Optical and Structural Characterization of Nanocrystallites \(\alpha\)-cordierite

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ABSTRACT— Nanocrystallite \(\alpha\)-cordierite glasses-ceramics are synthesized using a modified Pechini method. The structural and lattice modes of the products are investigated via XRD and Micro Raman back-scattering spectroscopy. The Debye-Scherrer formula is used to confirm the grain sizes estimated by the SEM slides. Dielectric coefficients calculation and DTA analysis are used to study the synthesized nanocrystallites properties.

KEYWORDS: Back-scattering Raman spectroscopy, Pechini, XRD, nanocrystallite, \(\alpha\)-cordierite, SEM, FTIR Spectroscopy, Vector Network Analyzer, VNA.

I. INTRODUCTION

\(\alpha\)-cordierite is one of the most popular glass ceramics for its interesting properties such as high mechanical strength, good wear resistance, high refractoriness and relatively low dielectric constant, [1]. \(\alpha\)-cordierite glass ceramics are widely used in important industrial application such as heat exchangers, gas turbines, high speed radomes, etc [2-4]. Low values of dielectric constant, dielectric loss and thermal expansion have made \(\alpha\)-cordierite glass ceramics the standard material in industrial and electrical applications, [5-7].

In recent years nanostructured materials have been intensively studied by many researchers. Pechini method has been used as an alternative to the conventional sol-gel technique because of low cost, versatility, the possibility of controlling the stoichiometry, its simplicity, low processing temperature and finally high degree of the homogeneity of the products [7].

In this method, first the chelates are formed between metal ions and a-hydroxycarboxylic acid (citric acid, CA). In the next step, a polyhydroxyl alcohol (ethylene glycol, EG) is added and heated to obtain polymeric resin. Heating process on the polymeric resin causes to break down the polymer. Final step is the calcinations process for several hours to break down the polymer at a known temperature to obtain the nanocrystalline material [8].

In this study a modified Pechini method, is used to synthesize nanocrystallite \(\alpha\)-cordierite. Consequently the products are characterized by X-ray diffraction, back-scattering micro-Raman and dielectric coefficient calculation.

II. EXPERIMENTAL PROCEDURES

\(\text{Mg (NO}_3\text{)}_2.6\text{H}_2\text{O (Merck), Al(NO}_3\text{)}_3.9\text{H}_2\text{O (Merck), SiO}_2\text{ (Merck) are used as precursor raw materials and CA is used for chelating metallic ions [9-13]. The precursor solution of Mg, Al and Si is prepared by adding the raw materials into an aqueous solution of CA and EG heating and stirring. By increasing the solution temperature in a steady stage and within 1-2 h, the solution changes to a resin. Further calcinations process is carried out at 1073 K for several hours. To produce finer particles, the calcinated powders were milled for various time durations. The pellet-shaped compacts were sintered at various temperatures.} \)
III. RESULTS AND DISCUSSION

A. XRD analysis

The X-ray diffraction patterns of the samples are collected by an Xpert X-ray diffractometer, model 1480 manufactured by Philips.

The XRD patterns of the heat-treated nanocrystallites of α-cordierite, at different temperatures (1200°C, 1250°C and 1300°C), are shown in Fig.1.

![Fig. 1. X-ray powder diffraction patterns of α-cordierite nanocrystallites calcinated at: a) 1200°C, b) 1250°C, and c) 1300°C.](image)

It is clear from Fig. 1 that the crystalline phase is present in the sample. All peaks in the XRD patterns are assigned to the α-cordierite. By increasing the temperature, the peak at 10°C becomes sharper and another sharp and clear peak appears. By increasing the temperature, the main structure of α-cordierite becomes dominant and the peaks due to other phases present in the structure disappear. The agreement between the XRD and the standard data in JCPDS file confirms the precipitation of α-cordierite [10, 14].

B. Raman spectra analysis

Raman spectra of the grown nanocrystallites of α-cordierite were collected at the Spectroscopy Laboratory, Atomic and Molecular Group, Physics Department, Tarbiat Modares University by using a Thermo Nicolet Almega dispersive micro-Raman scattering spectrometer operating by a 532 nm line as the second harmonic of a Nd:YLF laser.

The analysis of the Raman active modes of the samples can be carried out according to the standard symmetrical analysis and selection rules correlation of the normal modes.

![Fig. 2. Raman spectra of the synthesized α-cordierite nanocrystallites calcinated at: a) 1200°C b) 1250°C c) 1300°C in the spectral region of 200-1500 cm⁻¹.](image)

The α-cordierite structure is hexagonal, space group P6/mcc, and the silicate framework contains corner-sharing tetrahedrals linked into six-membered rings [11, 15]. The strongest Raman mode has been appeared at 566 cm⁻¹.
By increasing the temperature the peaks become sharper [12, 16].

C. Scanning Electron Microscope (SEM) imaging

The SEM study of the produced samples shows that the formed grains of crystalline powders were almost round-shaped, Fig. 3. The nanocrystallites sizes were determined to be in the range of 30-100 nm. However, the sizes of the grains also were calculated by Debye-Scherrer relation using the XRD patterns and were found to be in the range of 27-120 nm which is in close agreement with the SEM imaging results. It was found that the size and the number of the grains of the nanocrystallite powders were increased at higher calcinations temperatures.

![Fig. 3. SEM images of the synthesized α-cordierite nanocrystalites at different calcinations temperatures: a) 1200°C, b) 1250°C, c) 1300°C.](image)

D. Dielectric coefficient measurement

For measuring the dielectric coefficient of the α-cordierite nanocrystallites, the setup shown in Fig. 4 was used. In this method, a transmitter and a receiver working in the microwave region of the electromagnetic waves is responsible for sending and receiving the signal and the proposed materials are placed inside the waveguide and the waves after passing through the input window, reach the sample in module partition. Some part of the radiation reflects back and the rest transmitted through the sample. By analyzing these two waves, the dielectric coefficient can be calculated according to the reflection and transmission formulas. The dielectric coefficient for α-cordierite nanocrystallites at 1200°C is around 5.19 for the electromagnetic waves with 9 GHz frequency.

![Fig. 4. The experimental setup used to measure dielectric coefficient](image)

E. FTIR spectra

The FTIR spectra of thermal shocked and calcined powder at 1200°C, 1250°C and 1300°C are shown in Fig. 5.

![Fig.5: FTIR spectra at 1200°C (bottom spectrum), 1250°C and 1300°C (top spectrum).](image)

As the temperature increased from 1200 to 1300°C, the intensities of spinel and μ-cordierite peaks were decreased but the
intensities of $\alpha$-cordierite were increased. It shows the phase transformation to $\alpha$-cordierite as the temperature reached 1300°C. also characterization FTIR spectra are shown in the Tables 1-3 [2, 17].

<table>
<thead>
<tr>
<th>Wave num. (cm$^{-1}$)</th>
<th>Phase Type</th>
<th>Structural Type</th>
<th>Bond Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>512</td>
<td>$\mu$ cordierite</td>
<td>Hexagonal AlO$_6$</td>
<td>Al-O</td>
</tr>
<tr>
<td>694</td>
<td>Spinal</td>
<td>Tetragonal SiO$_4$</td>
<td>Si-O-Si Symm.</td>
</tr>
<tr>
<td>948</td>
<td>$\alpha$ cordierite</td>
<td>Tetragonal AlO$_4$</td>
<td>Al-O-Si Symm.</td>
</tr>
<tr>
<td>1085</td>
<td>$\mu$ cordierite</td>
<td>Tetragonal SiO$_4$</td>
<td>Si-O-Si AntiSymm.</td>
</tr>
</tbody>
</table>

Table 1: FTIR Spectra results for 1200°C

Table 2: FTIR spectral results for the sample synthesized at 1250°C calcinations temperature

<table>
<thead>
<tr>
<th>Wave num. (cm$^{-1}$)</th>
<th>Phase Type</th>
<th>Structural Type</th>
<th>Bond Type</th>
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</thead>
<tbody>
<tr>
<td>509</td>
<td>Spinal</td>
<td>Tetragonal SiO$_4$</td>
<td>Si-O-Si Symm.</td>
</tr>
<tr>
<td>692</td>
<td>$\alpha$ cordierite</td>
<td>Tetragonal SiO$_4$</td>
<td>Si-O-Si Symm.</td>
</tr>
<tr>
<td>949</td>
<td>$\alpha$ cordierite</td>
<td>Tetragonal AlO$_4$</td>
<td>Al-O-Si Symm.</td>
</tr>
<tr>
<td>1085</td>
<td>$\alpha$ cordierite</td>
<td>Tetragonal SiO$_4$</td>
<td>Si-O-Si AntiSymm.</td>
</tr>
</tbody>
</table>

Table 3: FTIR spectral results for the synthesized at 1300°C calcinations temperature

<table>
<thead>
<tr>
<th>Wave num. (cm$^{-1}$)</th>
<th>Phase Type</th>
<th>Structural Type</th>
<th>Bond Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>$\alpha$ cordierite</td>
<td>Hexagonal MgO$_6$</td>
<td>Mg-O-Si</td>
</tr>
<tr>
<td>685</td>
<td>Spinal</td>
<td>Tetragonal SiO$_4$</td>
<td>Si-O-Si Symm.</td>
</tr>
<tr>
<td>761</td>
<td>$\alpha$ cordierite</td>
<td>Tetragonal SiO$_4$</td>
<td>Si-O-Si Symm.</td>
</tr>
<tr>
<td>952</td>
<td>$\alpha$ cordierite</td>
<td>Tetragonal AlO$_4$</td>
<td>Al-O-Si Symm.</td>
</tr>
<tr>
<td>1169</td>
<td>$\alpha$ cordierite</td>
<td>Tetragonal SiO$_4$</td>
<td>Si-O-Si AntiSymm.</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

Several routes are proposed to synthesize cordierite that they are categorized in two main groups: solid-state reaction of stoichiometric oxides and wet chemical methods such as sol-gel, hydrolysis, spray pyrolysis and combustion synthesis [19, 20]. Expensive precursors, low yield and sophisticated processing route are main disadvantages of wet chemical methods. Substituting natural and cheaper raw materials instead of high purity oxides has been widely investigated in recent years [20, 21].

Nanocrystallites of $\alpha$-cordierite with the SEM estimation of the grain size of 50–100 nm are synthesized by modified Pechini method. The Debye-Scherrer grain size calculations, by using the X-ray diffraction patterns, are in good agreement with the SEM results. Micro-Raman scattering, were used to assign the relevant recorded Raman active modes of the synthesized nanocrystallites.

V. REFERENCES


Akbar Cheraghi was born in Esfahan, Iran in August, 27, 1974. He received his B.Sc. degree in Control Engineering from Shahid Sattari University in September 1997 and M.Sc. in Physics, from Tarbiat Modares University, with the title of his MSc project “The growth and structural analysis of nonlinear crystal of KTA and its applications in designing of tunable LASERs and LIDARs systems”. Currently he is a PhD student in Physics, Tarbiat Modares University.

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