Advanced Ceramics: Particle Size and the Challenge of Determining Suitable Refractive Indices

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Overview

- Ceramic Formulations
- Importance of particle size
- Problems in particle sizing
- Approaches to index determination
- Examples
  - Fuel cell electrode
  - Dielectric formulation
Ceramic Formulations

- Mixtures of two or more materials
  - Electronic Ceramics
    - Raw material mixtures
      - Oxides and carbonates of most of the Periodic Chart!
    - Doped BaTiO$_3$
      - Dopants containing >5 different materials
  - Solid Oxide Fuel Cell Materials
    - Raw material mixtures
    - La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$
    - Y$_2$O$_3$-ZrO$_2$
    - Gd$_2$O$_3$-CeO$_2$
    - Ni-Y-ZrO$_2$
Importance of Particle Size

- MLCC’s
  - >100 in a cell phone
  - ~0.5 mm
  - 10 to >200 layers of ceramic
  - 1 – 10 µm thick

- Thinner layer = Higher capacitance

MLCC's internal structure:
- TIN NICKEL (BARRIER LAYER) (Ag, Cu)
- TERMINATION
- INTERNAL ELECTRODE (Ag/Pd, Ni)
- CERAMIC DIELECTRIC

~1.5 µm layer
Importance of Particle Size

- **Size Effect in BaTiO$_3$ Ceramics**
  - K decreases below $\sim 300$ nm

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*Freyet al.: Ferroelectrics, 206-207 337 (1998).*
Importance of Particle Size

- Solid Oxide Fuel Cell
  - Each cell ~ 1 volt
  - 3 layers/cell
  - Thin electrolyte better
    - 10 to 40 µm
  - Flat plate and tube designs
Importance of Particle Size

Solid Oxide Fuel Cell Structure

- **Cathode**
  - ~50% porosity
  - $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$

- **Electrolyte**
  - Fully dense
  - $\text{Y-ZrO}_2$, $\text{Gd}_2\text{O}_3$-$\text{CeO}_2$

- **Anode**
  - ~40% porosity
  - $\text{NiO/ Y-ZrO}_2$
Problem

- Background
  - Laser scattering instruments are based on Mie theory for interaction of light with particles.
  - Requires knowledge of the complex refractive index of the particles.
    \[ n^* = n' + \kappa i \]

- Problem
  - Determining a suitable refractive index for accurate particle size determination of mixtures by laser scattering.
Index Determination

**Approaches**

- **Guess**
  - OK for process control
  - When relative value is adequate
- **Mixture Rule**
  - Usually suggested
  - Doesn’t help with imaginary component
- **Software based**
  - Statistical comparisons
  - Measured vs. calculated intensities

\[
\begin{align*}
    n_{\text{mixture}} &= \text{refractive index of mixture} \\
    V_i &= \text{volume fraction of } i\text{th component of mixture} \\
    n_i &= \text{refractive index of } i\text{th component of mixture} \\
    z &= \text{number of components}
\end{align*}
\]
Software Approach

- Horiba LA-950
- Software Ver. 3.56
- Creation of new refractive index kernels
- Measured vs. Calculated Scattered Intensities
- Goodness of fit parameters:
  - Degree of similarity between distribution calculated using the input optical properties and distribution of actual scattering data.
    - Chi Square ($\chi^2$)
    - R Parameter
Goodness of Fit Parameter $\chi^2$

- $y_i = \text{actual scattering measurement}$
- $y(x_i) = \text{theoretical scattering measurement}$
- $\sigma_i = \text{standard dev. of scattering data}$
Intensity Data

- Software Output:
  - Intensity vs. Channel
    - Measured
    - Theoretical
    - Residual (Actual – Theo.)

!! $\chi^2$
Software Based Approach

- Step 1: Make a representative measurement with best guess at R.I. (i.e. Mixture rule)
- Step 2: Vary imaginary component to minimize $\chi^2$
- Step 3: Vary real component to minimize $\chi^2$
- Step 4: Verify via image analysis
Image Analysis

- Deposit powder
- Collect images
- Process
  - ImageJ 1.38x Software (NIH)
- Data analysis
Examples

- Fuel Cell Cathode Mixture
- Dielectric Formulation
Fuel Cell Cathode

Unreacted mixture of raw materials

- La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3
  - La_2O_3, n = 2.51
  - SrCO_3, n = 1.61
  - CoO, n = 1.84
  - Fe_2O_3, n = 2.90
- Surface Area \sim 5 \text{ m}^2/\text{g}

Mixture Rule

- n_{\text{mixture}} = 2.29
Fuel Cell Cathode (cont’d)

1. Make Representative Measurement
2. Vary Imaginary component
   1. 0.0i to 1.0i
   2. Take i at min $\chi^2$
3. Vary real component
4. Verify via SEM
5. Min $\chi^2$ at $n_{mixture} = 3.0-0.20i$
6. Better match at $n_{mixture} = 2.0-0.20i$
Dielectric Formulation

- Dielectric formulation
  - BaTiO₃, \( n = 2.39 \)
  - Dopant mixture, \( n \approx 1.5 \)
  - Surface Area \( \sim 5 \text{ m}^2/\text{g} \)

- Mixture Rule
  - \( n_{\text{mixture}} = 2.32 \)
Dielectric Formulation (cont’d)

1. Make Representative Measurement
2. Vary Imaginary component
   1. 0.0i to 0.10i
   2. Take i at min $\chi^2$
3. Vary real component using 0.01i
4. Verify via SEM
5. No match – adjust Index
6. New imaginary – 0.10, vary Real component
7. $n_{mixture} = 3.0-0.1i$
### Dielectric Formulation (cont’d)

<table>
<thead>
<tr>
<th>Index</th>
<th>Mean</th>
<th>Median</th>
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</thead>
<tbody>
<tr>
<td>SEM</td>
<td>0.28</td>
<td>0.18</td>
</tr>
<tr>
<td>4.4-0.01i</td>
<td>0.51</td>
<td>0.47</td>
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<tr>
<td>3.0-0.10i</td>
<td>0.28</td>
<td>0.22</td>
</tr>
<tr>
<td>2.32-0.10i</td>
<td>0.09</td>
<td>0.08</td>
</tr>
</tbody>
</table>
Summary

- Knowledge of a R.I. that provides a correct particle size is critical
- $\chi^2$ is a good guide to find “correct” complex refractive index for a mixture
- Mixture rule calculation gives good starting point
- Must be realistic
- Still no substitute for actually looking at particles
Additional Reading


2) Algorithm Iterations, TN149, Horiba Instruments Technical Note

3) Guide to Selecting Refractive Index, TN118, Horiba Instruments Technical Note


5) http://www.webmineral.com/help/Gladstone-Dale.shtml


THANKS!

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Expertise in ceramic formulation and processing, new product development, and characterization.