Optical and Structural Characterization of Nanocrystallites α-cordierite

A. Cheraghi[a,b] and R. Malekfar[a,*]
[a]Physics Department, Faculty of Basic Sciences, Tarbiat Modares University, Tehran P.O. Box 14115-175, I.R. Iran
[b]Faculty of Sciences, Shahid Sattari University, Tehran, I.R. Iran

***Corresponding Author email:** malekfar@modares.ac.ir

ABSTRACT— **Nanocrystallite α-cordierite glass-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, α-cordierite, SEM, FTIR Spectroscopy, Vector Network Analyzer, VNA.

I. INTRODUCTION

α- 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]. α- 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 α-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 α-cordierite. Consequently the products are characterized by X-ray diffraction, back-scattering micro-Raman and dielectric coefficient calculation.

II. EXPERIMENTAL PROCEDURES

$Mg(NO_3)_2.6H_2O$ (Merck), $Al(NO_3)_3.9H_2O$ (Merck), SiO_2 (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.

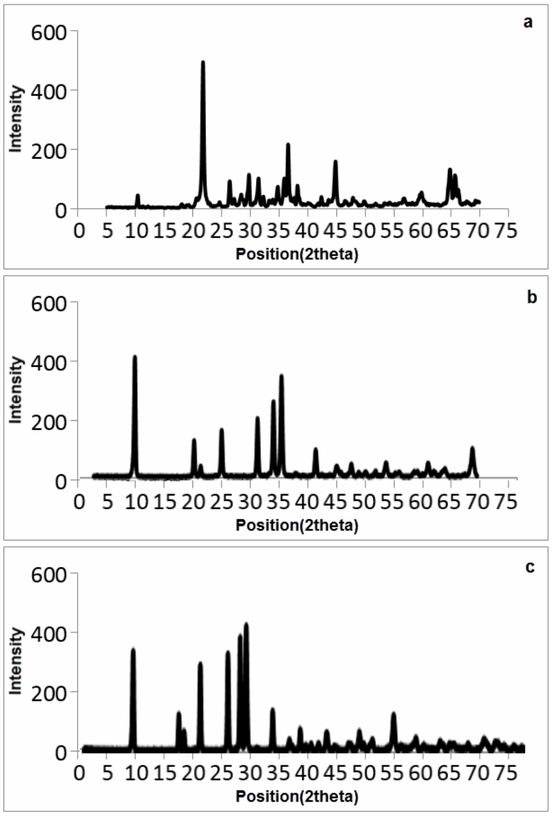

Fig. 1. X-ray powder diffraction patterns of α-cordierite nanocrystallites calcinated at: a) 1200°C, b) 1250°C, and c) 1300°C.

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 incresing 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.

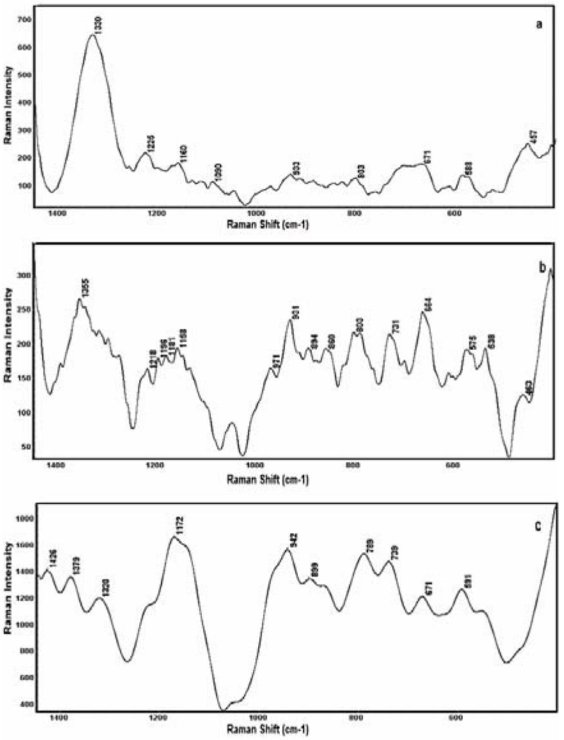

Fig. 2. Raman spectra of the synthesized α-cordierite nanocrystallites calcinated at: a) 1200°C b) 1250°C c) 1300°C in the spectral region of 200-1500 cm^{-1}.

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.

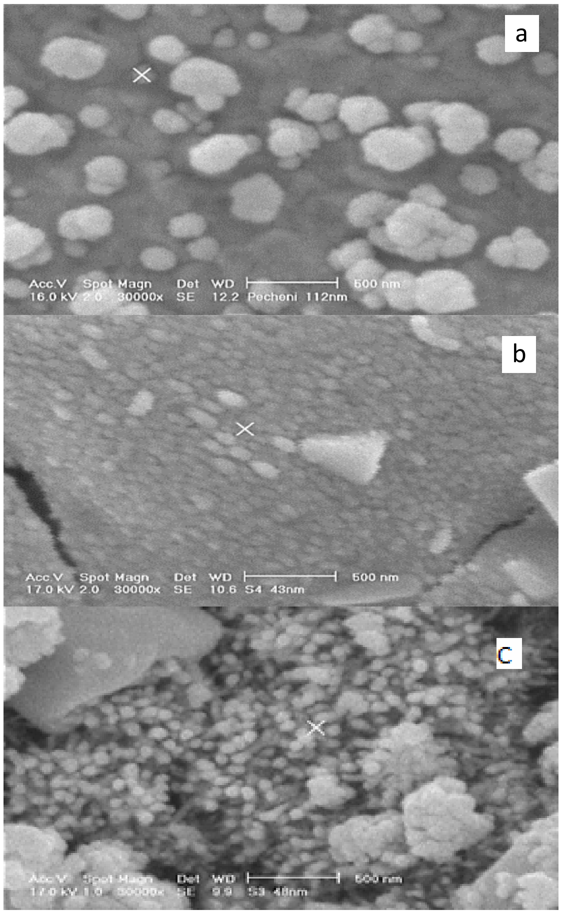

Fig. 3. SEM images of the synthesized α-cordierite nanocrystalites at different calcinations temperatures: a) 1200°C, b) 1250°C , c) 1300°C.

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 micrwave 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 nanocrystalites at 1200°C is around 5.19 for the electromagnetic waves with 9 GHz frequency.

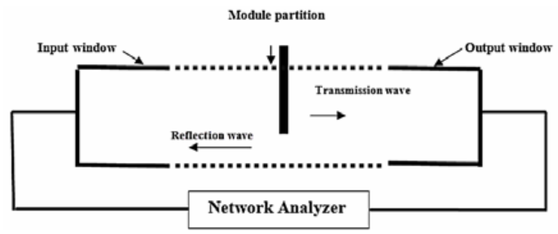

Fig. 4. The experimental setup used to measure dielectric coefficient

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.

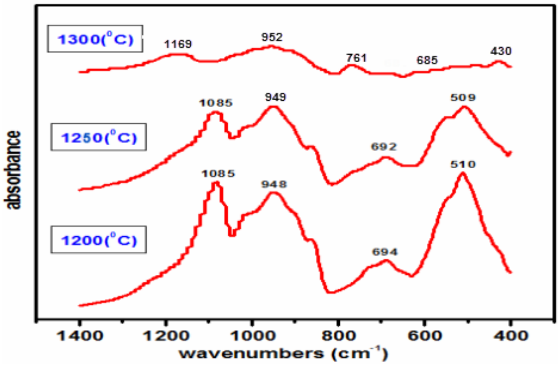

Fig.5: FTIR spectra at 1200°C (bottom spectrum), 1250°C and 1300°C (top spectrum).

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

Table1: FTIR Spectra results for 1200°C

Wave num. (cm^{-1})	Phase Type	Structural Type	Bond Type
512	μ cordrite	Hexagonal AlO_6	Al-O
694	Spinal	Tetragonal SiO_4	Si-O-Si Symm.
948	α cordierite	Tetragonal AlO_4	Al-O-Si Symm.
1085	μ cordierite	Tetragonal SiO_4	Si-O-Si AntiSymm.

Table2: FTIR spectral results for the sample synthesized at 1250°C calcinations temperature

Wave num. (cm^{-1})	Phase Type	Structural Type	Bond Type
509	Spinal	Tetragonal SiO_4	Si-O-Si Symm.
692	α cordierite	Tetragonal SiO_4	Si-O-Si Symm.
949	α cordierite	Tetragonal AlO_4	Al-O-Si Symm.
1085	α cordierite	Tetragonal SiO_4	Si-O-Si AntiSymm

Table3: FTIR spectral results for the synthesized at 1300°C calcinations temperature

Wave num. (cm^{-1})	Phase Type	Structural Type	Bond Type
430	α cordierite	Hexagonal MgO_6	Mg-O-Si
685	Spinal	Tetragonal SiO_4	Si-O-Si Symm.
761	α cordierite	Tetragonal SiO_4	Si-O-Si Symm.
952	α cordierite	Tetragonal AlO_4	Al-O-Si Symm.
1169	α cordierite	Tetragonal SiO_4	Si-O-Si AntiSymm

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 α-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

[1] E.M.M. Ewais, Y.M.Z. Ahmed, and A.M.M. Ameen, “Preparation of porous cordierite ceramic using a silica secondary resource (silica fumes) for dust filtration purposes,” J. Ceramic Process. Research Vol. 10, No. 6, pp. 721-728, 2009.

[2] Y.N. Shieh, R.D. Rawlings, and R.F. West, “Constitution of laser melted Al_2O_3–MgO–SiO_2 ceramics,” Mater. Sci. Technol. 11, pp. 863–869, 1995.

[3] C. Ghitulica, E. Andronescu, O. Nicola, A. Dicea, and M. Birsan, “Preparation and characterization of cordierite powders,” J. Eur. Ceram. Soc. 27, pp. 711–713, 2007.

[4] A. Douy, “Synthesis of cordierite powder by spray drying,” J. Non-Cryst. Solids, Vol. 147, pp. 554–558, 1992.

[5] A.J. Blodgett, D.R. Barbour, “Thermal conduction module: a high performance multilayer ceramic package,” J. Res. Dev. Vol. 26, pp. 30-36, 1982.

[6] P.W. McMillan, “Development of Alpha-Cordierite Phase in Glass,” Soc. Glass Technol. Vol. 6, pp. 286-292, 1985.

[7] M. P. Pechini, US Patent, 3, 330, 679, 1967.

[8] R. Malekfar, G. Ahmadi, A. Cheraghi, J. Rohollahnejad, F. Sahraiyan, M. Khanzadeh, “Micro-Raman scattering of KTP (KTiOPO4) nanocrystallites synthesized by modified sol–gel Pechini method,” Vibrational Spectroscopy, Vol. 51, pp. 308–312, 2009.

[9] S.J. Lee and W.M. Kriven, “Crystallization and Densification of Nano-size, Amorphous Cordierite Powder Prepared by a Solution-

Polymerization Route," J. Am. Ceram. Soc. Vol. 81, pp. 2605-2612, 1998.

[10] G. Chen, "Sintering, rystallization, and properties of CaO doped cordierite-based glass–ceramics," J. Alloys and Compounds. Vol. 455, pp. 298-302, 2008.

[11] C. Weikusat and U.A. Glasmacher, "Raman spectroscopy of heavy ion induced damage in cordierite," J. Nuclear Instruments and Methods in Phys. Research B, Vol. 266, pp. 2990-2993, 2008.

[12] A. Putnist and E. Salje, "Structural states of Mg cordierite: IV.Raman spectroscopy and local order parameter behaviour," J. Phys. Condens. Matter, Vol. 2, pp. 6361-6372, 1990.

[13] H. Esfahani, "Sintering, crystallization and mechanical properties of a gel-cast cordierite glass–ceramic body," Ceramics International, Vol. 38, pp.1523–1527, 2012.

[14] J. Zhou, Y. Dong, and S. Hampshire, "Utilization of Sepiolite in the Synthesis of Porous Cordierite Ceramics," Appl. Clay Science, Vol. 52, pp. 328–332, 2011.

[15] C. Qi, "New tetranuclear macrocyclic complex: Crystal structure, magnetic property and DNA cleavage activity," Solid State Sciences, Vol. 13, pp. 929-933, 2011.

[16] J. Banjuraizah and H. Mohamad, "Effect of impurities content from minerals on phase transformation, densification and crystallization of cordierite glass-ceramic," J. Alloys and Compounds Vol. 509, pp. 7645–7651, 2011.

[17] I. Jankovic, "Crystallization behavior and sintering of cordierite synthesized by an aqueous sol–gel route," Ceramics International, Vol. 38, pp. 1835-1841, 2012.

[18] G. Brunoa, A.M.D. Efremov, and W. Brown, "Evidence for calculation of microstrain in porous synthetic cordierite," Scripta. Materialia, Vol. 63, pp. 285–288, 2010.

[19] A. Yamuna, S. Honda, K. Sumita, M. Yanagihara, S. Hashimoto, and H. Awaji, "Synthesis, sintering and thermal shock resistance estimation of porous cordierite by IR heating technique," Microporous Mesoporous Mater. Vol. 85, pp. 169–175, 2005.

[20] R. Bejjaoui, A. Benhammou, L. Nibou, B. Tanouti, J.P Bonnet, A. Yaacoubi, and A. Ammar, "Synthesis and characterization of cordierite ceramic from Morocca stevensite and andalusite," Appl. Clay Sci. Vol. 49, pp. 336–340, 2010.

[21] Y.C. Dong, X.Q. Liu, Q.L. Ma, and G.Y. Meng, "Preparation of cordierite-based porousceramic micro-filtration membranes using wastefly ash as the main raw materials," J. Membr. Sci. Vol. 285, pp. 173–181, 2006.

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 tiltle 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.

Rasoul Malekfar received his BSc in Physics in 1980 from Pars College, Tehran, I.R. Iran, MSc in theoretical Physics in 1984 from University of Kent at Canterbury, U.K. and PhD in experimental Physics, laser Raman spectroscopy, from King's College, University of London in 1989. He is currently engaged as a Professor of Physics in Atomic and Molecular Group, Physics Department, Tarbiat Modares University, Tehran, I.R. Iran.