Processing, Properties, and Design of Advanced Ceramics and Composites

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Preface

This volume contains 33 papers presented during the Materials Science & Technology 2015 Conference (MS&T’15), held October 4–8, 2015 at The Columbus Convention Center, Columbus, Ohio. Papers from the following symposia are included in this volume:

- Controlled Synthesis, Processing, and Applications of Structural and Functional Nanomaterials
- Advances in Dielectric Materials and Electronic Devices
- Innovative Processing and Synthesis of Ceramics, Glasses and Composites
- Advances in Ceramic Matrix Composites
- Rustum Roy Memorial Symposium on Processing and Performance of Materials Using Microwaves, Electric, and Magnetic Fields
- Sintering and Related Powder Processing Science and Technology
- Thermal Protection Materials and Systems
- Surface Protection for Enhanced Performance
- Ceramic Optical Materials, and
- Alumina at the Forefront of Technology

These conference symposia provided a forum for scientists, engineers, and technologists to discuss and exchange state-of-the-art ideas, information, and technology on advanced methods and approaches for processing, synthesis, characterization, and applications of ceramics, glasses, and composites.

Each manuscript was peer-reviewed using The American Ceramic Society’s review process. The editors wish to extend their gratitude and appreciation to all the authors for their submissions and revisions of manuscripts, to all the participants and session chairs for their time and effort, and to all the reviewers for their valuable comments and suggestions.

We hope that this volume will serve as a useful reference for the professionals working in the field of synthesis and processing of ceramics and composites as well as their properties.

Gurpreet Singh
Amar Bhall
Controlled Synthesis, Processing, and Applications of Structural and Functional Nanomaterials
ASSESSING THE LIMITS OF ACCURACY FOR THE TAUC METHOD FOR OPTICAL BAND GAP DETERMINATION

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ABSTRACT

Scientists and engineers working with nanotechnology and thin film optical devices often make use of “Tauc plots” to determine band gaps and evaluate the effect of processing conditions on the quality of coatings made for these applications. Broad-band optical data are easy to acquire and usually exhibit a region of reasonable transparency and then a sharp rise in absorption with increasing photon energy as the band-gap energy is exceeded. The shape of the onset of absorption is diagnostic of whether the band-gap is direct or indirect. Then, an appropriate linear regression can be used to extrapolate to the band gap value, though sometimes the extrapolation is quite far in absolute energy terms from the data used to make the extrapolation. This paper covers some of our recent work where we use known materials to standardize the fitting protocols and assess the accuracy of this simple method.

INTRODUCTION

In our earlier work with thin films (and for many studies in the literature that use the Tauc method) we’ve noticed that the distance of extrapolation in the fitting process may be relatively large, and the tail of sub-band-gap absorption can also be quite large. This raised the basic question about how accurate the Tauc method would be, and how to establish procedures that improve the accuracy of the fitting results[1]. We delved deeply into this problem by looking at ZnO thin films because they are an extremely well-studied material and ZnO is known to have a direct band gap. By looking closely at a population of over 120 thin film Tauc fits we found the band-gap results overall were consistent with a value of 3.27 +/- 0.05 eV, with evidence for two small outlier populations [1]. A subpopulation of higher gap values appeared to be caused by nanoparticle quantum confinement effects (not surprisingly), while a subpopulation of lower gap values appeared to be correlated with more defective samples. These were essentially cases that had stronger sub-band-gap absorption, which has the mathematical effect of shifting the intercept point somewhat to the left and making the confidence interval of the band-gap determination wider (less accurate). To quantify this effect and provide a figure of merit for identifying the more accurate samples, we introduced the “near-edge absorptivity ratio (NEAR)”. And, when using the NEAR to focus on the more accurate data sets, we found that the Tauc method generally gave an experimental distribution of results with a standard deviation of only 0.033 eV, thus emphasizing the relatively high accuracy of the method in general.

We extend that work to the case of indirect band-gap materials and examine accuracy limits based on absorption coefficient values and coating thickness effects that can influence the signal-to-noise ratio of real optical absorption data. Indirect band-gaps are more difficult to characterize because their absorption intensities are characteristically weaker, which provides an added difficulty when most optical data are determined from thin film samples. We address this problem by working with single crystal data from silicon, probably the most well-characterized indirect band-gap material available.

BACKGROUND

The seminal work of Tauc, Grigorovici, and Vancu [2] presented a simple method that uses broad band absorption spectra and interpreted the shape of the absorption edge to arrive at a
determination of the band gap, and its character. Their method was further developed in Davis and Mott’s more general work on amorphous semiconductors [3, 4]. Together they’ve shown that the optical absorption strength depends on the difference between the photon energy and the band gap as shown in (Eq. 1):

\[(a \nu)^{1/n} = A(\nu - E_g)\]  

(1)

where \(h\) is Planck’s constant, \(\nu\) is the photon’s frequency, \(\alpha\) is the absorption coefficient, \(E_g\) is the band gap and \(A\) is a proportionality constant. The value of the exponent denotes the nature of the electronic transition, whether allowed or forbidden and whether direct or indirect:

- For direct allowed transitions \(n=1/2\)
- For direct forbidden transitions \(n=3/2\)
- For indirect allowed transitions \(n=2\)
- For indirect forbidden transitions \(n=3\)

Typically, the allowed transitions dominate the basic absorption processes, giving either \(n=1/2\) or \(n=2\), for direct and indirect transitions, respectively.

Thus, the basic procedure for a Tauc analysis is to acquire optical absorbance data for the sample in question that spans a range of energies from below the band gap transition to above it. Then, plotting the \((\alpha \nu)^n\) with various test exponents versus photon energy allows the researcher to decide which of the exponents gives the most linear plot. Finally, with this exponent, the line is extrapolated down to intersect the X-axis, which will be the band-gap value (as can be interpreted from Equation 1). Of the four exponent choices listed, it is usually found that either the \(1/2\) and 2 exponents are most frequently used (being associated with the allowed transitions).

ANALYSIS OF DIRECT-GAP MATERIALS

Zinc oxide was a good candidate for evaluating the Tauc method because it has been widely studied for a number of useful applications [5-13]. Among these applications the band-gap plays a central and fundamental role as it controls many absorption and conductivity phenomena. Single crystal optical studies have found a direct band gap of 3.3 eV[14-16], though many of the papers surveyed in our thin film analysis were collected from very well crystallized films or even epitaxially grown layers[1]. ZnO was also attractive as a reference material because of its high level of stoichiometry. While every stoichiometric compound must thermodynamically have point defects at some level (and therefore by definition be non-stoichiometric), the phase of ZnO has been experimentally studied and found to have very little deviation from the ideal 1:1 ratio. For example, the early work of Allsopp and Roberts found a slight zinc excess, but less than 50 ppm [17]. This is much more stoichiometric than many phases and thus provided a good calibration test-case for the Tauc method.

Figure 1 gives one example Tauc plot for ZnO where the absorption coefficient times the photon energy to the second power is plotted versus the incident photon energy[18]. The second power was used as zinc oxide is well known to have a direct allowed transition. The characteristic features of Tauc plots are evident: at low photon energies the absorption approaches zero – the material is transparent; near the band-gap value the absorption gets stronger and shows a region of linearity in this squared-exponent plot. This linear region has been used to extrapolate to the X-axis intercept to find the band gap value (here about 3.28 eV).
Assessing Limits of Accuracy for Tauc Method for Optical Band Gap Determination

Figure 1: Example Tauc Plot from UV-Vis analysis of a ZnO thin film, illustrating the method of fitting the linear region to extrapolate the band-gap at the X-axis intercept, here about 3.28 eV. Data replotted from ref.[18].

At even higher energies the absorption processes saturate and the curve again deviates from linear. To select and justify a linear region for extrapolation one must understand the reasons for these lower and upper deviations from linear behavior. On the low energy end, the deviation from linearity can be associated with defect absorption states that are near the band edge. This phenomenon has been investigated by Urbach [19] and in subsequent years, therefore, identified as an “Urbach Tail.” These states are usually described by an exponential function, corresponding to a typical distribution of density of states, evident in the absorption behavior seen in the example Tauc plot (Figure 1). On the high energy end, saturation of available transition states can be responsible for a leveling out of absorption strength in most collected spectra.

The absorption data are rooted in the possible optical transitions within the electronic structure of the material. Figure 2 (next page) shows the band diagram for ZnO[20], showing that the material is direct and that the band-gap derives from states at, Γ, the center of the Brillouin Zone. A representative direct optical transition is shown for a photon energy slightly larger than the band-gap energy.

Selecting the “right” points to use for fitting from Figure 1 is largely subjective, but could also have a profound effect on the extrapolated value for the band-gap. In our earlier work on ZnO, we tried to develop a completely unbiased method for picking the linear portion of the plot and finding the band gap value[1]. Digital data were processed in a spreadsheet to achieve a
series of linear regressions corresponding to incremental portions of the data set. We typically fitted using an 11-data-point window for evaluating the local linear regression (using +/- 5 datapoints on either side for any given local fit), and then we slid this fitting-window along and tested the fit at every possible location. The impact of fitting window width can be illustrated in Figure 3 where we plot the $R^2$ value for each incremental linear regression fit for the data we extracted from the graph shown in Figure 1. Three different curves are presented that cover 5, 11, and 15 datapoint fitting windows, respectively. When fewer data points are used for fitting then better $R^2$ results are generally obtained (as a mathematical certainty). However, if the actual linear region is relatively short then using a bigger span of datapoints will force the inclusion of points that are clearly not part of the linear region and the $R^2$ value will be reduced. Or, similarly when fitting a line to a clearly curved part of the dataset, the same $R^2$ reduction will occur. Figure 3 illustrates this behavior with the general trend downward for the energy values between 3.2 and 3.3 eV (see arrow). Referring back to Figure 1, it can be seen that this is a
Assessing Limits of Accuracy for Tauc Method for Optical Band Gap Determination

region of upward curvature for the Tauc plot, so that extending the fit to larger ranges of data can force the inclusion of more curvature and therefore poorer fits (as shown). The best fit values are found in the mid-point photon energy region between 3.30 and 3.35 eV (as marked with the red ellipse in Figure 3). In our analysis, each linear regression can be evaluated to find the X-axis intercept (the band gap value). Figure 4 shows how this band gap/intercept value changes depending on which set of adjacent datapoints was used for linear regression fitting. The best $R^2$ values for fitting correspond to the band gap values highlighted with the ellipse, all around 3.28 eV. Note that the choice of the width of fitting window imposes only a slight change in extrapolated band gap value establishing a method-imposed precision of about +/-0.005 eV. Interestingly, the standard regression error from any specific fit can be used to calculate a confidence interval for specific fit’s extrapolated bandgap value. For the data shown in Figure 1-4 the best-fit region is found to have 95% confidence intervals of +/-0.0025 eV, +/-0.0015 eV, and +/-0.0023 eV, for the 5, 11, and 15 point fitting windows, respectively. The smaller fitting window has a better $R^2$ value, but the extrapolation is poorer because it is based on a narrower range of energy values and fewer data points. The largest fitting window has a wider basis for making the extrapolation, but the $R^2$ value is a little lower and the confidence interval a little wider, too. In any case, these confidence intervals must be considered the best precision values for the technique, though when many measurements are considered and compared the accuracy is not as good as this.

![Figure 4: Fitted Tauc gap obtained from linear regression fits covered in Figure 1 and 3. The region where the best $R^2$ values resulted is also the region where the fitting slope is steepest and the largest Tauc gap intercept is found: (●) 5, (■) 11, and (▲) 15 sequential points used.](image-url)
In view of the importance of the overlap between the linear region used for Tauc gap fitting and the lower energy Urbach tail absorption effects we also have tried to provide a quantitative measure for comparing different plots and data\[1\]. We noted that if there were no Urbach tail at all then the absorption would be zero up to the optical gap and then rise linearly according to equation (1). So we suggest that the \((a(h\nu)^2\) value measured at the Tauc gap should relate to the size of the Urbach tail, though perhaps not to its energy breadth or shape in detail. Often the Tauc plots are put on an arbitrary units scale, so we normalize this value by comparing it to a \((a(h\nu)^2\) value at slightly higher energy. To make it generalizable we suggested normalizing using a value taken at 2% higher energy than the Tauc gap that has been determined by the fitting process, ie. \(h\nu = 1.02E_g\). To generalize this further and make the concept applicable to indirect materials, also, we take the square root and correct for the 2% difference in photon energy to arrive at a factor we call the “Near-Edge Absorptivity Ratio”, or NEAR, which is essentially the ratio of the absorption coefficients at those two energy values.

\[
NEAR = 1.02 \left( \frac{a(E_{gap})}{a(1.02E_{gap})} \right) = \frac{a(E_{gap})}{a(h\nu = 1.02E_{gap})} \]

Note that this ratio is dimensionless and can thus be evaluated from \((a(h\nu)^2\) graphs even when arbitrary units are used in the plots. The +2% offset is arbitrary and merely intended to probe how steep the curve is close to the Tauc gap. Similarly, when the NEAR factor would be applied to an indirect-gap material (where the \((a(h\nu)^n\) would have been plotted with a \(\frac{1}{2}\) power, then the ratio would need to be squared to yield a dimensionless absorption coefficient ratio.

This NEAR factor was shown to be correlated with the accuracy of the band-gap determined using the Tauc method [1]. Certainly, sharper absorption data that come closer to the X-axis before exhibiting their Urbach tail will be mathematically more likely to have a more accurate band-gap value.

**ANALYSIS OF INDIRECT-GAP MATERIALS**

The case of indirect band-gap materials is quite a bit more complicated since every indirect band-gap material will also, eventually, have direct band optical transitions that start to come into play at photon energies above the indirect gap value. In this regard, many publications provide both the \(n=1/2\) and \(n=2\) plots and use these to extract the indirect edge as well as the lowest of the direct band transitions. And, in many of these analyses, the transition from indirect to direct is not so starkly delineated; there is often a rather broad energy range where the data might be contributing to the linear regression fit for both values – even though each line would have to be built from the assumption of having a dominant contribution from one type or the other.

We address this situation by using the best optical data possible for silicon, an indirect-band-gap material, as a proxy for well crystallized thin film indirect-gap materials. This allows us, eventually, to assess the limits that might be found for distinguishing the indirect and direct band edges and key data signatures that help quantify these assessments. Figure 5 (next page) shows a band-diagram for silicon [21-23]. Silicon is an indirect band-gap material where the indirect transition goes from the center of the Brillouin Zone (Γ) and requires the simultaneous absorption or emission of a phonon in one of the \(<100>\) directions of the lattice (denoted X), resulting in the slanted vector shown. Direct optical transitions happen vertically, but will require larger energy for silicon because the electron must be excited from a filled state into an available
state at higher energy. One such direct transition is shown. Interestingly, the earliest direct transitions for silicon happen up near 3 eV, which is quite a bit larger than the room temperature band-gap of around 1.12 eV. Figure 6 (next page) shows the rapid rise in absorption coefficient for energies above 3 eV and much lower values between 1.1 and 3 eV (associated with indirect optical transitions).

In the basic understanding of how the energy levels vary with electron momentum (k) result in shapes that often have parabolic shapes at symmetry points (for example at the valence band edge and other high symmetry points. And, this parabolic shape is the mathematical reason that the Tauc exponents were found to be the values listed above in equation (1).

![Figure 5: Band structure for silicon showing the indirect transition that is responsible for the onset of absorption and a direct transition (blue arrow) that occurs at certain higher energy values (figure adapted from Chelikowsky [21]).](image)

Knowing that silicon is an indirect material we immediately move to replotting the data using the ½-exponent (the n=2 case from Equation 1, above). Figure 7 (next page) shows this plot for photon energies up to 3 eV (before the sharp rise caused by direct transitions). It can be seen that a large segment of the data can be well represented by a moderately straight light, supporting Tauc’s formalism for an indirect material. The data deviate upward from the nominally-linear part for energies above about 2.2 eV, which could be expected for the following reasons. First, the E-vs-k energy level lines must be parabolic to yield the exponents derived by
Assessing Limits of Accuracy for Tauc Method for Optical Band Gap Determination

Figure 6: Dispersion of absorption coefficient at 300°K for intrinsic silicon. Open symbols are data from Aspnes and Studna[24]; filled symbols are from Green and Keevers[25]. The rapid rise above 3 eV (indicated by the arrow) comes from the onset of direct transitions.

Figure 7: Overview Tauc plot examination of the single crystal silicon absorption data of Green and Keevers[25]. Data are plotted up to 3 eV showing the long region of good linearity (from the band edge up to about 2.2 eV) and including the higher energy range where there is strong upward deviation from the ideal $\frac{1}{2}$-power indirect correspondence.
Tauc. However, as seen in Figure 5, there may be a central region of nice parabolic shape, but there is usually inflection and leveling of the lines at some point. This indicates a higher density of states, which will translate into a larger differential absorption effect as we evaluate at increasingly large photon energies. It is also possible that we might start to have the early contributions from direct transitions which will be added to the basic starting indirect behavior. Further, we might have other secondary indirect transitions that might begin to add into the main transition that was illustrated as the mechanism in Figure 5. All of these factors will lead to an upward deviation of the Tauc plot at higher energy values. For the present discussion we confine our assessment to the region that is nicely linear.

Since we are especially interested in using the Tauc method to extrapolate back to the X-axis to solve for the indirect optical band-gap, we turn our attention to the lower left part of this curve, as shown in Figure 8. Interestingly, the indirect plot displays two linear regions indicating two different indirect transitions. These correspond to the cases where a phonon needs to be either (A) absorbed from the lattice or (B) is emitted into the lattice[26]. Case A has the shallower line, which intersects at (E_{gap} – Eph), where Eph is the energy of the phonon vibration. Case B, with the steeper line, intersects at (E_{gap} + Eph). The intersection points found here were 1.0490 ± 0.0094 and 1.1351 ± 0.0012, resulting in a nominal phonon energy of 0.043 ± 0.010 eV, which is quite consistent with experimental and modeling studies of the phonon dispersion in silicon[27-30].

While the single crystal data for silicon can be resolved into both phonon absorption and emission processes, it would be rather unusual for thin film optical absorption data to extend down this low and thus band-gap values derived by the Tauc method are usually reported without acknowledging the phonon processes inherent in these indirect transitions. Notably, then,
experimental Tauc plots are derived from the steeper sloped region (case B) that extends to higher absorption coefficient values.

Now, we focus our attention more broadly to assess our ability to extrapolate from more limited optical absorption data. This is required because thin film samples may not be thick enough to accurately measure the relatively small absorption coefficient values covered in Figure 8. For example, if we had a 200 nm film that had $\alpha = 1000 \text{ cm}^{-1}$ at a certain wavelength, then still 98% of the light intensity would be transmitted, so depending on the film quality and the spectrometer used it might be difficult to measure that $\alpha$ value. Figure 9 signifies this limit showing that the larger $\alpha$ values will necessarily be more accurate (for a given film thickness and spectrometer) and that the linear regression of the type shown in Figures 7 and 8 would most sensibly be done for the photon energies above some threshold. This issue is further complicated by the fact that many thin films may be defective to some degree and exhibit sub-band-gap absorption or band tailing, the “Urbach tail mentioned above [19]. These states are usually described with an exponential function having absorption coefficient values that remain well above zero quite further into the gap.

Now, referring back to Figure 7, we test the degree of linearity that would be found (and the extrapolated band-gap) if we were fitting a Tauc plot using data only above some selected lower limit absorption coefficient value and working upwards with the more confident data. For simplicity we take a linear regression that is based on 10 adjacent data points (though one would normally select that fitting window to be as large as reasonable for the existing data set, as discussed before in our direct-gap work[1]). Figure 10 (next page) gives the band-gaps and extrapolated confidence interval values found when we do each of the possible 10-adjacent-point linear regressions for the silicon data in Figure 7. The X-axis in Figure 10 is draw to correspond to the photon energy of the left-most data point used in the linear regression. The typical width of

Figure 9: Absorption coefficient values for silicon in the region from 1.05 through 2.20 eV [25]. The parabolic shape associated with an indirect transition is clear.
energy values thus used for these test fits spanned about 0.1 eV at the lower energies and grew to about 0.3 eV when fitting at the higher energies. For example, referring back to Figure 4, the 10-point-regression that starts at 1.1 eV (on the flatter line) will extend well into the area on the steeper line, resulting in a somewhat poorer fit.

Figure 10: Fitted indirect band-gap values for each 10-point linear regression window (small circles) including their mathematical confidence interval based on the variability within each 10-point window. The specific values of mathematical confidence interval are referenced to the right side scale (open diamonds).

So, if we were working with a thin coating of single crystal silicon we might have trouble measuring the smaller $\alpha$ values and could be forced to fit a linear regression through a part of the data that appeared linear but might already be including some of the data from incipient direct transitions, for example, or a wider range of indirect transitions. It is no surprise that if we use a fitting window that is at higher energies then the confidence interval gets gradually wider (because we are extrapolating further). Overlaid onto Figure 10 is a flat line at the indirect band-gap value (determined using the steeper line from Figure 8, above). The higher-photon-energy-base fitted lines (those using the larger absorption coefficient values) find band-gap intercept values that are much higher above the $E_g$ value than would have been predicted by the linear-regression’s projected confidence interval. As noted above, this is partly attributable to the change in curvature for the $E$-vs-$k$ energy levels in Figure 5, which provides for slightly more absorption at higher photon energies and slight upward curvature of the $\alpha(h\nu)$ curve, compared with what would have been predicted by the lowest energy threshold responses. Thus, we find that systematic error might be relatively large when associated with fitting using a range of energy values somewhat far from the lowest absorption coefficient values. The $R^2$ values and calculated confidence intervals must be considered the precision of the measurement, not the accuracy.
Assessing Limits of Accuracy for Tauc Method for Optical Band Gap Determination

DISCUSSION
Application of the Tauc method to thin films is then especially strongly influenced by the thickness of the coating being measured. If the coating is especially thin then only the larger \( \alpha \) values are sampled leading to a likely systematic bias that over-estimates the band-gap value. And, since the \( \alpha \) values associated with those indirect transitions can be rather small it is questionable whether indirect materials can be fairly evaluated using this method. For example, as shown with silicon, there will always be some form of direct transition that eventually overshadows the indirect transition.

CONCLUSIONS
Direct and indirect band-gap model material data have been examined to help understand in greater detail the limitations of the Tauc method when applied to thin film materials. Direct-gap materials have been shown to have band-gap accuracy in the 1% range when considering the whole range of error contributions that might be important for real thin film sample preparation and characterization. A figure-of-merit has been applied that can help differentiate datasets that might have more mathematical likelihood of providing high accuracy band-gap values. This figure of merit is also applicable to indirect materials, but the absorption coefficient values found near the indirect-gap are frequently too low to be measured with typical samples, raising the question of whether good indirect-gap determinations can be made with the Tauc method.

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INVESTIGATION OF PYROAURITE-TYPE ANIONIC CLAY-DERIVED MIXED OXIDES WITH VARIOUS COMPOSITIONS

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ABSTRACT
Pyroaurite, a natural mineral with the formula Mg₆Fe₂(OH)₁₆(CO₃)₄H₂O belongs to the large class of anionic clays and contains positively charged Mg(II) and Fe(III) layers alternating with layers containing carbonate ions and water molecules. Mesoporous pyroaurite-type anionic clays with different Mg/Fe molar ratios (1:3-5:2) have been successfully synthesized by coprecipitation method. The corresponding oxides were obtained by thermal treatment at 550°C and 900°C. The effect of samples’ composition on the structural and textural characteristics of starting pyroaurite and corresponding oxides has been investigated. The crystallite size, the phase composition and BET surface area values were found to strongly depend on the Mg/Fe ratios. TEM micrographs revealed that sheet-like morphology of the high Mg(II) content samples was preserved at 550°C, due to a special decomposition mechanism of pyroaurite.

INTRODUCTION
Pyroaurite and sjögrenite compounds are two closely similar minerals that are two stacking modifications of typical composition Mg₆Fe₂(OH)₁₆(CO₃)₄H₂O¹. Their structure is based on Mg(OH)₂ – brucite-like layers, in which some of the Mg(II) ions are randomly substituted by Fe(III) leading to positively charged layers, their charge being compensated by carbonate (CO₃²⁻) ions, located in the interlayer region along with water molecules. Those two minerals are polypeptides that differ only in layer stacking, the rhombohedral pyroaurite (3R polytype) and the hexagonal sjögrenite (2H polytype) creating two subgroups that belong to the much larger class of layered compounds called anionic clays⁰¹². The anionic clays have been largely investigated due to their applications as anion exchangers, catalysts and catalysts precursors, adsorbents and UV stabilizers, just to mention a few³. Cationic compositions along with specific characteristics of the interlayer play an important role in numerous applications⁴.

Lately, anionic clays derived mixed oxides have been proved to be effective in desulfurization processes⁵. A high level of sulfur in fuels is not desired due to the formation of SOₓ from the combustion of sulfur-containing compounds. SO₂ causes acid rain and this in turn causes damage to buildings and affects dramatically the ecosystem balances⁵. Moreover, sulfur compounds poison the noble metal catalysts used in automobile catalytic converters and this leads to fuel to be incompletely combusted and consequently to emissions of incompletely combusted hydrocarbons, carbon monoxide, nitrogen oxides⁷. An interesting promising potential application of derived oxides is as absorbents for sulfur based compounds, due to their basic properties⁷. So far, different types of absorbents have been used, such as supported metal oxides (support is typically alumina or carbon), mixed metal oxides, metal ion-exchanged zeolites. While all these materials are quite effective, the main difference that anionic clays derived
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oxides bring is that they show very good promise to work at ambient temperature, as opposed to elevated temperatures required for the other absorbents\textsuperscript{7}. Based on the particularities of the layered structure and decomposition mechanism, the metal oxides have increased basicity relative to the clay precursor\textsuperscript{7}. Due to these properties, anionic clays derived mixed oxides have been top candidates for absorbent applications for acidic species, such as CO\textsubscript{2}, NO\textsubscript{x} and SO\textsubscript{x}, mercaptans, organosulfides, CS\textsubscript{2} and thiophene\textsuperscript{7}.

Surface properties and morphology of the oxides, and subsequently their absorption capacities, catalytic activity and efficiency as supporting material is strongly dependent on their chemical composition. The mixed oxides obtained after such a calcination process have very interesting properties, such as: high surface area, basic properties, formation of homogeneous mixture of oxides with very small crystallite size\textsuperscript{8}. The key to these special characteristics resides in the distinctiveness of anionic clays decomposition that occurs in two steps: first, dehydration followed by the collapse of the lamellar structure\textsuperscript{9}. The intermediate structure preserves the layered characteristics of anionic clays, and the overall topology is unchanged. Second, the decomposition of the anions and collapse of the structure leads to formation of a new 3-dimensional network\textsuperscript{8}. The increase of surface area occurs together with this contraction of the layers and is possibly related to the associated strain development in the material. The calcination temperature is the key parameter to be controlled in this process.

This present work describes synthesis and characterization of a series of mixed oxides derived from synthetic phases structurally related to pyroaurite minerals. Pyroaurite-like materials with three different Mg/Fe molar ratios have been synthesized by precipitation and then calcined at two different temperatures. The structural and morphological characterization of the mixed oxides and their precursors indicated differences in structure, thermal behavior and surface characteristics as a function of the cation composition.

EXPERIMENTAL

Materials

All materials (Reagent grade) were used as received, without further purification. All solutions have been prepared with deionized water. Magnesium nitrate hexahydrate, >99\% and iron nitrate nonahydrate, >98\% (Sigma Aldrich) have been used for pyroaurite synthesis, along with sodium carbonate >99.5\% and sodium hydroxide >98\% (Sigma Aldrich).

Sample preparation

The pyroaurite-type samples with Mg/Fe molar ratios of 1:3, 2:1 and 5:2 were synthesized by the coprecipitation method at a constant pH=8. An 0.5M aqueous solution of Mg(NO\textsubscript{3})\textsubscript{2} \textcdot 6H\textsubscript{2}O and Fe(NO\textsubscript{3})\textsubscript{3} \textcdot 9H\textsubscript{2}O containing Mg(II) and Fe(III) in the required ratios was added dropwise under mechanical stirring (600 rpm) simultaneously with a basic solution containing 0.5M Na\textsubscript{2}CO\textsubscript{3} and 0.5M NaOH in a reaction vessel at a constant pH=8. The reaction vessel was equipped with a heating mantle that maintained a constant temperature of 60\degree C during the reaction. Once the reaction was completed, the samples were aged for an hour at 60\degree C, then filtered, washed at room temperature with deionized water, and subsequently dried at 110\degree C overnight. Thermal treatment was carried out at 550\degree C and 900\degree C, respectively, at a heating rate of 5\degree C/min. Samples were kept at each temperature for 1h.

Sample characterization

Powder X-Ray diffraction patterns were recorded using a Rigaku Ultima IV Theta-Theta with a Cu K\textalpha\ radiation (1.54056 Å) in the 2\theta range 5-80\degree, step size 0.02 at a speed of 0.1\degree/min. For the determination of the average crystallite size, Williamson-Hall method has been employed:

\[ \beta_i = K \lambda / L \cos \theta \]

where \( \lambda \) is the wavelength (CuK\textalpha\), \( \beta_i \) is the size broadening, \( \theta \) the Bragg angle.