of passive film and corrosion layer is generally confirmed.

In the last 20–30 years an increasing number of electrochemists working in the field of corrosion have been attracted by this technique owing to its versatility and ability to scrutinize “in-situ” corrosion layers and passive films having semiconducting or insulating behavior. In previous as well as in very recent works1–7 we have shown that PCS is able to provide detailed information on characteristic energy levels of passive film/electrolyte junctions (flatband potential: U_{FB}; internal photoemission threshold: E_{o}; bandgap value: E_g). Such information is necessary for a deeper understanding of the possible mechanisms of charge transfer (electrons and ions) at the metal/corrosion layer/electrolyte interface. Further advantages stem from the fact that the PCS technique does not require particular surface finishing control, it can be used both on large areas as well as in microscopic regions of the electrode, and can reach high sensitivity by using a lock-in amplifier coupled to a mechanical light chopper to detect the photocurrent signal. According to this, numerous experimental studies have shown how it is possible to scrutinize corrosion layers and passive films of very limited thickness grown on metals and alloys (Fe, Cr, Ni and SS) of relevant industrial interest.3,4,2 In an attempt to make more quantitative the characterization of corrosion layer and passive film by PCS, in previous works3,6,8,9 we have shown that it is possible to correlate semi-empirically the E_g values of numerous binary oxides to their composition by means of the following expressions:9

\[ E_g = 2.17(\chi_M - \chi_O)^2 - 2.71 \text{ in eV} \quad \text{for s,p metal oxides} \]

[1a]

\[ E_g = 1.35(\chi_M - \chi_O)^2 - 1.49 \text{ in eV} \quad \text{for d metal oxides} \]

[1b]

where \( \chi_M \) and \( \chi_O \) are the electronegativity parameters of metal and oxygen, respectively, on the Pauling scale. Eqs. 1a and 1b were able to fit with a reasonable accuracy the E_g values of sp-metal oxides (2 and 13–15 groups in the periodic table of the elements), whilst Eq. 1b was able to reproduce with good accuracy the experimental E_g values of many d-metal oxides (3–12 groups). In the original paper,9 the E_g values of passive films oxides and of most common crystallographic structures have been used by neglecting the differences in the bandgap values of different polymorphs. When possible, E_g values derived from PCS studies by means of Tauc’s treatment of data have been used. As for the electronegativity values of different elements, the values of Pauling scale,10 integrated with other data11,12 for Mg and Sn in different oxidation states, have been used in previous studies9 and in the following.

In several successive works we extended Eqs. 1a and 1b to ternary oxides, M_mN_nO_o, using an average electronegativity defined as the arithmetic mean between those of partner metals, \( \chi_M \) and \( \chi_N \), each weighted according to their corresponding atomic fraction. This procedure allowed correlation of the bandgap values measured by PCS with the mixed oxide composition, as confirmed with several mixed oxides of known composition.1–4,6,8,9

In this work, we will discuss the limits of validity of Eqs. 1a and 1b for binary and ternary oxides spanning a large range of bandgap values (from \( \sim 1 \text{ eV} \) to \( \sim 9 \text{ eV} \)) by discussing data reported in the literature pertaining to ternary mixed oxides prepared by different techniques and including anodic passive films grown on metallic alloys. Moreover, we will compare the bandgap values of mixed d-d metal oxides, of large interest in corrosion studies, theoretically derived by Density Functional Theory (DFT), to those estimated by PCS. Possible explanations for the difference between experimental and theoretical data will be presented and discussed in order to highlight the limits and possibilities of the PCS technique in providing information on the chemical composition of passive films and corrosion layers. Finally, a generalization of Eq. 1a and 1b to the case of ternary s,p-d mixed oxides will be presented and discussed by using the literature data of mixed Zn Mg_{1-x} O oxides covering all the range of composition (0 < x < 1) and both wurtzite (WZ) and rock-salt (RS) crystalline structures.

Theoretical Background

Following previous works of Manca13 and Vijh14–16 we suggested to write the following relationship for the bandgap of inorganic

\[ E_g = \epsilon - \frac{\chi_M + \chi_O}{2} \]

where \( \epsilon \) is the energy of the highest filled level of the metal, and \( \chi_M \) and \( \chi_O \) are the electronegativity parameters of the metal and oxygen, respectively. This relationship is derived from the assumption that the bandgap is the energy difference between the highest filled and lowest empty levels of the material.
At the heart of the debate about the nature of semiconducting and insulating compounds lies the understanding of the bandgap, a parameter that defines the energy required for an electron to transition from the valence to the conduction band. In the case of d-metal oxides, this energy is particularly complex due to the unique properties of these materials. The Pauling equation, a cornerstone in inorganic chemistry, offers a framework to estimate the bandgap (Eg) of semiconducting and insulating compounds as:

$$E_g = 2 \left( \Delta H_{eq} - U_R \right)$$  \hspace{1cm} \textbf{[2a]} \nonumber$$

where $\Delta H_{eq}$ is the heat of atomization per equivalent, in the case of polyatomic compounds, and $U_R$ is an energy term including repulsive and London components.\(^{13}\) Moreover, we modified Eq. 2a for a polyatomic oxide $\text{MO}_y$ by using for $\Delta H_{eq}$ the Pauling equation\(^ {10}\) for the average single bond energy $D_{M-O}$ and re-writing Eq. 2a as:

$$E_g = 2 \left\{ \left( \chi_M - \chi_O \right)^2 + \frac{1}{2y} \left[ \left(D_{M-M} + yD_{O-O} \right) - R_{M-O} \right] \right\}$$  \hspace{1cm} \textbf{[2b]} \nonumber$$

where $D_{M-M}$ and $D_{O-O}$ are the enthalpies of dissociation of $M_2$ and $O_2$ in the gaseous phase, $\chi_M$ and $\chi_O$ are the electronegativities of metal and oxygen on the Pauling scale and $R_{M-O}$ is the repulsive term (see below). The Pauling equation\(^ {10}\) was modified according to Phillips’ suggestion\(^ {17}\) introducing the parameter $E_I$ assumed “to vary with hybridization configuration, i.e., with different atomic coordination in different crystal structures” in order to take into account the possible influence of different types of bonds on the “extraatomic energy” as defined in Pauling’s classical book. After substitution of the Pauling equation in Eq. 2a it was possible to get a general expression for the bandgap of semiconducting and insulating compounds as:

$$E_g = 2 \left[ E_I (\chi_{av} - \chi_M)^2 + \frac{1}{2} \right]$$  \hspace{1cm} \textbf{[2c]} \nonumber$$

where $\chi_{av}$ and $\chi_M$ are Pauling electronegativity values of the oxygen (or generally speaking of the most electronegative non-metallic element) and metal, respectively, present in the compound. The term:

$$\Xi = \frac{1}{2y} \left[ \left( D_{M-M} + yD_{O-O} \right) - R_{M-O} \right]$$  \hspace{1cm} \textbf{[2d]} \nonumber$$

contains the average bond energies of the diatomic molecules in the gas phase ($1/2(D_{DA} + D_{DM})$) and the repulsive term $R_{M-O} = (U_{bond} - U_{lance})$. In the ionic limit, $U_{bond}$ coincides with the Madelung energy, while in the covalent limit a quantum mechanical calculation of the bonding energy is required.\(^ {18}\) In spite of the widely discussed limitations, the use of Pauling equation is still very attractive owing to limitations, the use of Pauling equation is still very attractive owing to its simplicity, reliable estimate of the heats of formation per equivalent of inorganic compounds, assumed as a measure of the bond strength in solids, and the possibility to relate this classical chemical concept with quantum mechanical derived concepts and parameters.\(^ {19,20}\) Moreover, owing to the periodic trends of the electronegativity values in the Pauling scale, strictly related to the periodic table of chemical elements, the use of Eq. 2c allows for easy identification of the expected general trend in the optical bandgap of inorganic semiconductor compounds. We would like to stress this aspect as one of the most rewarding results of our previous studies on pure sp-metal and d-metal oxides together with the possibility to tailor, to some extent, the bandgap values of mixed oxides.

As assumed in previous works,\(^ {3,6,8,9}\) in so far as the $\Xi$ term is constant, Eq. 2c predicts that the bandgap of semiconducting compounds is linearly dependent on the square of the difference of electronegativity between the most electronegative element (oxygen in the case of oxides) and the metallic element. According to this, Eq. 2c was fitted according to a general expression as:

$$E_g = A (\chi_{av} - \chi_M)^2 + B$$  \hspace{1cm} \textbf{[3]}$$

where $A$ and $B$ have been determined by a linear best fitting procedure of experimental $E_g$ values vs $(\chi_{av} - \chi_M)^2$. In the case of pure sp and d-metal oxides, two different interpolating straight lines were derived with:

- For d-metal oxides: $A_{d-metal}$ = 1.35 and $B_{d-metal}$ = -1.49 in eV \hspace{1cm} \textbf{[3a]} \nonumber$$

- For s,p-metal oxides: $A_{s,p-metal}$ = 2.17 and $B_{s,p-metal}$ = -2.71 in eV \hspace{1cm} \textbf{[3b]} \nonumber$$

We have to mention that NiO was a noticeable exception of the d-metal oxides owing to the fact that its $E_g$ value (3.50–3.60 eV, according to the literature)\(^ {9}\) is about 50% higher than that estimated ($E_g$ = 2.40 eV) by Eq. 3 and Eq. 3a valid for d-metal oxides. Interestingly, the $E_g$ value of NiO was fitted by using the s,p-metal oxide correlation ($E_g$ = 3.56 eV according to Eq. 3b) with a $\chi_{Ni}^{av}$ value of 1.8.\(^ {12}\) Analogously, three oxides of s,p-metals of higher atomic number (In$_2$O$_3$, PbO, Ti$_2$O$_3$) were better interpolated by using the d-metal oxides correlation (Eq. 3a). An indirect optical bandgap value of 2.80 eV was reported for In$_2$O$_3$\(^ {9}\) by using the value measured\(^ {21}\) for the thermal oxide film grown on In. Such a value compares well with the value foreseen by the d-metal correlation (2.87 eV) by assuming the Pauling electronegativity value of 1.70.\(^ {3,4}\) In this case, however, we have to mention that the most common $E_g$ quoted in literature is a direct band gap ~0.7–0.9 eV higher than the previous one.\(^ {22}\) Although still controversial, the most recent $E_g$ value (2.70 eV) for single crystal c-In$_2$O$_3$\(^ {23}\) seems to support our initial assumption of In$_2$O$_3$ based on the d-metal correlation. We will come back on these aspects in the following.

**Regular (sp,sp or dd-metals) mixed oxides.—** We previously attempted\(^ {6}\) to extend Eqs. 1 to mixed oxides ($M_nN_mO_{n+m}$) by replacing $\chi_M$ with an average electronegativity, $\chi_{av}$, parameter defined as the arithmetic mean between the electronegativity of partners metals ($\chi_M$ and $\chi_N$), each weighted by the corresponding atomic fraction as:

$$E_g (M_nN_mO_{n+m}) = A (\chi_{av} - \chi_M)^2 + B$$  \hspace{1cm} \textbf{[4a]} \nonumber$$

$$\chi_{av} = \frac{m \chi_M + n \chi_N}{m + n} = x_M \chi_M + x_N \chi_N$$  \hspace{1cm} \textbf{[4b]} \nonumber$$

The selection of $A$ and $B$ is straightforward when $M$ and $N$ are both d-metals or s,p-metals (regular) mixed oxides, whilst the problem of coefficients selection arises for s,p-d metals (non-regular) mixed oxides (see below). We also suggested that if the difference of electronegativity (in the Pauling scale) between the partner metals in the mixed oxide is higher than ~0.5, the bandgap of the mixed oxide was very close to that of the oxide of the most electronegative metal (lower bandgap oxide, see Table I).\(^ {9}\) Although, initially, this observation seemed limited to the s,p-d mixed oxides more recent data confirm that analogous results can be expected also for regular solutions (d-d metal or s,p-s metal mixed oxides) when a large difference in the electronegativity values of the cations is observed (see Table II). This finding is in agreement with the results of Eng et al.,\(^ {24}\) where the bandgap value of a series of MITiO$_3$ (M = Ca, Sr) mixed oxides is reported to be not significantly influenced by the presence (and concentration as reported in Table III) of Sr or Ca ions, therefore, described as “cation spectators”. The small influence of the cation spectator on the optical bandgap value, in such mixed oxides, has been attributed to the steric action of the different cation spectator through local distortion of bond angle and lengths. Our observation allows prediction of which metallic element combination could originate such a behavior, although it is not yet clear if the threshold value of $\Delta \chi_{cat}$, marking the onset of such a behavior, is equal or slightly different for regular ($\geq 0.7$) and non-regular ($\geq 0.5$) mixed oxides.

| Mixed Oxide | $\chi_{average}$ | $E_{g,exp}$ (eV) | $E_{g,th,sp}$ (eV) | $\Delta \chi$ | $E_{g,th}$ (eV) |
|-------------|------------------|-----------------|-----------------|-------------|----------------|
| NaTaO$_3$  | 1.2              | 3.8             | 7.20            | 0.60        | 3.90           |
| LiTaO$_3$  | 1.25             | 3.8             | 6.80            | 0.50        | 3.90           |
| KNbO$_3$   | 1.3              | 3.8             | 7.20            | 0.80        | 3.35           |
| LiNbO$_3$  | 1.3              | 3.8             | 6.41            | 0.60        | 3.35           |
| SrTiO$_3$  | 1.3              | 3.15            | 6.30            | 0.63        | 3.05–3.2       |
| BaTiO$_3$  | 1.25             | 4.1             | 6.86            | 0.80        | 3.20           |
derive from Eqs.1a, 1b the following relationship for the composition dependence of the bandgap value of mixed regular oxides:29

In a previous work,28 we have shown that in the case of regular mixed the bowing parameter assumes usually small values well below 1 eV . Coworkers noted that for regular mixed cationic semiconductor alloys where \( b \) represents the so-called bowing coefficient. Zunger and coworkers25–27 discussed the role of the composition in determining structural phase transitions in alloys or electronic direct-to-indirect bandgap crossover the physical properties \( P(x) \) were traditionally assumed to be simple continuous functions of the composition. Obviously, from Eq. 4 it follows that for \( x_N \leq 1 \) of the traditional bowing equation, represented by a linear term plus a small quadratic correction term, which can be written as:27

\[
E_g(x) = (1 - x) E_g(M) + x E_g(N) - bx (1 - x) \tag{5}
\]

where \( b \) represents the so-called bowing coefficient. Zunger and coworkers noted that for regular mixed cationic semiconductor alloys the bowing parameter assumes usually small values well below 1 eV . In a previous work,29 we have shown that in the case of regular mixed nitrates following Eq. 4 it is possible to get an expression analogous to Eq. 5 by simple algebraic manipulation of Eq. 4. By following the same procedure in the case of regular mixed oxides it is possible to derive from Eqs. 1a, 1b the following relationship for the composition dependence of the bandgap value of regular oxides:29

\[
E_g(x) = E_{g,M} + 2A x_N (\chi_M - \chi_N) (\chi_{an} - \chi_M) + A x_N^2 (\chi_N - \chi_M)^2 \tag{6a}
\]

where \( E_{g,M} \) (or \( E_{g,N} \)) is the bowgap of pure MO (or NO) oxide, \( x_N \) (or \( x_M \)) is the cationic fraction (0 \( \leq x \leq 1 \) ) of N (or M) into the oxide. Obviously, from Eq. 4 it follows that for \( x_N = 1 \) Eq. 6a gives the bandgap of pure NO oxide.

After algebraic manipulation, Eq. 6a can be rewritten in a manner similar to the bowing equation usually reported for semiconductor alloy as:

\[
E_g(x) = E_{g,M} + S_1 x_N + S_2 x_N^2 \tag{6b}
\]

where the linear term is now: \( S_1 = 2A (\chi_M - \chi_N) (\chi_{an} - \chi_M) \), and the quadratic term (bowing coefficient) is:

\[
b = S_2 = A (\chi_N - \chi_M)^2 \tag{6c}
\]

in Eq. 6 A is the coefficient derived by Eq. 4, therefore \( A = 1.35 \) or \( A = 2.17 \) for regular d,d metals and s,p-s,p metals mixed oxides, respectively.

In previous papers,30–32 we have shown that conditions such as those mentioned above in the paper of Zunger et al. can be encountered in practice in the case of passive films grown on valve-metals alloys where, in suitable electrolytic solutions, the oxide composition maintains the same cation ratio present in the metallic alloy. This is reported in Figures 1–3 for d,d-metals mixed oxides, where the measured optical band gaps as a function of the alloys composition are reported for passive films grown on Ti-Zr and Ta-Nb alloys as well as for physically deposited \((\text{Gd}_x\text{Y}_1-x)_2\text{O}_3.30–34\) The amorphous nature of the passive film on Nb-Ta alloys and the absence of any indirect-to-direct optical transition crossover in the case of crystalline films grown on Ti-Zr alloys, allowed testing of the suggestion of Zunger and coworkers25,26 for the regular semiconducting alloys reported above.

Figures 1 and 2 show the dependence of experimental \( E_g \) values of thin anodic passive films vs alloys composition for Ti-Zr and Ta-Nb

![Figure 1. Experimental bandgap values of Ti-Zr mixed oxides as a function of base alloy composition. (Data taken from the literature) Green line: theoretical bandgap values estimated according to Eq. 4a.](image1)

![Figure 2. Experimental bandgap values of Nb-Ta mixed oxides as a function of base alloy composition. (Data taken from the literature) Green line: theoretical bandgap values estimated according to Eq. 4a.](image2)
mixed oxides. In these figures the experimental optical bandgap values were obtained by PCS, whilst the theoretical data were calculated by using Eq. 4a with the average electronegativity parameter value of the cations calculated according to Eq. 4b. The cation ratio in the anodic film, derived from RBS analysis, was estimated to be almost coincident to that in the alloys. As shown in Figure 2, the experimental $E_g$ values of anodic oxides, grown on Nb-Ta sputtered alloys, follow the expected trend as a function of the oxide composition but with values slightly higher (about 0.1 eV) than the values of crystalline counterparts. As discussed in literature, a larger (mobility) gap with respect to the $E_g$ of crystalline counterparts is expected for stoichiometric amorphous semiconductors. In the absence of stoichiometric deviations, the disordered structure of the a-SC induces the localization of electronic states close to the conduction and/or valence band edges, as described by the density of states (DOS) model proposed by Mott-Davis for amorphous semiconductors.

A further support to our approach to the estimate of the bowing parameter comes out from the data of Figure 3 pertaining to mixed $(Y,Gd_{1-x})_2O_3$ oxides for which a good agreement between experimental and theoretical values is also observed by assuming for the two d-metal cations $A = 1.35$ and $B = -1.5$ (see Eq. 3b) and an electronegativity parameter of 1.2 and 1.27 for Y and Gd respectively, in quite good agreement with the Pauling scale and uncertainty limits. The value of 1.27 for $\chi_{Gd}$ was derived from Eq. 3a considering an optical $E_g$ value for Gd$_2$O$_3$ pure oxide of 5.22 eV.

Eq. 6c shows that for regular mixed oxides the bowing coefficient $b$ is always positive or zero, whilst the linear term can be positive or negative depending on the sign of the term ($\chi_M - \chi_N$). The linear term will be positive (negative) if $E_{g,M} < E_{g,N}$ ($E_{g,M} > E_{g,N}$) i.e. $\chi_M > \chi_N$ ($\chi_M < \chi_N$). According to our correlations, lower bandgap materials have higher Pauling electronegativity parameters and vice versa. Positive $b$ values are expected for regular mixed oxides together with a linear dependence of the bandgap as a function of the composition, as long as the difference of electronegativity of the cationic partners present into the alloy is small ($\Delta \chi \approx 0.2$ for regular s,p- or d-metals mixed oxides).

Critical Issues in the Field
Composition dependence of optical band gap in mixed oxides.— Regular ($sp,sp$ or $d,d$-metals) mixed oxides.—The previous correlations are mainly based on a semi-empirical approach and thus subjected to the criticism reported in literature, where the authors discuss the limits of the ability to predict the expected $E_g$ values of different oxide polymorphs, as well as the lack of any dependence of $E_g$ on the nature of optical transitions (direct or indirect) determining the optical bandgap values. Even if such criticism is valid in general terms, it is less relevant in the case of passive films grown on metals and alloys that are frequently amorphous. Moreover, from a general point of view, we want to stress that in many cases oxide polymorphs display $E_g$ values (see Table IV) which can be fitted within the proposed correlations by assuming small changes in the parameter $B$ and by leaving unchanged the coefficient $A$ of each correlation. This suggestion derives from the fact that according to Eqs. 2c and 3 the term $B$ includes the repulsive term $R$, which can be assumed dependent on the crystallographic structure of each polymorph through the difference ($U_{bnd} - U_{unique}$). We are aware that reasonable changes in the R values cannot always account for the differences in the reported or estimated bandgap values of several polymorphs, and that changes in the A value of the employed correlation can be also necessary (see below for $\alpha$-(Ga$_{1-x}$Al$_x$)$_2$O$_3$).

We would like to stress, however, that predicting the $E_g$ of pure and mixed amorphous semiconducting compounds is not an easy task even for the more sophisticated quantum-mechanical based DFT techniques and it is not yet, extensively, used to determine the $E_g$ values as a function of the composition of passive films or corrosion layers having amorphous or strongly disordered nature. This aspect must be taken into account owing to the fact that there are few techniques at our disposal able to correlate the gathered in-situ information on the solid state properties ($E_g$, flatband potential, $U_{fb}$, and internal photocurrent) of passive films and corrosion layers with their chemical composition, as a function of chemical and electrical variables employed in the experiments.

A theoretical support to the use of Eqs. 1 can be found in seminal papers of Zaanen, Sawatsky, and Allen who suggested that the $E_g$ of transition-metal compounds (i.e. oxides, sulfides and halides) is of charge-transfer type, i.e. $E_g \propto \Delta$, provided that the charge transfer energy, $\Delta$, is less than the d-d coulomb and exchange interactions term $U$, used in the theory for the calculations of band structure in transition metals compounds. In these works it was suggested that the $\Delta$ term is directly related to the electronegativity of the anion and the Madelung potential of the solid. The semi-empirical correlation proposed for the dependence of $E_g$ values on the nature of the partner involved in the solid agrees, in principle, with the suggestion by Zaanen-Sawatsky-Allen as long as the lowest measured optical gap value is related to an inter-atomic charge transfer process. However, lower $E_g$ values in transition metal oxides are foreseen by their model as long as the charge transfer term $\Delta$ is larger than the d-d coulomb repulsion and exchange interactions term $U$ used in the theory for the calculations of band structure.

Table IV. Comparison between the experimental $E_g$ values of some oxides polymorphs and $E_g$ estimated according to Eqs. 1.

| Polymorphs | $\chi_{P}$ | $E_{g,exp}$ (eV) | $E_{g,th}$ (eV) |
|------------|------------|----------------|----------------|
| $\alpha$-Bi$_2$O$_3$ | 1.9 ± 0.05 | 2.85–3.10 | 2.85 ± 0.35 |
| $\beta$-Bi$_2$O$_3$ | 1.9 ± 0.05 | 2.58–2.81 | 2.85 ± 0.35 |
| $\gamma$-Bi$_2$O$_3$ | 1.9 ± 0.05 | 2.7–3.0 | 2.85 ± 0.35 |
| $\alpha$-Ga$_2$O$_3$ | 1.6 ± 0.025 | 5.3 | 5.12 ± 0.21 |
| $\beta$-Ga$_2$O$_3$ | 1.6 ± 0.025 | 4.8 | 5.12 ± 0.21 |
| $\gamma$-Ga$_2$O$_3$ | 1.6 ± 0.025 | 5.0 (dir) | 5.12 ± 0.21 |
| $\alpha$-Sb$_2$O$_3$ | 1.9 ± 0.05 | 3.40 | 2.85 ± 0.35 |
| $\beta$-Sb$_2$O$_3$ | 1.9 ± 0.05 | 2.50 | 2.85 ± 0.35 |
| $\gamma$-Sb$_2$O$_3$ | 1.9 ± 0.05 | 2.80 | 2.85 ± 0.35 |
| rutile-TiO$_2$ | 1.625 ± 0.025 | 3.05 | 3.25 ± 0.12 |
| anatase-TiO$_2$ | 1.625 ± 0.025 | 3.2 | 3.25 ± 0.12 |
| brookite-TiO$_2$ | 1.60 ± 0.025 | 3.1–3.3 | 3.25 ± 0.12 |
| $\alpha,\beta,\gamma,Y,\bar{c},\bar{h},\bar{c},\bar{h}$-WO$_3$ | 1.70 ± 0.025 | 2.75 ± 0.25 | 2.87 ± 0.15 |

Figure 3. Experimental bandgap values of Y-Gd mixed oxides as a function of base alloy composition. (Data taken from the literature) Green line: theoretical bandgap values estimated according to Eq. 4a.
In the case of oxides, the charge transfer process frequently occurs from oxygen p orbital, forming the valence band, to the conduction band made mainly from the orbital of the cationic counterparts. According to this it can be generally inferred that $E_g$ values of pure or mixed oxides not in agreement with the proposed correlations could be rationalized by assuming the onset of intra-atomic transitions owing to the fact that the electronic exchange and d-d coulomb interaction can be accounted for. Further complications to this scheme can be expected in the presence of passive films containing transition metal cations with d-band partially filled originating from possible intra-atomic d-d optical transitions. For this purpose, we need to compare some recent theoretical results pertaining to the bandgap of mixed iron-chromium oxides with the experimental data derived from PCS investigations of passive films grown on SS and Fe-Cr alloys.

As previously reported, and in agreement with the proposed correlations, increasing optical bandgap values are expected for passive films grown on pure iron ($E_g$ values range from 1.5 to 2.3 eV) and for SS alloys, where at least 13% of Cr metal is present. In the case of oxides, the charge transfer process frequently occurs from oxygen p orbital, forming the valence band, to the conduction band made mainly from the orbital of the cationic counterparts. According to this it can be generally inferred that $E_g$ values of pure or mixed oxides not in agreement with the proposed correlations could be rationalized by assuming the onset of intra-atomic transitions owing to the fact that the electronic exchange and d-d coulomb interaction can be accounted for. Further complications to this scheme can be expected in the presence of passive films containing transition metal cations with d-band partially filled originating from possible intra-atomic d-d optical transitions. For this purpose, we need to compare some recent theoretical results pertaining to the bandgap of mixed iron-chromium oxides with the experimental data derived from PCS investigations of passive films grown on SS and Fe-Cr alloys.

As previously reported, and in agreement with the proposed correlations, increasing optical bandgap values are expected for passive films grown on metallic alloys obtained by alloying pure iron (Fe) with Cr or both ferritic and austenitic SS. Table V indicates that in the case of mixed iron-chromium oxides with the experimental data derived from PCS for such mixed oxides of extreme relevance for a correct interpretation of the corrosion behavior of these technologically important alloys.

In order to test the general validity of Eq. 4a and Eqs. 6 in predicting the composition dependence of $E_g$ values also in the case of s-p metals mixed oxides, and in agreement with the general rules of the regular semiconductor alloys above mentioned, in Figure 4a we report the optical bandgap of mixed $\alpha$-(Ga$_{1-x}$Al$_x$)$_2$O$_3$ as a function of the square of the difference of electronegativity between oxygen and the average electronegativity of cations derived according to Eq. 4a. As indicated in Figure 4a, $E_g$ linearly depends on $(\chi_O - \chi_{\text{Al}})^2$ by assuming $(\chi_O - \chi_{\text{Ga}})^3 = 1.61$ and $(\chi_{\text{Ga}} = 1.475$, in agreement with the Pauling scale and within the accepted uncertainty. Moreover, from the data shown in Figure 4b, it is evident that the dependence on composition of the band gaps of mixed $\alpha$-(Ga$_{1-x}$Al$_x$)$_2$O$_3$ can be nicely fitted according to the following expression:

$$E_g = (\chi_O - (\chi_{\text{Al}}_{1-x} + \chi_{\text{Ga}}_x)) = 8.4751 - 3.241x_{\text{Ga}} + 0.1287x_{\text{Ga}}^2$$

By using the A value of 5.8866 derived from the data fitting in Figure 4a we obtain (see Eqs. 6b, 6c) a bowing parameter $b = S_b = 5.89 \times (0.135)^2 = 0.107$ and a linear term $S_l = 2 \times 5.89 \times (3.5 - 1.475) \times (-0.135) = -3.22$ in very good agreement with linear and quadratic values derived from experimental data fitting equation (see Figure 4b). In the case of $\alpha$-Ga$_2$O$_3$, the bandgap reported in the literature is around 5.30 eV in agreement with the value reported previously and with the $E_g$ values derived by using Eq. 3b valid for s-p metal oxides (see also Table IV). It is of some interest to stress that the linear correlation reported in Figure 4a is able to provide also a value of bandgap of $\alpha$-In$_2$O$_3$ (corundum structure) equal to 3.40 eV ($\chi_{\text{Ga}} = 1.70$ in the Pauling scale) in quite good agreement with the bandgap value of 3.6 eV reported in the literature for In$_2$O$_3$ by assuming direct optical transitions as for mixed $\alpha$-(Ga$_{1-x}$Al$_x$)$_2$O$_3$. According to the literature the value of $E_g = 3.6$ eV is not the fundamental bandgap but the lowest direct optical bandgap value of $\alpha$-In$_2$O$_3$. Moreover, recently, it has been experimentally shown that the fundamental gap for single crystal cubic-In$_2$O$_3$ is indirect with a value of $\sim 2.70$ eV. This last value well compares with the experimental value reported for plasma grown polycrystalline In$_2$O$_3$ better interpolated by the d-metal correlation as, initially, suggested previously. In fact, by assuming for In the Pauling electronegativity value $\chi_{\text{In}} = 1.70 \pm 0.05$, an $E_g$ value of 2.87 $\pm$ 0.24 eV is obtained from d-metal correlation, whilst a bandgap value of 4.30 $\pm$ 0.385 eV is derived according to the s-p metal correlation, quite far from the values experimentally measured in the literature.

In the case of Al$_2$O$_3$, the $E_g$ values experimentally measured (or derived by DFT studies) for different polymorphs span a quite large range of energies well outside the range of energies (5.5–6.40 eV)
Figure 4. (a) Experimental bandgap values of mixed α-(GaₓAl₁₋ₓ)₂O₃ as a function of the square of the difference of electronegativity of oxygen and the average electronegativity of cations. (b) Eₓ,exp values as a function of the composition. (Data taken from the literature.) Green line: theoretical bandgap values estimated according to Eq. 6b. (c) Experimental (dots) and calculated according to Eq. 7 (triangles) bandgap values of mixed α-(GaₓAl₁₋ₓ)₂O₃.

Non-regular (s,p-d metals) mixed oxides and estimates of polymorphs Eₓ.—In the case of ternary oxide containing cationic elements belonging both to sp-metal and d-metal groups (non-regular mixed oxides), the choice of the coefficients A and B to be used in Eq. 3 becomes undetermined. In order to overcome such a difficulty and in agreement with the model previously suggested for regular mixed oxides, we here generalize Eq. 4 to mixed non-regular systems by assuming that for mixed oxides the bandgap value can be written as:

\[
E_{x,sp-d} = x_1 E_{x,1}(\chi_{av}) + x_2 E_{x,2}(\chi_{av})
\]

where:

\[
E_{x,1}(\chi_{av}) = A_1(\chi_{av} - \chi_{av})^2 + B_1 \quad E_{x,2}(\chi_{av}) = A_2(\chi_{av} - \chi_{av})^2 + B_2
\]

with \(\chi_{av} = x_1 \chi_1 + x_2 \chi_2\) in which \(x_i\) and \(\chi_i\) representing the cationic fraction (in at%) and electronegativity parameter, respectively, of each metal \(M_i\) present in the mixed oxides. \(E_{x,1}\) and \(E_{x,2}\) represent the bandgap values of pure oxides assumed to follow the previous correlations according to Eq. 3.

Eq. 7 after simple algebraic manipulations can be rewritten as:

\[
E_{x,sp-d} = S_1 x_1 + S_2 x_1^2 + S_3 x_1^3
\]

where:

\[
S_1 = 2A_2(\chi_{av} - \chi_{av})(\chi_{av} - \chi_{av}) + (B_1 - B_2) + (A_1 - A_2)(\chi_{av} - \chi_{av})^2
\]

\[
S_2 = 2(A_1 - A_2)(\chi_{av} - \chi_{av})(\chi_2 - \chi_1) + A_2(\chi_1 - \chi_2)^2
\]

\[
S_3 = (A_1 - A_2)(\chi_1 - \chi_2)^2
\]
MgO (rock salt) for $x\text{Mg}$.

stable polimorphs WZ-ZnO (wurtzite) for $x\text{Mg}$ in almost all the range of composition corresponding to the different bandgap of 4.49 eV has been reported and it will be also taken into account in the fitting procedures discussed below.

The zinc-magnesium mixed oxides system presents further advantages owing to the fact that:

(a) we have no further complications related to the possible presence of partially full d-atomic orbital (Zn$^{2+}$ is a 3d$^{10}$ transition metal);

(b) the two pure oxides, under standard conditions, display bandgap values (7.8 eV for MgO (RS) and 3.25 ± 0.1 eV for ZnO (WZ)) in good agreement with the bandgap values predicted by the s,p-metal ($E_{\text{corr,sp-d}} = 7.80$ eV for MgO) and d-metal ($E_{\text{corr,d}} = 3.37$ eV for ZnO) correlations by assuming Pauling electronegativity parameters of 1.3 and 1.6 for Mg and Zn, respectively.

Moreover, very recently, a very recent study on the electronic band structure of MgO, based on DFT techniques, reports values of 6.06 eV and 6.2 eV for WZ-MgO and ZB-MgO (zincblende structure), respectively.

Furthermore, a very recent study on the electronic band structure of ZnO film defines a range of electronegativity values of Zn ($\chi_{\text{Zn}} = 1.625 ± 0.025$) within the uncertainty range of the Pauling scale of electronegativity;

c) all experimental bandgap values pertain to direct optical transitions so that of the simplifying assumptions mentioned above by Zunger that one “in absence of electronic direct-to-indirect bandgap crossover” is also satisfied for mixed oxides in both RS and WZ structure (although RS-ZnO under pressure seems to display indirect optical gap);

d) the large number of $E_g$ values vs composition data reported in literature, covering all the compositional range where both RS and WZ phases are stable, allow for a reliable extrapolation of the missing $E_g$ values for pure WZ-MgO and RS-ZnO phases, under ambient conditions, as well as a clear separation of the dependences of $E_g$ values from the composition of the mixed oxides in the two crystallographic structures;

e) the difference of electronegativity values between Mg and Zn (0.3 unity according to the Pauling scale) is meaningful but still below the limit for the onset of the cation spectator behavior.

In Figures 5a and 5b we report the optical bandgap values of mixed (Zn$_{1-x}$Mg$_x$)O$^{76-84}$ oxides both in the RS as well as in WZ phase as a function of the square of the difference of electronegativity of oxygen and of the average electronegativity of cations ($\chi_{av} = 1.615 \times x_{\text{Zn}} + 1.315 \times x_{\text{Mg}}$). By direct visual inspection it is evident that the mixed oxides belonging to different crystallographic systems can be much better linearly fitted, separately, as confirmed by the improved $R^2$ value of the two interpolating lines ($R^2 = 0.985$ for RS and

![Figure 5](image-url)

In order to get a test on the validity of the suggested approach in predicting the composition dependence of bandgap of non-regular mixed oxides a detailed analysis of the composition dependence of $E_g$ values of the Zn$_{1-x}$Mg$_x$O system has been carried out. The choice of this system was suggested by the fact that numerous experimental data ($E_g$ values and cationic ratios) are available from the literature in almost all the range of composition corresponding to the different stable polimorphs WZ-ZnO (wurtzite) for $x_{\text{Zn}} \leq 0.40$at% and RS-MgO (rock salt) for $x_{\text{Mg}} \geq 0.45$ at% according to the Pauling scale; moreover, very recently, a metastable wurtzite phase containing 51at% of Zn with an optical bandgap of 4.49 eV has been reported and it will be also taken into account in the fitting procedures discussed below.

We have to mention that, as for the pure oxides, there are not experimental data for the bandgap values of RS-ZnO and WZ-MgO under ambient conditions, although experimental $E_{\text{opt}}$ values ranging between 2.50–2.80 eV have been reported for the optical bandgap of RS-ZnO under high-pressure conditions as nano-crystals.

| Mixed Oxide | $\chi_{\text{s,p-metal}}$ | $\chi_{\text{d-metal}}$ | $E_{\text{g,exp}}$ (eV) | $E_{\text{g,th,sp-d}}$ (eV) |
|-------------|--------------------------|--------------------------|--------------------------|--------------------------|
| BiFeO$_3$   | 1.9                      | 1.9                      | 2.30–2.80               | 2.40                     |
| Bi$_{0.5}$Dy$_{0.5}$VO$_4$ | 1.9                      | 1.9, 1.25               | 3.06 ± 0.02             | 3.03                     |
| Bi$_2$Ti$_2$O$_7$ | 1.9                      | 1.65                    | 2.83±0.04               | 3.13                     |
| Bi$_2$TiO$_4$ | 1.9                      | 1.6                    | 3.40±0.04               | 3.25                     |
| BiVO$_4$    | 1.9                      | 1.9                    | 2.40–2.80               | 2.40                     |
| Bi$_2$WO$_6$ | 1.9                      | 1.70                    | 2.80–3.00               | 2.96                     |
| CdAl$_2$O$_4$ | 1.5                      | 1.725                   | 4.70 ± 01              | 4.73                     |
| CdGa$_2$O$_4$ | 1.625                    | 1.725                   | 3.5–4.05               | 4.12                     |
| Cd$_2$SnO$_4$ | 1.85                    | 1.725                   | 2.97–3.18              | 2.97                     |
| CdSnO$_3$   | 1.85                     | 1.725                   | 3.07 ± 01              | 3.06                     |
| CuAlO$_2$   | 1.5                      | 1.90                    | 3.50–3.60               | 3.60                     |
| CuGaO$_2$   | 1.6                      | 1.90                    | 3.60 ± 05              | 3.30                     |
| Cd$_2$Al$_2$O$_4$ | 1.475                   | 1.3                    | 5.87 ± 01              | 5.88                     |
| LaAlO$_3$   | 1.5                      | 1.2                    | 5.8–6.3 ± 01           | 6.03                     |
| Pr$_2$Sn$_2$O$_7$ | 1.9                      | 1.3                    | 4.20 ± 08              | 4.25                     |
| Y$_2$Al$_2$O$_7$ | 1.475                   | 1.175                 | 6.40 ± 06–6.50 ± 05    | 6.25                     |
| ZnAl$_2$O$_4$ | 1.475                   | 1.76                    | 5.15 ± 09              | 5.15                     |
| ZnAlGaO$_4$ | 1.5                      | 1.6                    | 4.60 ± 09              | 4.73                     |
| ZnGa$_2$O$_4$ | 1.625                    | 1.6                    | 4.55 ± 10              | 4.54                     |
| Zn$_2$SnO$_4$ | 1.85                    | 1.6                    | 3.30–3.70±111–113      | 3.45                     |
| ZnSnO$_3$   | 1.85                     | 1.6                    | 3.00–3.90±111–113      | 3.44                     |

*From Ref. 12: $\chi_{av} = 1.90$.\*

\[(\chi_{av})^{5+1} = 1.90.\]
Figure 6. Experimental bandgap values of mixed Zn(1-x)MgxO as a function of the composition. (Data taken from the literature78–84) (a) Best fitting line relating to the experimental bandgap values regardless of crystallographic system (squares and diamonds) and theoretical bandgap values (triangles) estimated according to Eq. 7. (b) Experimental (squares) and calculated (triangles) bandgap values of mixed Zn(1-x)MgxO in wurtzite phase. (c) Experimental (diamonds) and calculated (triangles) bandgap values of mixed Zn(1-x)MgxO in rock-salt phase (see text).

R² = 0.984 for WZ) reported in Figure 5b for mixed oxides, with respect to that one reported in Figure 5a (R² = 0.956).

Furthermore, from Figure 5b, it is possible to derive a bandgap value of WZ-MgO polymorph of about 5.71 eV by extrapolating the interpolating line of WZ-ZnO system up to the value of \((\chi_O - \chi_{av})^2 = (3.5–1.3)^2\), i.e. \(\chi_{av} \equiv \chi_{Mg}\). This last value is in good agreement with the analogous value estimated by extrapolating the theoretical \(E_g\) values calculated by DFT in a range of Mg concentration \(\leq 0.40\). No experimental data for such a phase have been reported in the literature but this extrapolated value is also in relatively good agreement with the direct bandgap value of 6.06 eV theoretically derived from a recent DFT study.88 It is also worth noting that a linear dependence of \(E_g\) from the composition \((x_{Mg})\) of Zn(1-x)MgxO ternary oxides was reported according to Eq.8:

\[
E_g = 3.35 + 2.33x_{Mg} \text{ in eV} \quad [8]
\]

where only the linear term is present in Eq. 8 whilst the bowing parameter is missing, in spite of the large difference in \(\chi\) values of the two cations, probably owing to the short composition range fitted88 (see below). From Eq. 8a \(E_g\) value of 5.68 eV is derived for WZ-MgO phase in very good agreement with the value above reported (Figure 5b).

Analogously, it is possible to derive an \(E_g\) value of 2.74 eV for ZnO in the rock salt structure (RS-ZnO) by extrapolating the interpolating line of RS-Zn,Mg(1-x)O system to the value of \((\chi_O - \chi_{av})^2 = (3.5–1.625)^2\), i.e. \(\chi_{av} \equiv \chi_{Zn}\) (see Figure 5b). Such a value is in quite good agreement with the experimental indirect optical bandgap values reported in the literature85–87 for RS-ZnO under high pressure conditions (\(E_g = 2.5 \pm 0.15\) eV) and with that (2.80 eV) reported for RS-ZnO nanocrystals embedded in MgO matrix.89 By using the uncertainty range of \(\chi_{Zn}\) values around the value assumed for WZ-ZnO, we estimate a range of possible \(E_g\) values for RS-ZnO equal to 2.74 ± 0.34 eV. We have to mention that indirect bandgap values ranging between 1.1 and 4.5 eV have been calculated by DFT for RS-ZnO.87

The data shown in Figures 5a and 5b seem to confirm the general validity of the correlation between \(E_g\) and the square of the difference of Pauling electronegativity between oxygen and the cationic average electronegativity initially proposed9 also for mixed s,p,d metal oxides. However the A values, obtained from the fitting lines for WZ-Zn,Mg(1-x)O (1.803) and RS-Zn,Mg(1-x)O (3.673) in Figure 5b, display no direct relationship with the initial A values derived for pure s,p-metal (2.17) and d-metal (1.35) oxides correlations,9 so that it is impossible to predict the composition dependence of mixed s,p-d,d ternary oxides also in presence of previous knowledge of the \(E_g\) values of pure s,p-metal and d-metal oxides.

On the other hand, according to Eqs. 7a–7d it should be possible to predict the bandgap value of mixed s,p-d metal oxides as a function of composition if \(E_g\) values of pure oxides are in agreement with the \(E_g\) values calculated by the correlations valid for s,p and d-metal oxides. According to this, we report in Figure 6a the best fitting of experimental data, derived from different authors,78–84 of Zn(1-x)MgxO films in the whole range of composition. All data have been used regardless of the crystallographic system in which each alloy is stable owing to the fact that \(E_g\) values of pure oxides can be calculated...
by d,d and s,p-metal oxides correlations as above mentioned and in agreement with the derivation of Eq. 7.

We like to stress that:

a) theoretical data calculated by using Eq. 7 (green triangles in Figure 6a) are close to experimental values of mixed oxides in both crystallographic systems (rock-salt structure up to 50at% in Mg content for stable phases and wurtzite structure with Mg content ≤ 20at%) by using as electronegativity parameters χ_{Mg} = 1.625 and χ_{Mg} = 1.30, in agreement with above mentioned uncertainty, and by assuming the usual values of A and B for pure d (1.35 and −1.49 respectively) and s,p-metal (2.17 and −2.71 respectively).

b) appreciable changes in the value of bowing parameter, b_{exp}, were obtained depending on the presence or not of experimental points relating to the metastable (x_{Mg} = 0.4) WZ-Mgₓ(Zn₁₋ₓ)O phases recently reported in literature.

Data shown in Figure 6a support the usefulness of the use of Eq. 7 in predicting, with reasonable accuracy, the optical bandgap values of non-regular mixed oxides provided that the bandgap value of both pure oxides can be expressed by means of Eq. 3. A rapid inspection of the bowing terms as expressed according to Eq. 6c (regular mixed oxides) and 7c (non-regular mixed oxides) indicates that for non-regular mixed oxides the quadratic term can assume positive as well as negative values and that bowing coefficients much larger than those expected for regular mixed oxides can be obtained also in the presence of a constant value of Δχ = (χ_{M} − χ_{Z}) term. This last statement can be easily checked by comparing the Sₜ term given by Eq. 7c (Sₜ = 1.142) with the analogous term of Eq. 6c (Sₜ = 0.360) calculated by using the A value (3.41) derived from fitting procedure shown in Figure 5a. It is clear that the large difference in the quadratic (bowing) term stems out from the fact that, with respect to the regular mixed oxides, a new contribution to the bowing parameter is now appearing in Eq. 7c: 2(A₁ − A₂)(B₂ − B₁) that accounts for the difference in the A values of the two original correlations and for the difference of electronegativity of the two cations. This fact can help to explain why in mixing different semiconductor alloys larger values of the bowing term are usually observed in alloys having different anionic partners but the same metallic cation. Different A values and larger difference in the electronegativity values of the anionic partner (the more electronegative atom) cooperate in magnifying the bowing coefficient. We will go into the details on this point in a forthcoming paper. The difference between the Sₜ term (1.142) and the bowing coefficient, b (1.271), reported in Figure 6a, must be attributable to the interpolating quadratic law used to compare the bowing equations of the experimental data and of the theoretical data calculated according to Eq. 7.

As previously noted, an improved fitting of the experimental data (E_{g} vs x_{Mg}) is clearly obtained by separating the mixed oxides for each crystallographic system in which they are stable (RS and WZ for Mg and Zn rich phase respectively). In Figure 6b we report the experimental E_{g} values as a function of Mg composition for mixed oxides crystallizing in wurtzite structure including also the metastable Mg richer phases (x_{Mg} = 0.51at%). The theoretical E_{g} values as a function of the Mg content were obtained by using Eq. 7a with a value of E_{g}(WZ-ZnO) = 3.35 eV, very close to that reported in literature for single crystal WZ-ZnO. The resulting equation is:

E_{g}(WZ − (Zn₁₋ₓ)MgₓO) = 3.35 + 1.93x_{Mg} + 0.718x_{Mg}/x_{Zn} + 0.0463x_{Mg}^² in eV [8a]

where the linear, quadratic and cubic coefficients (see Eqs. 7b, 7c, 7d) were derived by assuming A_{d} = 1.35, B_{d} = −1.50, x_{Zn} = 1.605 for the WZ-ZnO and A_{d} = 0.9, B_{d} = −3.025, x_{Mg} = 1.931 for WZ-MgO. The values of A_{d} and B_{d} were chosen in order to have the best agreement between experimental data and theoretical values and by taking into account that, in absence of any experimental value for WZ-MgO, any value comprised between the estimated ones, 5.69 eV (see above) and 6.07 eV, could be a reasonable E_{g} value for pure MgO.

As for the results of this fitting procedure we want to stress that:

a) it is noteworthy that the data derived from Eq. 8a provide a very nice fitting of the experimental data by using the original A (1.35) and B (−1.50) values valid for d-metal oxides as well as an electronegativity value x_{Zn} = 1.605, well below the Pauling electronegativity uncertainty, and in agreement both with the value of WZ-ZnO = 3.30 eV, experimentally derived, and with that one calculated by using Eq. 3. Moreover, for the A_{d} (1.90) and B_{d} (−3.025) parameter derived from the best fitting procedure, we like to stress that such values differ a little from the A (14%) and B (11%) values originally reported for s,p-metals oxides correlations. This difference is quite reasonable if we take into account that according to Eq. 2b these parameters, empirically derived, can be expressed as: A = 2E_{g} and B = 1/[(Δχ_{M} + Δχ_{Z})] with both E_{g} and Δχ_{M} (the repulsive term) expected to vary with changing crystal structure;

b) the bandgap value of WZ-MgO derived from Eq. 8a (6.05 eV) coincides practically with the one estimated by DFT (6.06 eV) and with the one estimated by using Eq. 3 with A_{d} and B_{d} and χ_{Mg} values reported above. Moreover, by using the same value of χ_{Mg} and B_{d}, and by assuming A_{d} = 1.93, it is possible to derive a bandgap value for zincblende MgO phase (E_{g}(ZB-MgO) = 6.19 eV) coincident, once again, with the value (6.20 eV) estimated previously. A similar result can also be obtained by assuming a value of χ_{Mg} = 1.30 and leaving unchanged the A and B values also for ZB-MgO.

From the best fitting procedures of RS-MgₓZn₁₋ₓO, i.e. Mg-rich phases, it is also possible to derive, in analogous manner, the E_{g} value for pure RS-ZnO as extrapolated point. The theoretical E_{g} values as a function of the Zn content were obtained by using Eq. 7a with a value of E_{g}(RS-ZnO) = 7.80 eV as reported in literature for single crystal RS-MgO. The resulting best fitting equation was:

E_{g}(RS − (MgSn−₁₋ₓ)O) = 7.80 − 6.35x_{Zn} + 1.473x_{Zn}/x_{Sn} − 0.092x_{Zn}^² in eV [9a]

where the linear, quadratic and cubic coefficient (see Eqs. 7b, 7c, 7d) were derived by assuming A_{d} = 1.3, B_{d} = −1.75, x_{Zn} = 1.625 as for the RS-ZnO and A_{d} = 2.17, B_{d} = −2.71, x_{Mg} = 1.30 for RS-MgO. The values of A_{d} and B_{d} for RS-ZnO were chosen by taking into account that, in absence of any experimental value for RS-ZnO under ambient conditions, a value of E_{g}(RS-ZnO) near to those reported for samples under high pressure (2.45–2.80) could be a reasonable choice.

The data of Eq. 9a suggest a value of E_{g}(RS-ZnO) equal to 2.83 eV in good agreement with experimental optical bandgap values reported. We want to stress that these values of A_{d} (4%) and B_{d} (15%) differ slightly from the values derived for d-d metal oxides and used for WZ-ZnO (see Eq. 3a).

We have to mention that the indirect bandgap values of E_{g}(RS-ZnO) estimated by DFT span a very wide range of values (0.75–5.5 eV) with a more recent one equal to 3.93 eV. From the quadratic fitting of experimental data point (including 2.8 eV for RS-ZnO) we derive a bowing parameter b_{th} = 1.19 whilst a value of b_{th} = 1.35 is obtained from the fitting of theoretical points derived by means of Eq. 9a.

The importance of the use of Eq. 7 in predicting the bandgap values of mixed oxides can be further appreciated by comparing the theoretical E_{g} values obtained by means of Eq. 7 with the experimental data of α-(Ga_{1−x}Al_{x})₂O₃, already discussed (Figure 4c), in order to extract the A and B parameters to be used in Eq. 3 for getting a theoretical bandgap value for α-Al₂O₃ polymorph closer to the experimental value (5.7 eV) by using also a value of χ_{Al} = 1.5 ± 0.05 eV equal to that one reported by Pauling. We have to recall that the E_{g} value for Al₂O₃ calculated by using the s,p-metals correlation (Eq. 3b) and a value of χ_{Al} = 1.475 is equal to 6.2 eV quite near to γ-Al₂O₃.
In this case we take advantage of the fact that the bandgap value of α-Ga2O3 agrees nicely with the value estimated by using the correlation valid for s,p-metal oxide. In fact, by using the $\chi_{Ga} = 1.60 \pm 0.05$ and the usual values for $A_{Ga}$ (2.17) and $B_{Ga} = (-2.71)$, we derive a value of $E_g(Ga_2O_3) = 5.12 \pm 0.40$ eV in agreement with the values reported in literature for α-Ga2O3 (see Table IV). By following the same approach described above for the non-regular mixed oxides, we obtain the A and B values for $\alpha - Al_2O_3$ by the best fitting procedure and by using Eqs. 7b and 7c to derive the unknown A1 and B1 values pertaining to $\alpha - Al_2O_3$. In Eqs. 7a – 7c $E_{g,2}$, $A_2$ and $B_2$ represent, respectively, the $E_g$ values of $\alpha - Ga_2O_3$ and the values of A (2.17) and B (-2.70) typical of the s,p-metal oxides.

The results of such a procedure are reported in Figure 4c showing that the agreement between theoretical $E_g$ values and experimental data was obtained by using the values of $A_{Ga-Al_2O_3} = 2.50$ and $B_{Ga-Al_2O_3} = -2.0$ and by keeping a constant to 1.475 the electronegativity parameter, $\chi_{Al}$, of aluminum. The increase in the value of A, about 15% larger for $\alpha - Al_2O_3$, would agree with the suggestion by Phillips reported above that the extra-ionic energy unit E1 can change “with different atomic coordinations in different crystal structures”. The parameter B is expected to change too, due to possible changes in the repulsive term contained in Eq. 2. Further investigations and more experimental data are necessary before reaching a deeper understanding of these aspects.

**Future Perspectives**

A critical assessment of the use of PCS in passivity studies to characterize the film composition has been presented aimed to clarify the limits of the semi-empirical correlation proposed by the present authors. It has been shown that in many cases the proposed correlation is able to provide quantitative information on the composition of mixed regular oxides for s,p-metals as well as of mixed TMO with d electronic configuration. It has been shown that some of the criticism pertaining to a chemical approach to the estimate of optical bandgap of different polycrystals can be accommodated within the theoretical framework underlying the proposed correlations. In particular, it has been suggested that changes in the empirically derived A and B parameters of the proposed correlations are able to fit the changes in $E_g$ values reported for different polymorphs of s,p and d-metal oxides by keeping almost constant, or within the Pauling’s claimed uncertainty, the electronegativity value of the metallic partners. We have shown that, by neglecting very minor changes in the electronegativity parameter, the semi-empirical correlation proposed is able to predict the bandgap value of different MgO, $Al_2O_3$ and ZnO polymorphs. Further investigations on the composition dependences of mixed oxides with different crystallographic structures are mandatory before reaching any definitive conclusion on the dependence of A and B parameters from the details of oxides crystallographic structure. These studies are particularly welcome in the case of oxides systems where the different polymorphs span a very large range of bandgap values ($Al_2O_3$, MgO, etc.).

We have also shown that the same semi-empirical approach can be used to predict the dependence of $E_{opt}$ values as a function of composition for mixed oxides as well as to derive the dependence of the bowing coefficient for both regular and non-regular mixed oxides. In the absence of change in the nature of optical transitions, the reported equation could help to explain the origin of the large difference in the bowing coefficient in presence of cationic partner having large difference in the electronegativity values as well as the large bowing coefficient values, usually observed, in presence of non-regular mixed oxide (or semiconducting alloys).

A physical approach based on the more recent models of DFT and quantum mechanical techniques, can provide a more reliable approach to the estimation of the optical bandgap of different crystalline polymorphs. However, such an approach, which is unavoidable in any attempt to put on physically sound basis any theory of electronic properties of materials or to get physical insights on any deviations from observed experimental regularities, is rather discouraging from a practical point of view in providing general indications on the role that the chemical nature of the oxides components plays in determining the optical bandgap value as well as on how it changes with changing oxide composition.

Further theoretical and experimental studies on well characterized systems, possibly including mixed oxides of TM with partially full d-orbital, are necessary before reaching final conclusions on the validity of the semi-empirical approach described above, and the PCS technique to extract reliable information on mixed oxides as a function of their composition. This is particularly true for very complex systems such as those represented by very thin anodic passive films on metallic alloys of large industrial interest (SS, Fe-Cr alloys etc.). However, we are confident that the efforts toward a generalization of the initial semi-empirical correlations will extend a more quantitative use of PCS technique beyond corrosion studies.

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