STATE UNIVERSITY OF MARINGÁ

POSTGRADUATE IN PHYSICS

Lívia Macková

VIBRATIONAL SPECTROSCOPY OF THE MULLITE-TYPE $BI_2(FE_xGA_{1-x})_4O_9$

Supervisor: Prof. Dr. Klebson Lucenildo da Silva Co-supervisor: Prof. Dr. Luiz Fernando Cótica

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Life is like riding a bicycle. To keep your balance you must keep moving.

Albert Einstein

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Resumo

Óxidos policristalinos do tipo mulita $\operatorname{Bi}_2(\operatorname{Fe}_x\operatorname{Ga}_{1-x})_4\operatorname{O}_9$ $(0 \le x \le 1)$ foram preparados por síntese mecânica-térmica e foram investigados por difração de raios X (DRX), microscopia eletrônica de varredura (MEV), espectroscopia no infravermelho (IR) e espectroscopia Raman. Os difratogramas de raios X mostraram uma fase única com a estrutura ortorrômbica e o grupo espacial *Pbam* (*No.55*). Observou-se uma mudança nas posições dos picos em direção aos ângulo menores no difratograma para números de onda menores na espectroscopia no infravermelho com o aumento do teor de ferro. Similaridades com os outros sistemas da mulita, as bandas IR em 850-400 cm⁻¹ e as bandas Raman 750-300 cm⁻¹ são atribuídas à estiramentos e torções das vibrações das coordenadas do sítio tetraédrico e octaédrico. Os modos IR de alta energia apresentaram presença de vibrações de alongamento Ga-O-Ga e Ga-O-Fe/Fe-O-Ga para x < 0.5. As micrografias de MEV revelaram não homogeneidade do tamanho de partícula e não homogeneidade da morfologia das partículas. Os histogramas revelaram que o tamanho médio das partículas aumenta com a dopagem do ferro.

Abstract

The polycrystal mullite-type $\operatorname{Bi}_2(\operatorname{Fe}_x \operatorname{Ga}_{1-x})_4 \operatorname{O}_9$ $(0 \leq x \leq 1)$ oxides were prepared by mechanochemichal-thermal synthesis and were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), infrared (IR) and Raman spectroscopies. XRD diffractograms show the samples are single phase with orthorhombic structure and space group *Pbam* (*No.55*). It has been observed a shift in the peak positions towards lower angles in X-ray diffraction and towards lower wavenumber in IR spectroscopy with increasing of iron content. In similarity with other mullite systems, IR bands 850-400 cm⁻¹ and Raman bands 750-300 cm⁻¹ are attributed to stretching and bending vibrations of the tetrahedral and octahedral site coordinates. High-energy IR modes showed a presence of Ga-O-Ga and Ga-O-Fe/Fe-O-Ga stretching vibrations for x < 0.5. SEM micrographs revealed non-homogeneity of the particle size and non-homogeneity of the morphology of the particles. The histograms revealed that the mean particle size is increasing with iron doping.

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Chapter

Introduction

Mullite system is a very perspective material due to the its outstanding properties as low thermal expansion, low thermal conductivity and high-temperature strength [1]. One of the subgroup of the mullite-type structure is the mullite with the chemical composition $Bi_2M_4O_9$ (M = transition metal ³⁺) [2]. This mullite-type family posses various technical applications, some of them are used as scintillation materials due to the high emission in the infrared region [3,4], others posses extraordinary ionic conductivity of anions [5,6] which is used in solid state oxide fuel cells and oxygen sensors in gas separation membranes [7].

In this work we are interested in the mullite-type $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$, where it was prepared using solid state reaction in the range of $0 \leq x \leq 1$. The ability to substitute a particular element directly into a specific crystallographic site can show up attractive magnetic, electrical and other interesting properties direct to the technological applications [8,9].

The crystal structure of the *Pbam* space group is defined by octahedral chains $(Fe,Ga)O_6$, which are connected with tetrahedral by dimers of $(Fe,Ga)O_4$ [1]. Both sites are parallel to the c-axis and octahedral site is parallel to the Bi³⁺ atoms. Per formula unit, the structure provides two octahedrally and two tetrahedrally coordinated non-equivalent sites for the metal cations Fe³⁺ and Ga³⁺ [7, 10].

Detailed vibrational studies were investigated on the mullite type $\operatorname{Bi}_2(\operatorname{Fe}_x\operatorname{Ga}_{1-x})_4\operatorname{O}_9$ ($0 \leq x \leq 1$) by infrared (IR) and Raman spectroscopy. Voll *et al.* [11] reported band assignment of the mullite-type $\operatorname{Bi}_2\operatorname{Al}_{4-x}\operatorname{Fe}_x\operatorname{O}_9$, with his own band assignment were published IR spectra of polycrystals $\operatorname{Bi}_2(\operatorname{Fe}_x\operatorname{Al}_{1-x})_4\operatorname{O}_9$ ($0 \leq x \leq 1$) by da Silva *et al.* [2] and single-crystals $\operatorname{Bi}_2\operatorname{Ga}_4\operatorname{O}_9$ by Beran [12]. Raman studies of the polycrystals of the mullite-type have not been published yet.

The goal of this work is to establish IR and Raman assignment of the polycrystalline samples $Bi_2(Fe_xGa_{1-x})_4O_9$ ($0 \le x \le 1$) measured by Fourier Transform IR and micro-Raman spectroscopy. Additional information were obtained and deduced by Gaussian fit of IR and Raman spectrum. The crystallite size were calculated by Scherrer and Williamson-Hall method. The results were compared with the mean particle size obtained by scanning electron microscope (SEM).

To easier work of the reader, the chapter 2 is dedicated to the theoretical part in which is defined the mullite in general, crystal structure of mullite compositions, methods of the synthesis and properties of the different mullite compositions. In this chapter are presented infrared spectroscopy, Raman spectroscopy, X-ray diffraction and scanning electron microscopy techniques. The reader can find information about vibrations of the molecules and the method for the calculation of crystallite size.

The chapter 3 brings the experimental part of the work. This chapter completely describes preparation of the samples, parameters and techniques used for the preparation and characterization of the samples.

In the chapter 4 are reported all results of this work. This chapter starts with the results measured by X-ray diffraction (XRD), IR and Raman spectra followed by scanning electron microscopy analysis.

The chapter 5 presents the conclusions of this work.

The Appendices contain the Williamson-Hall Curves, the bond length values calculated by FT-IR and fitted parameters used in infrared spectroscopy.



Theoretical part

2.1 Mullite

2.1.1 Introduction to the mullite

The word mullite is known less than a century. It is derived from Isle of Mull in Western Scotland, where this mineral has been discovered for the first time like a result of post-Caledonian volcanic activities [13].

It occurs hardly in the nature because for its synthesis are needed high temperature and low pressure. This conditions are provided in the nature particularly at the contact of superheated basaltic lavas with Al_2O_3 -rich sediments [1] or more typical is that the mullite is a subject of the various synthesis investigated in Brazil [2], Germany [11], India [14], etc.

Mullite has more often occurrence in conventional ceramics like in porcelains, sanitary or can be a component of building bricks or pipes [1]. Besides that, it has an enormous impact in advanced structural and functional ceramics due its excellent properties like low thermal expansion, low thermal conductivity, excellent creep resistence, high-temperature strength and good chemical stability [1].

2.1.2 Structure of the mullite

Usually mullite system possess a chemical composition given by $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$. For x = 0 we obtain aluminosilicate mineral $Al_4Si_2O_{10}$, which is called sillimanite. For x = 0.25 we get relatively silica-rich $3Al_2O_3.2SiO_2$, famous as 3:2 mullite and for x = 0.4 we get $2Al_2O_3.SiO_2$, known as 2:1 mullite. In fact, according to the diffusion studies [15], the chemical formula is given by:

$$Al_{(\frac{4}{3}+\frac{14}{3}x)}^{VI} [Al_{\frac{8}{3}}^{IV} Si_2]_{(1-x)} O_{10-x} \Box_x$$

$$(2.1)$$

where the symbol \Box means the oxygen vacancies and IV and VI represent tetrahedral and octahedral coordination site of aluminium cations, respectively.

The crystal structure of mullite is orthorhombic with the space group Pbam [16]. The mullite contains 2 types of chains. The first type is octahedral created by AlO₆ chains and the second are double tetrahedral represented by (Al,Si)O₄ [1]. Octahedral and tetrahedral sites are connected and both are parallel to the c-axis.

The topological arrangement of the chains is a common feature of whole group of mullites called "mullite-type family". These mullites are differed by their chemical composition and by their crystallographic subgroup [1]. In this work we are interested in the subgroup MUL - IV.12, Pbam: Bi₂M₄O₉, which will be introduced in the next subsection.

2.1.3 MUL - IV.12, *Pbam*: $Bi_2M_4O_9$ Group

This group contains the compounds with the chemical composition $Bi_2M_4O_9$ (M = Al³⁺, Fe³⁺, Ga³⁺ and In³⁺) and their derivatives $Bi_{2-2x}A_{2x}M_4O_9$ (A = Sr²⁺, M = Al³⁺, Fe³⁺, Ga³⁺) including also $Bi_2Mn_4O_{10}$ [1,2].

The orthorhombic compounds studied in this work crystallize in the space group Pbam [2,8,9]. The structure of this group is defined by octahedral chain MO₆, which are connected with tetrahedral by dimers of MO₄ [1,9]. Both sites are parallel to the c-axis and octahedral site is parallel to the Bi³⁺ atoms (Figure 2.1).

 $Bi_2M_4O_9$ mullite-type compositions are important due to their various applications. Some of them are used as scintillation materials, others are proper materials for membranes, sensors and electrodes, especially in solid oxide fuel cells [17–19].

2.1.4 Methods of synthesis

Here we report some methods for the preparation of the mullite materials. They can be classified according to the preparation (for example sinter-mullite or chemical mullite) or according to the starting materials (mixture of solids or salts, etc.).

The single crystals of $Bi_2Fe_4O_9$ were prepared by E. Kostiner *et al.* [20] by a chemical method. They used muffle furnace at 950°C during 1 h and after cooled it

approximately $9^{\circ}/h$ to $750^{\circ}C$ in a flowing dry oxygen atmosphere.

The polycrystals $Bi_2Al_4O_9$, $Bi_2Fe_4O_9$, $Bi_2Ga_4O_9$ and $Bi_2Mn_4O_{10}$ were prepared by K. J. D. MacKenzie [21]. The synthesis was by solid state reaction using high energy ball milling during 12 h in 2-propanol, followed by heat treatment in flowing air. The temperature 865°C was for $Bi_2Al_4O_9$ and $Bi_2Ga_4O_9$, 920°C for $Bi_2Fe_4O_9$ and 760°C for $Bi_2Mn_4O_{10}$.

The polycrystalline $\text{Bi}_2(\text{Al}_{1-x}\text{Ga}_x)_4\text{O}_9$ ($0 \le x \le 1$) were prepared by K. L. Da Silva *et al.* [10] by mechanochemical/thermal synthesis method using a high-energy ball mill. The precursors Bi_2O_3 , Ga_2O_3 and Al_2O_3 were milled during 3 h at 600 rpm in free atmosphere, followed by 24 h heat treatment in the air at 800°C.

The polycrystalline $\text{Bi}_2\text{Fe}_{4-x}\text{Ga}_x\text{O}_9$ samples were prepared by Giaquinta *et al.* [9] by solid state reaction. Stoichiometric calculated oxides Bi_2O_3 , Fe_2O_3 and Ga_2O_3 were grounded under acetone, after were created pellets and heated at 850°C in the air atmosphere during 2 weeks.

Pollycrystals of mullite series $Bi_2(M'_xM_{1-x})_4O_9$, where M'/M = Ga/Al, Fe/Al and Fe/Ga were synthesized by Debnath *et al.* [22] applying glycerine method followed by gelation and calcination in an open Pt crucible at 850°C during 24 h.



Figure 2.1: Crystal structure of the Bi₂Fe₂Ga₂O₉ mullite-type composition [8]

2.1.5 Some properties of the $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ and $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ mullite-type compositions

Rietveld refinements of R. T. Santiago [8] (Figure 2.2) and Giaguinta [9] revealed that the lattice parameters and the lattice volume of the $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ samples increase linearly with iron content (x) according to the Vergard's law. This is the consequence of the replacement of Ga^{3+} ions by Fe^{3+} ions due to the different ionic radius (0.47 Å for $\text{Ga}^{3+}(\text{IV})$ and 0.49 Å for Fe^{3+} (IV), 0.62 Å for $\text{Ga}^{3+}(\text{VI})$ and 0.645 Å for Fe^{3+} (VI)) [23].



Figure 2.2: Lattice parameters (a, b, c) and lattice volume (V) of the $Bi_2(Fe_xGa_{1-x})_4O_9$ as a function of iron content (x) [8]

As we can see in Figure 2.3 the results obtained by XRD and Mössbauer spectroscopy are in the good agreement and show the iron ion occupational preference for the octahedral sites. These results also reveal the gallium ion has preference to occupy the tetrahedral sites, which was also reported by Giaguinta [9].

The quadrupole splitting derived from Mössbauer spectroscopic results of ferric ions decrease with the iron content (Figure 2.4) because of the formation more symmetrical environments of ferric ions due to the smaller electric field gradients acting on iron nuclei [8].



Figure 2.3: Concentration of ferric cations in tetrahedral sites and octahedral sites as a function of iron content (x) in the mullite-type $Bi_2(Fe_xGa_{1-x})_4O_9$ [8]

Table 2.1: Band notation, band positions and band assignment of the mullite-type $Bi_2Al_4O_9$ and $Bi_2Fe_4O_9$ according Voll [11]

Band	Band position		Band assignment	
notation	Bi–Al	Bi–Fe		
D	922	812	M–O stretch (MO ₄)	
E	777	648	M–O stretch (MO ₄)	
F	730	600	M-O-M bend (MO ₄)	
F'	694	570	M-O-M bend (MO ₄)	
G"	656	527	O-M-O bend (MO ₄)	
G	601	497	O-M-O bend (MO ₄)	
H"	572	471	$M-O$ stretch (MO_6)	
H'	526	437	$M-O$ stretch (MO_6)	
Н	498	n.o.	$M-O$ stretch (MO_6)	
Ι	468	n.o.	M–O–M bend (MO_6)	

Voll *et al.* [11] published the assignment of the infrared absorption bands for the $Bi_2Al_{4-x}Fe_xO_9$ compounds. The results revealed 3 distinct groups, which were fitted by Gaussian functions. The classifications of the vibrational band modes is



Figure 2.4: Quadrupole splittings for tetrahedrally and octahedrally coordinated ferric cations in $Bi_2(Fe_xGa_{1-x})_4O_9$ as a function of iron content (x) [8]

shown in Table 2.1.

K. L. da Silva in his Phd thesis [2] also studied the infrared spectroscopy in the mullite-type $Bi_2(Fe_xAl_{1-x})_4O_9$. The concentration for x = 0.5 showed in Figure 2.5, in the range of high energy group, presented three vibrational band modes: D, D' and D' which corresponds to the symmetrical stretching of Al-O-Al, Al/Fe-O-Fe/Al and Fe-O-Fe vibrations, respectively.



Figure 2.5: IR absorption spectrum of the $Bi_2(Fe_{0.5}Al_{0.5})_4O_9$ [2]

2.2 Infrared spectroscopy

2.2.1 Introduction to the IR spectroscopy

Infrared spectroscopy (known as IR spectroscopy) is a spectroscopy which study the interactions of the infrared radiation with the matter. The infrared spectrum is divided into 3 regions: Near Infrared (NIRS), Mid Infrared (MIRS) and Far Infrared region (FIRS) [24]. In this work the IR radiation was in the range of 4000-400 cm⁻¹, so in the Mid Infrared region, are typical region for molecular vibrations.

Radiation	Wavenumber (cm^{-1})	Transition
Visible, UV	> 14000	electronic transitions
Near IR	14000 - 4000	molecular vibrations
Mead-Infrared	4000 - 400	molecular vibrations
Far Infrared	400 - 4	molecular vibrations
Microwaves	< 4	molecular rotations

Table 2.2: A part of the electromagnetic spectrum [24]

When a molecule interacts with the electromagnetic radiation, a quantum of the energy is absorbed or emitted (Figure 2.6). The energy of the quantum is given by:

$$\Delta E = h\nu \tag{2.2}$$

where h is the Planck's constant and ν is the equivalent to the classical frequency.

Then the frequency of the transition between the energy states E_1 and E_2 is expressed with the equation:

$$\nu = (E_2 - E_1)/h \tag{2.3}$$



Figure 2.6: Absorption and emission of IR radiation

2.2.2 Vibrations of the molecules

Vibration of a diatomic molecule

To explain a molecular vibration we use the example of the classical harmonic oscillator (Figure 2.7). Two atoms connected via a chemical bond can be understood as two masses connected by a spring [25].



Figure 2.7: Masses m_1 and m_2 connected by a spring

In the classical mechanics, following Hooke's law, the restoring force, f, is given by:

$$f = -K(x_1 + x_2) \tag{2.4}$$

where K means the force constant, x_1 and x_2 are displacements of atoms 1 and 2 from their equilibrium positions, respectively. Minus sign is due to the opposite direction of the restoring force and atomic displacement [25].

The displacements are calculated by the conservation of the center of the gravity and the results are given by:

$$x_1 = (\frac{m_2}{m_1})x_2 \tag{2.5}$$

or

$$x_2 = (\frac{m_1}{m_2})x_1 \tag{2.6}$$

Then we get:

$$f = -K(\frac{m_1 + m_2}{m_1})x_2 = -K(\frac{m_1 + m_2}{m_2})x_1$$
(2.7)

Using Newton's equation of motion we obtain:

$$m_1 \frac{d^2 x_1}{dt^2} - K(\frac{m_1 + m_2}{m_2}) x_1 \tag{2.8}$$

$$m_2 \frac{d^2 x_2}{dt^2} - K(\frac{m_1 + m_2}{m_1}) x_2 \tag{2.9}$$

By using (2.8) and (2.9), we get one equation expressed as:

$$\frac{m_1 m_2}{m_1 + m_2} \left(\frac{d^2 x_1}{dt^2} + \frac{d^2 x_2}{dt^2}\right) = -K(x_1 + x_2) \tag{2.10}$$

Rewriting the result with effective mass $(\mu = \frac{m_1m_2}{m_1+m_2})$ and the displacement $(q = x_1+x_2)$ we get:

$$\mu \frac{d^2 q}{dt2} = -Kq \tag{2.11}$$

The solution of this differential equation is given by:

$$q = q_0 \sin(2\pi v_0 t + \varphi) \tag{2.12}$$

where q_0 is the maximum of the displacement and φ is the phase constant and v_0 is the vibrational frequency expressed as:

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \tag{2.13}$$

In the quantum mechanics, the potential energy is given by:

$$V = \frac{1}{2}Kq^2 \tag{2.14}$$

The Schrödinger equation for this system is expressed as:

$$\frac{d^2\Psi}{dq^2} + \frac{8\pi^2\mu}{h^2} (E - \frac{1}{2}Kq^2)\Psi = 0$$
(2.15)

Resolving the Schrödinger equation with the condition that Ψ must be singlevalued, finite and continuous [25], then we obtain:

$$E_v = (v + \frac{1}{2})h\nu$$
 (2.16)

where v is the vibrational quantum number with the values 0, 1, 2, 3, ...

Fundamental vibrations

Molecular vibrations and rotations are associated with the changes in the molecular dipoles. The amount of the possible vibrations depends on the degree of the freedom of the molecule [26]. The degree of the freedom depends if the molecule is linear or non-linear. Therefore, the number of vibration modes for non-linear molecule is 3N-5 and for linear 3N-6.

The normal modes of the vibrations are stretching and bending (Figure 2.8). Stretching is connected with changes in the bond length between the atoms and can be symmetric or antisymmetric. Bending corresponds to the changes in the angles between the atoms and can be in the plane or out of the plane. In the plane are called scissoring and rocking, out of the plane are known as twisting and wagging.



Figure 2.8: Types of molecular vibrations [27]

2.2.3 FT-IR

The equipment which is used for the measuring IR spectrum is an IR spectrometer. There are two types of the IR spectrometers, the classical IR spectrometer and Fourier Transform IR spectrometer [28].

The IR spectra in this work were measured by FT-IR. This type of the spectrometer uses Michelson interferometer instead of the dispersing element as it is in the classical IR spectrometer. The basic components of the Michelson interferometer are the beam splitter, the fixed and the moving mirror. If the moving mirror moves, it creates phase difference between two beams and appear constructive and destructive interference [29].

The Fourier Transform Infrared Spectroscopy (FT-IR) is based on the relationship between intensity of the radiation $\bar{I}(\delta)$ and $B(\bar{\nu})$ the spectral power density of a given number of wave $\bar{\nu}$ [29]. In Figure 2.9 is the schematic diagram of the FT-IR. IR source $B_0(\bar{\nu})$ makes the light on the interferometer. The output beam $I_0(\delta)$ from Michelson interferometer goes trough the sample, where absorptions exist to generate $I(\delta)$ of the sample. This signal $I(\delta)$ is detected by the detector and it is recorded as a function of optical path difference δ . The interferogram which bring us all information about material is calculated from the transcript $[\bar{I}(\delta) = 2I(\delta) - I(0)]$ [29] and $B(\bar{\nu})$ is gained from the Fourier transform of $\bar{I}(\delta)$.



Figure 2.9: The interference method for the measuring spectrum

Using the Fourier integral theorem it is obtained:

$$B(\bar{\nu}) = \int_{-\infty}^{+\infty} \bar{I}(\delta) \cos(2\pi\bar{\nu}\delta) d\delta \qquad (2.17)$$

Equation 2.17 is also known as fundamental integral of FT-IR [29].

2.2.4 IR spectrum

An infrared spectrum is a plot of the measured infrared light intensity to the property of the light. In this work it is used the plot of the absorbance/absorption versus the wavenumber.

The wavenumber W is the number of the waves in one centimetre and it is given by the equation:

$$W = 1/\lambda \tag{2.18}$$

where λ means wavelength.

The wavenumber is proportional to the light energy, how it shows the relation:

$$E = hcW \tag{2.19}$$

where E is light energy, h is Planck's constant and c is the velocity of the light.

The frequency of the wave is inversely connected with wavenumber according this equation:

$$c = \nu/W \tag{2.20}$$

where ν means frequency in Hz.

The absorbance of the sample is calculated from this equation:

$$A = logI_0 - logI = log(I_0/I) \tag{2.21}$$

where I_0 is the intensity of the light entering to the sample and I is the intensity of the light transmitted by the sample.

The transmittance is defined as:

$$T = I/I_0 \tag{2.22}$$

The percentage transmittance is also often used. It is the transmittance multiplied by 100.

$$\%T = 100 * T \tag{2.23}$$

Then we have:

$$A = -log(I/I_0) = -logT \tag{2.24}$$

Using percentage transmittance values, it is easy to understand the numbers. For example, 50 % transmittance reveals that the half of the light is transmitted and half is absorbed.

2.3 Raman spectroscopy

2.3.1 Introduction to Raman spectroscopy

Although Raman spectroscopy is also the vibrational spectroscopy, it differs by IR spectroscopy. In Raman spectroscopy, the sample is irradiated by a laser beam and the scattered light is normally detected. There are two types of the scattering, Rayleigh scattering (an elastic process) and Raman scattering (an inelastic process) (Figure 2.10). Although Rayleigh scattering is the dominant of the scattered light, we are interested in the the inelastic process, where the energy of scattered light is different from the incident light. For the first time was Raman scattering (Raman effect) observed by Chandrasekhara Venkata Raman in 1928 [30].



Figure 2.10: Types of the scattered light

When incident light (laser beam) irradiates the sample, it induces an electric dipole moment P given by:

$$P = \alpha E = \alpha E_0 \cos 2\pi v_0 t \tag{2.25}$$

where α is a polarizability, E is the electric field strength of the laser beam, E₀ is the vibrational amplitude and v₀ is the frequency of the laser.

The nuclear displacement q is expressed as:

$$q = q_0 sin 2\pi v_m t \tag{2.26}$$

where v_m is the frequency of the molecule and q_0 is the vibrational amplitude.

Using the small amplitude approximation, the polarizability is the linear function of the displacement. Then we obtain:

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 + \dots \tag{2.27}$$

where α_0 is the polarizability at the equilibrium and $\left(\frac{\partial \alpha}{\partial q}\right)_0$ is the velocity of the change α with the acceptance of the change in q at the equilibrium.

Creating the combination of the previous equations 2.29, 2.30 and 2.31 we get:

$$P = \alpha E = \alpha E_0 \cos 2\pi v_0 t + \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \cos 2\pi v_0 t \cos 2\pi v_m t \tag{2.28}$$

Using the relation between cosines:

$$\cos(a)\cos(b) = \frac{1}{2}[\cos(a+b) + \cos(a-b)]$$
 (2.29)

We obtain:

$$P = \alpha E_0 \cos 2\pi v_0 t + \frac{1}{2} (\frac{\partial \alpha}{\partial q})_0 q_0 E_0 [\cos \left\{ 2\pi (v_0 + v_m) t \right\} + \cos \left\{ 2\pi (v_0 - v_m) t \right\}] \quad (2.30)$$

Corresponding to the classical theory, the first term means Rayleigh scattering in the frequency v_0 and the second term represents Raman scattering. As we can see, Raman scattering can be in 2 different frequencies, v_0+v_m and v_0-v_m . The increasing of the frequency is knows as anti-Stokes shift and decreasing is Stokes shift. The last equation also reveals that if $(\frac{\partial \alpha}{\partial q})_0$ is equal zero, the vibration is Raman-inactive.

To better imagine the scattering it will be introduce the quantum particle interpretation. As we can see in Figure 2.11 the incident photon interact with the molecule and excite it into the unstable virtual state and the photon is rapidly emitted as the scattered light. In Rayleigh scattering the electron in the ground state is excited and falls to the original ground state. In Stokes Raman scattering an electron in ground state is excited and falls to the vibrational state. Anti-Stokes Raman scattering is the process opposite to the Stokes Raman scattering, an electron is excited from the vibrational state and fall to the ground state.



Figure 2.11: Quantum energy diagram of the scattered light

2.3.2 Raman spectrum

The Raman spectrum is given in the form of the Raman intensity versus Raman shift. Raman intensity is the name for the intensity of the scattered light and Raman shift is the wavenumber. Raman shift (R.S.) is obtained by:

$$R.S. = \left(\frac{1}{\lambda_{exc.}} - \frac{1}{\lambda_{Ram.}}\right) \tag{2.31}$$

where $\lambda_{exc.}$ is the wavelength of the excitation and $\lambda_{Ram.}$ is the wavelength of the Raman peak.

2.4 Scanning electron microscopy

2.4.1 Introduction to SEM

SEM (Scanning Electron Microscopy) was created due to the necessity of the bigger magnification of the samples. In a scanning electron microscope the analogy of the photons have the electrons. As the source of the electrons is often used tungsten filament. Accelerated electrons are focused into the thin beam by series of lens and coils (Figure 2.12).

The final image depends on the interaction between the primary electrons with the scanned surface. The incident electron beam interact with the atoms of the sample and cause the elastic and non-elastic interactions. Back scattered electrons (BSE) are the consequence of the elastic interactions, but subsequent release of secondary electrons (SE), Auger electrons (AE), X-rays and cathodoluminescence are due to the inelastic interactions. The detector can detect back scattered electrons (BSE), secondary electrons (SE) and X-rays.

Setting the acceleration voltage of the electrons we are able to affect the quality of the image, magnifying the image we can reach a nanoscopic scale and take a scan. By the scan of images we can study surface and structure of the surface, even it can be determined the size of the particles. Using energy-dispersive X-ray spectroscopy (EDX) are detected X-rays and it is possible to obtain chemical composition of the material.



Figure 2.12: Schematic diagram of SEM [31]

2.5 X-ray Powder Diffraction

2.5.1 Introduction to XRD

XRD (X-ray Powder Diffraction) is a classical method to determine crystal structure and chemical composition of solid substances. This method is based on the diffraction of X-rays on the atoms of atomic grid. It is used X-rays because the wavelength of the incident beam should be similar to grid constant.

Diffracted light subsequent interfere with the crystallographic planes and are created diffractive maximum (Figure 2.13). Diffracted light interfere constructively when is completed Bragg's law:

$$2dsin\theta = n\lambda \tag{2.32}$$

where λ is the wavenumber of the beam, d is the distance of 2 neighbouring planes of the atoms, n is any integer and θ is the incident angle.



Figure 2.13: Schematic diagram of Bragg's law [32]

The typical X-ray diffractometer is made up of source of X-ray, detector of diffracted beam and goniometer. The exact position of the source, sample and detector is determined by goniometer. Usually it is measured numbers of signals on detector in dependence on double of the incident angle.

2.5.2 Crystallite

Crystallites are tridimensional domains which propagate an incident X-ray or neutron wave in a coherent way without phase loss [33]. In the crystallography they are also called "coherent domains". Single crystal contain only one crystallite but polycrystal is an aggregate of crystallites of varying number, shape, size and crystalline state [33].

How Figure 2.14 reveal, the samples are made up of grains. A grain is an ensemble of crystallites and crystallites are an ensemble of crystallographic planes. In contrast to crystallites, grains can be observed by scanning electron microscopy.



Figure 2.14: Definitions of grains (bold), crystallites (hatched zones) and crystallographic planes (hatchings) in a polycrystalline sample [33]

It can be determined crystallite size using Scherrer and Williamson-Hall method. By Williamson-Hall method is also possible to estimate lattice strain. In this work these analysis will be provided.

Scherrer and Williamson-Hall method

In 1918 Paul Scherrer first observed that small crystallite size could give rise to peak broadening [34]. He derived the relation between crystallite size and peak width, known as Scherrer's equation:

$$L = \frac{K\lambda}{B\cos\theta} \tag{2.33}$$

where K is the Scherrer constant in the range 0.87-1.0, λ is the wavelength of X-ray, B is the broadening of the diffraction peak measured at half of its maximum intensity (FWHM) and θ is the incident angle (Bragg angle).

Normally X-ray diffraction peak broadening is not only caused by crystallite size, it is also contributed by instrumental and lattice strain present in the material [34]. Any lattice imperfection as dislocations, vacancies, interstitials, substitutional and similar defects provoke lattice strain [35]. The relation between the lattice strain and the width of the peak is given by:

$$B_{strain} = \eta \, tan\theta \tag{2.34}$$

Then, the total X-ray diffraction peak broadening can be expressed as:

$$B_t = \frac{K\lambda}{L\cos\theta} + \eta\,tan\theta\tag{2.35}$$

Multiplying by $\cos\theta$ we obtain:

$$B_t \cos\theta = \frac{K\lambda}{L} + \eta \sin\theta \tag{2.36}$$

The total X-ray diffraction peak broadening is estimated as:

$$B_t = \sqrt{B_{measured}^2 - B_{instrumental}^2} \tag{2.37}$$

Plotting $B_t \cos\theta$ along y-axis and $\sin\theta$ along x-axis, after this graph is fitted by linear fit. Therefore, the crystallite size is extracted from the intercept of the linear fit and the lattice strain from the slope of the linear fit (Figure 2.15).



Figure 2.15: Williamson-Hall Curve



Experimental part

3.1 Preparation of the samples

The samples $\operatorname{Bi}_2(\operatorname{Fe}_x\operatorname{Ga}_{1-x})_4\operatorname{O}_9$ $(0 \le x \le 1)$ were prepared by mechanochemical/thermal synthesis method using a high-energy ball mill. With the precursors $\operatorname{Bi}_2\operatorname{O}_3$ (Alfa Aesar, 99.999%), $\operatorname{Ga}_2\operatorname{O}_3(\operatorname{Alfa}\operatorname{Aesar}, 99.99\%)$ and α -Fe₂O₃(Alfa Aesar, 99.998%) stoichiometries were calculated (Table 3.1), then were weighted and mixed. In the next step the precursors were milled in a planetary mill (Pulverisette 6, Fritsch) during 3 h at 600 rpm in the air. The volume of the used chamber was 250 cm³ with 10 mm diameter balls. The both are made of the tungsten carbide. The ratio 22:1 was used between the mass of the sample and the mass of balls. Then, it was followed by 24 h heat treatment in the air at 800°C. The samples were placed into the oven and taken out of the oven at the temperature 800°C. A fast heating rate is approximately 20° C/s.



Figure 3.1: The photos of the $Bi_2(Fe_xGa_{1-x})_4O_9$ ($0 \le x \le 1$) mullite-type prepared samples

x	$\operatorname{Bi}_2(\operatorname{Fe}_x\operatorname{Ga}_{1-x})_4\operatorname{O}_9$
0	$\mathrm{Bi}_{2}\mathrm{Ga}_{4}\mathrm{O}_{9}$
0.1	${\rm Bi}_2({\rm Fe}_{0.1}{\rm Ga}_{0.9})_4{\rm O}_9$
0.2	$\operatorname{Bi}_2(\operatorname{Fe}_{0.2}\operatorname{Ga}_{0.8})_4\operatorname{O}_9$
0.3	${\rm Bi}_2({\rm Fe}_{0.3}{\rm Ga}_{0.7})_4{\rm O}_9$
0.5	${\rm Bi}_2({\rm Fe}_{0.5}{\rm Ga}_{0.5})_4{\rm O}_9$
0.7	${\rm Bi}_2({\rm Fe}_{0.7}{\rm Ga}_{0.3})_4{\rm O}_9$
0.8	$\mathrm{Bi}_{2}(\mathrm{Fe}_{0.8}\mathrm{Ga}_{0.2})_{4}\mathrm{O}_{9}$
0.9	$\mathrm{Bi}_{2}(\mathrm{Fe}_{0.9}\mathrm{Ga}_{0.1})_{4}\mathrm{O}_{9}$
1	$\mathrm{Bi}_{2}\mathrm{Fe}_{4}\mathrm{O}_{9}$

 Table 3.1: Chemical formula of the prepared samples

3.2 Characterization techniques

3.2.1 FT-IR spectroscopy

The infrared spectra were measured by FT-IR with the spectrometer Bruker, Vertex 70v at UEM, in the range of 4000-400 cm⁻¹. Background and sample spectra were obtained from 128 scans each with a nominal resolution of 4 cm⁻¹. For the measurements 2 mg of sample and 198 mg of KBr pellets were created. As a reference, 200 mg of KBr pellet was used. The spectra were obtained in transmittance and converted to absorbance.



Figure 3.2: The spectrometer Bruker, Vertex 70v

3.2.2 Raman spectroscopy

The Raman spectra were measured by the confocal spectrometer Senterra at UEM in the range between 3267-56 cm⁻¹ configured with 2 s integration time, 60

scans and $3-5 \text{ cm}^{-1}$ spectral resolution. A 633 nm red laser with a nominal power of 20 mW was used for the excitation. The samples were measured on Raman sample holder.



Figure 3.3: The confocal spectrometer Senterra

3.2.3 SEM

To obtain the micrographs of the samples, it was used the scanning electron microscope FEI (Quanta 250) at COMCAP-UEM. A few amount of sample in the powder form was dispersed in acetone by a sonicator during 5 minutes and after a drop was placed on an aluminium stand and dried. Then, the samples were sputtered during 60 seconds to get a gold layer.

3.2.4 XRD

X-ray diffractograms were obtained by a X-ray diffractometer Shimadzu XRD-7000 at GDDM-UEM using Cu-K α radiation ($\lambda = 1.54439$ Å). X-ray data were measured in the range of 10 °-80 ° in 2 θ with a step size of 0.02 °. The powdered samples were measured on a glass substrate.



Results and discussion

4.1 XRD

The XRD patterns of the $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ samples with $0 \le x \le 1$ are shown in Figure 4.1. All diffraction peaks correspond to the orthorhombic mullite-type phase with space group *Pbam* without any spurious or minority phases [8]. The mullite-type $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ pure phase with increasing of iron content (x) showed a linear shifting of diffraction peaks (121), (211) and (002) towards low angle as can be seen in Figures 4.2 and 4.3 due to the bigger ionic radii of Fe^{3+} compared with Ga^{3+} . The almost linear decreasing in the intensity of the peaks (121), (211) and (002) can be attributed to the smaller scattering factor of Fe when compared with Ga atoms (Figures 4.2 and 4.4).

Crystallite size was determined by Scherrer and Williamson-Hall methods in the range of 24 °-40 ° and the results are shown in Table 4.1. In Schrerrer method was the full width at half maximum (FWHM) of this peaks obtained by Pseudo-Voigt fit and by Rietveld refinements of R. T. Santiago [8]. As we can see in Figure 4.5, the results obtained by both methods are in the good accordance. Also it is in the good agreement with the results obtained by Wiliamson-Hall method by Rietveld refinements of R. T. Santiago [8]. We expected the crystallite size increasing with iron content (x) as the consequence that the ionic radii of Fe³⁺ is bigger than Ga³⁺. Our results obtained by both methods reveal that the crystallite size decreasing roughly with iron content (x). It could be the outcome of the long time of heating or by high angular velocity of milling process during the preparation of the samples.



Figure 4.1: XRD patterns of $Bi_2(Fe_xGa_{1-x})_4O_9$ $(0 \le x \le 1)$ compositions

Lattice strain estimation, where it was calculated by Williamson-Hall method from Rietveld refinements shown in Figure 4.7, does not correspond to the lattice disorder, which has been already mentioned (Figure 2.4), where with bigger amount of iron content a quadrupole splitting decreases almost linearly, what is not in good agreement with lattice strain calculated from Williamson-Hall method. Negative lattice strain is created, when the crystal lattice is influenced by compressive forces [36]. The lattice strain is increasing with iron content (x) what can be caused by the expansion of the lattice parameters and the lattice volume derived from Rietveld refinements (Figure 2.2).


Figure 4.2: XRD patterns of ${\rm Bi}_2({\rm Fe}_x{\rm Ga}_{1-x})_4{\rm O}_9~(0\le x\le 1)$ of peaks in the range of 21 °-36 °

Table 4.1: Crystallite size (L) and lattice strain (η) calculated by Scherrer (L_S) and Williamson-Hall (L_W, η_W) method

$\mathbf{Bi}_2(\mathbf{Fe}_x\mathbf{Ga}_{1-x})_4\mathbf{O}_9$	$L_S(nm)$ (PV. fit)	$L_S(nm)$ (Rietveld)	$\mathbf{L}_W(\mathbf{nm})$	$\eta_W(\%)$
${\rm Bi}_2({\rm Fe}_{0.1}{\rm Ga}_{0.9})_4{\rm O}_9$	38.08	64.41	52.60	-0.184
$\operatorname{Bi}_2(\operatorname{Fe}_{0.2}\operatorname{Ga}_{0.8})_4\operatorname{O}_9$	38.20	70.05	60.32	-0.119
${\rm Bi}_2({\rm Fe}_{0.3}{\rm Ga}_{0.7})_4{\rm O}_9$	37.45	77.74	62.67	-0.164
${\rm Bi}_2({\rm Fe}_{0.5}{\rm Ga}_{0.5})_4{\rm O}_9$	33.36	64.42	51.48	-0.210
${\rm Bi}_2({\rm Fe}_{0.7}{\rm Ga}_{0.3})_4{\rm O}_9$	42.13	70.46	55.89	-0.194
$\operatorname{Bi}_2(\operatorname{Fe}_{0.8}\operatorname{Ga}_{0.2})_4\operatorname{O}_9$	30.50	65.03	53.42	-0.176
$\mathrm{Bi}_2(\mathrm{Fe}_{0.9}\mathrm{Ga}_{0.1})_4\mathrm{O}_9$	39.11	66.83	50.97	-0.244



Figure 4.3: Positions of diffraction peaks (121), (211) and (002) as a function of iron content (x)



Figure 4.4: Intensity of diffraction peaks (121), (211) and (002) as a function of iron content (x)



Figure 4.5: Crystallite size of $Bi_2(Fe_xGa_{1-x})_4O_9$ compositions calculated by Scherrer method



Figure 4.6: Crystallite size of $Bi_2(Fe_xGa_{1-x})_4O_9$ compositions calculated from Rietveld refinament



Figure 4.7: Lattice strain of $Bi_2(Fe_xGa_{1-x})_4O_9$ compositions calculated by Williamson-Hall method

4.2 FT-IR spectroscopy

The infrared absorption spectra of $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ ($0 \le x \le 1$) solid solutions were measured in the range of 4000-400 cm⁻¹ and were analysed in the range of 1000-400 cm⁻¹ because this region gives us an information about inorganic material. As we can see in Figure 4.8, the infrared spectra are described by three band groups (group I, group II and group III) [12]. Every group of the spectrum was adjusted using Gaussian functions and the infrared absorption bands were classified with the infrared band assignment used by the Voll *et al.* [11, 37] in Table 4.2.



Figure 4.8: The infrared absorption spectra of $Bi_2(Fe_xGa_{1-x})_4O_9$ ($0 \le x \le 1$) compositions

It is possible to observed (Figure 4.8) a shift in the band positions to lower wavenumber with iron content (x). It is probably caused by a decrease of the vibrational force constant proportionately to the the bigger distance of Fe³⁺-O (~ 1.8 Å for Bi₂Fe₄O₉) with comparation to the Ga³⁺-O distances (~ 1.75 Å for Bi₂Ga₄O₉) due to the difference of ionic radii in the both sites position ($r_{Fe} > r_{Ga}$) [23].

Band notation	Band position (cm^{-1})	Band assignment
D (symmetrical)	849.3	M-O stretch (MO_4)
D^* (symmetrical)	831.5	M-O stretch (MO_4)
D^{**} (symmetrical)	814.3	M-O stretch (MO_4)
E (symmetrical)	708.2	M-O stretch (MO_4)
\mathbf{F}	682.4	M-O-M bend (MO_4)
F^*	638.5	M-O-M bend (MO_4)
G^{**}	607.8	$O-M-O$ bend (MO_4)
G	552.8	O-M-O bend (MO_4)
H^{**}	518.3	M-O stretch (MO_6)
H^*	494.8	M-O stretch (MO_6)
Н	469.4	M-O stretch (MO_6)
Ι	449.7	M-O-M bend (MO_6)

Table 4.2: Band notation, band positions and band assignment of the mullitetype $Bi_2(Fe_{0.5}Ga_{0.5})_4O_9$ compositions

For the polycrystals $Bi_2Ga_4O_9$ and $Bi_2Fe_4O_9$ all the sites are occupied only by the one type of atom, Ga or Fe, respectively. In that case we have just one vibrational peak in the group I for both concentrations. In both of samples the vibration peaks are attributed to Ga-O-Ga and Fe-O-Fe symmetrical stretching vibration, respectively, for tetrahedral site coordination, see Figures 4.9 and 4.17.

The FT-IR measurements in the range of 0 < x < 0.5 are characterized by a doublet band splitting (Figures 4.10, 4.11 and 4.12). In group I, the two vibration peaks are assigned to Ga-O-Ga stretching mode in the highest energy (D band) and the lowest energy vibrational peak (D^{*}) to Ga/Fe-O-Fe/Ga stretching mode [11]. It is worth to note that for small concentration of iron (x < 0.5) the two peaks, fitted with two Gaussian functions, are not so clearly distinguished as in the work of $Bi_2(Fe_xAl_{1-x})_4O_9$ [2] for the same range. This can be explained using the fact that for low concentration (x < 0.5) iron has strongly preference for octahedral site.

In the solid solutions with $x \ge 0.5$ a triplet splitting is observed in the group I (Figures 4.13, 4.14, 4.15 and 4.16). As the amount of iron content (x) increases, a third peak in the group I started to comes out, even trough grossly. This peak is attributed to the Fe-O-Fe stretching mode (D^{**}) with lower energy band than D and D^{*}. The triplet splitting is not so visible like in the case of the compounds $Bi_2(Fe_xAl_{1-x})_4O_9$ studied by da Silva [2]. This is due to the iron preference to the

octahedral site. As the consequence of this preference of iron to the octahedral sites, the peaks (triplets) in the group I are not so defined for lower iron contents. This preference to the octahedral site can be observed by the stretching mode of the vibrations (H, H^{*} and H^{**}), when these bands for x < 0.5 are more intense than for $x \ge 0.5$. These results are in the good concordance with the results given by the Rietveld refinament and Mössbauer spectroscopy [8], which confirm the preference of the Fe³⁺ ions to the octahedral site for the solutions x < 0.5 (Figure 2.3). Similar results also were deduced by da Silva [2] in his study about the compounds $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ ($0 \le x \le 1$).

The E band is attributed to the symmetrical stretching vibrational mode in tetrahedral site coordination. The tetrahedral Ga/Fe-O₄ vibrates approximately perpendicular to the (001) plane [11]. The F bands are assigned to the bending vibration Ga/Fe-O-Ga/Fe in tetrahedral site, what has a big influence on the E band [11]. The G bands are attributed to O-Ga/Fe-O bending vibrations [11]. Supposedly the I band is assigned to bending vibrations Ga/Fe-O-Ga/Fe [11].



Figure 4.9: IR absorption spectrum of the $Bi_2Ga_4O_9$ composition



Figure 4.10: IR absorption spectrum of the $Bi_2(Fe_{0.1}Ga_{0.9})_4O_9$ composition



Figure 4.11: IR absorption spectrum of the $Bi_2(Fe_{0.2}Ga_{0.8})_4O_9$ composition



Figure 4.12: IR absorption spectrum of the $Bi_2(Fe_{0.3}Ga_{0.7})_4O_9$ composition



Figure 4.13: IR absorption spectrum of the $Bi_2(Fe_{0.5}Ga_{0.5})_4O_9$ composition



Figure 4.14: IR absorption spectrum of the $Bi_2(Fe_{0.7}Ga_{0.3})_4O_9$ composition



Figure 4.15: IR absorption spectrum of the $Bi_2(Fe_{0.8}Ga_{0.2})_4O_9$ composition



Figure 4.16: IR absorption spectrum of the $Bi_2(Fe_{0.9}Ga_{0.1})_4O_9$ composition



Figure 4.17: IR absorption spectrum of the $\mathrm{Bi}_2\mathrm{Fe}_4\mathrm{O}_9$ composition

The band shifting of the all samples at the high energy band (group I) is shown in Figure 4.18. It can be observed that the every band of the band splitting at high energy changes linearly with the iron content obtained from Mössbauer. The similar linear band shifting of the band E is revealed in Figure 4.19 but this band is a lower energy band of group II. D, D^{*}, D^{**} and E bands belong to stretching vibrational mode of tetrahedral site. It changes linearly with iron content, therefore it belongs to symmetrical stretching vibrations.

It is also interesting to analyse full width at half maximum (FWHM), intensity and area of the bands as a function of iron content (x) (Figures 4.21 and 4.22). In Figure 4.21 is shown full width at half maximum of stretching modes of tetrahedral bands as a function of iron content (x). According with M. Bradley [38], the line width is inversely proportional to the effective lifetime τ . The term lifetime is used for the relaxation when the excited state molecules return fastly to the ground state. Therefore, the long lifetime (long τ) causes narrow peaks in contrast to rapid loss of the excitation (short τ) which creates broad peaks [38]. For the samples in this work it can be seen that with increasing of iron content the FWHM of Ga-O-Ga stretching is decreasing and then the peaks become more narrow. FWHM of Fe-O-Fe stretching is firstly decreasing due to the preference of gallium ions to the tetrahedral site for x < 0.5 and for x \geq 0.5 is increasing with iron content due to the presence iron ions. A similar behaviour can be noted for FWHM of Ga-O-Ga stretching for x < 0.5 and for FWHM of Fe-O-Fe stretching for x \geq 0.5.

Figure 4.22 reveal very similar variation of intensity and area of stretching modes of tetrahedral bands as a function of iron content (x). According M. Bradley [38] the area of the peak is a better indicator of concentration (number of present molecules). Intensity and area of the Ga-O-Ga stretching is decreasing linearly with iron content. Figure 4.22 better reveals area of the Fe-O-Fe stretching varying linearly with the iron content. For x < 0.5 intensity and area of Ga-O-Ga stretching is increasing with iron content and for $x \ge 0.5$ intensity and area of Ga-O-Fe/Fe-O-Ga stretching is decreasing.

Figure 4.20 illustrates area of the octahedral bands as the function of iron content in the group III. From Figures 4.8-4.16 is not clearly to distinguish three individual modes of vibration, i. e., the Ga-O-Ga, Ga/Fe-O-Fe/Ga and Fe-O-Fe stretching peaks on octahedral sites and assigned to each band peak H, H^{*} and H^{**}. For that it was plotted the total area versus iron content (x). As it is shown in

Figure 4.20 the total area decreases with iron content (x) in opposite behaviour of area in the tetrahedral bands in the group I (Figure 4.22).

This results give some light to understanding and estimate the site occupancy tendencies using an infrared spectroscopy method. The vibrational method goes in good agreement with the results of Mössbauer and Rietveld analyses, where iron shows a preference for octahedral sites (Figure 4.20).



Figure 4.18: Positions of the tetrahedral bands in group I as a function of iron content (x)



Figure 4.19: Positions of the tetrahedral E band in group II as a function of iron content (x)



Figure 4.20: Area of the octahedral bands in group III as a function of iron content (x)



Figure 4.21: FWHM of the tetrahedral bands in group I as a function of iron content (x)



Figure 4.22: Intensity and area of the tetrahedral bands in group I as a function of iron content (x)

The bond length values of the tetrahedral bond Ga/Fe-O-Ga/Fe calculated by FT-IR spectra are shown in Table 4.3. For this calculation we used the relation between vibrational frequency and force constant mentioned in equation 2.13 with effective mass $\mu = \frac{m_1m_2}{m_1+m_2}$ to obtain force constant K. By the equation between force constant and average bond length $B_L = (\frac{17}{K})^{1/3}$ [39], we calculated bond lengths and compared with Rietveld analysis (Figure 4.23). The results obtained in both technique showed slightly linear increasing on bond length with iron doping. As it was expecting by comparation of ionic radii between the two ions. Also, from the Rietveld analysis, the bond lengths are inversely proportional to the linear band shift, as expected (Figure 4.18).

In Figure 4.24 are shown the bond length values of the tetrahedral bonds Ga-O-Ga and Fe-O-Fe calculated by FT-IR spectra as a function of iron content (x). It can be observed that the bond length values of Ga-O-Ga stretching are increasing with iron content and the bond length values of Fe-O-Fe stretching are decreasing with iron content. For x = 0.5 the bond length of Fe-O-Fe stretching is bigger than the bond length of Ga-O-Ga stretching but for x = 0.7 and x = 0.8 the bond lengths of Fe-O-Fe stretching are smaller than the bond lengths of Ga-O-Ga stretching. This result is also the consequence of the occupational preference of iron ions for octahedral sites for x < 0.5.

Conc.	$W(cm^{-1})$	$\mu(10^{-26}\mathrm{kg})$	K(N/cm)	$\mathbf{B}_L(\mathbf{\mathring{A}})(\mathrm{FT}\text{-}\mathrm{IR})$	$\mathbf{B}_L(\mathbf{\mathring{A}})(\mathrm{Riet.})$
x = 0.1	835.67	1.815	4.4974	1.5577	1.7573
x = 0.2	834.28	1.804	4.4565	1.5625	1.7653
x = 0.3	833.28	1.794	4.4203	1.5668	1.7674
x = 0.5	831.50	1.773	4.3508	1.5750	1.7634
x = 0.7	828.39	1.744	4.2470	1.5878	1.7694
x = 0.8	826.47	1.726	4.1837	1.5957	1.7404
x = 0.9	824.41	1.708	4.1191	1.6040	1.7405
$\mathbf{x} = 1$	810.00	1.688	3.9321	1.6291	1.8023

Table 4.3: Tetrahedral Ga/Fe-O-Ga/Fe bond lenght values B_L calculated by FT-IR using wavenumber (W), effective mass (μ), force constant (K) compared with Rietveld



Figure 4.23: Bond lengths of the tetrahedral bands in group I as a function of iron content (x)



Figure 4.24: Bond lengths of the tetrahedral bands in group I as a function of iron content (x)

4.3 Raman spectroscopy

Raman spectra of the polycrystals $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ ($0 \le x \le 1$) are shown in Figure 4.25. It can be seen a shift of Raman modes with the bigger iron content towards lower wavenumbers. According S.R. Mohapatra *et al.* [14] it could be caused by lower atomic mass of Fe and lower lattice disorder. The atomic mass of Fe (55.845 *amu*) is significantly lower as compared to Ga (69.723 *amu*). With increasing amount of iron content the shift is increased. The lattice disorder already have been mentioned in Figure 2.4, with the increasing of iron content (x) the lattice disorder has decreased due to the creation of more symmetrical cations and this can corresponds to the shift in the wavenumber.



Figure 4.25: Raman spectra of $Bi_2(Fe_xGa_{1-x})_4O_9$ $(0 \le x \le 1)$ compositions

A detailed Raman study of the monocrystals $Bi_2Ga_4O_9$ and the assignment of Raman modes was reported by Beran *et al.* [12]. In the region between 300 cm⁻¹ and 800 cm⁻¹ are occurred Ga-O stretching and bending vibrations but below 300 cm⁻¹ they are assigned to Bi-O stretching and bending modes. Raman spectra were fitted by using Gaussian functions and the Raman band assignment was in the same way as Beran *et al.* [12]. To avoid extremely big values of the intensity, the intensity was normalized in the Raman mode 202 cm^{-1} for every spectrum.

In Figure 4.26 are fitted the vibrational modes for the $Bi_2Ga_4O_9$ compound and the modes are marked with numbers which correspond to the assignment according to Beran *et al.* [12]. We fitted more vibrational modes than are reported by Beran *et al.*, probably it is due to the several kinds of orientation that polycrystal presents instead the single crystal. Another explanation can be due to the stabilization of FeO₆ octahedron [40]. For lower iron content it is possible to observe two separated peaks between 500 cm⁻¹ and 400 cm⁻¹, which are missing for higher iron content because are overlapped.

Vibrational mode 1 is assigned to GaO_4 tetrahedral site stretching vibrations, Raman mode 2 is attributed to Ga-O-Ga bending vibrations. Vibrational modes in tetrahedral site are also Raman modes 3 and 4 which are probably due to the bending vibrations of O-Ga-O. Vibrational mode 5 is assigned to stretching vibration of GaO_6 octahedral site.



Figure 4.26: Raman spectrum of the $Bi_2Ga_4O_9$ composition



Figure 4.27: Raman spectrum of the $Bi_2(Fe_{0.1}Ga_{0.9})_4O_9$ composition



Figure 4.28: Raman spectrum of the $Bi_2(Fe_{0.2}Ga_{0.8})_4O_9$ composition



Figure 4.30: Raman spectrum of the $Bi_2(Fe_{0.5}Ga_{0.5})_4O_9$ composition



Figure 4.32: Raman spectrum of the $Bi_2(Fe_{0.9}Ga_{0.1})_4O_9$ composition



Figure 4.29: Raman spectrum of the $Bi_2(Fe_{0.3}Ga_{0.7})_4O_9$ composition



Figure 4.31: Raman spectrum of the $Bi_2(Fe_{0.7}Ga_{0.3})_4O_9$ composition



Figure 4.33: Raman spectrum of the $Bi_2Fe_4O_9$ composition

In Figures 4.34 and 4.35 are shown the 5 Raman bands as a function of iron content (x) obtained from Mössbauer. It can be seen the linearly shift varying with the increasing of iron content (x). For the band 5 it can be observed not so deeply linearly shifting for x < 0.5 with comparison to the band 1 (Figure 4.35), probably it is due to the occupational preference of Fe in octahedral site as it was also deduced by infrared measurements. Therefore, significantly lower atomic mass of Fe and lower lattice disorder with the comparison to Ga caused not so deeply linearly shifting.



Figure 4.34: Positions of the tetrahedral bands as a function of iron content (x)



Figure 4.35: Positions of the bands as a function of iron content (x)

4.4 SEM

The SEM images of the mullite system $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ ($0 \le x \le 1$) show non-homogeneity of particle size and also non-homogeneity of morphology of the particles. To obtain mean particle size the histograms were adjusted using Lognormal distribution.

The obtained mean particle size are in the range between 0.38 μ m and 1.83 μ m. For the doped samples, it can be observed that the grains are increasing with iron doping. Therefore, the medium particle size are in concordance with the lattice parameters behaviour mentioned in Figure 2.2, where with increasing of iron content the lattice parameters are increasing too. For the solution x = 0.7 (Fig. 4.49) and x = 0.8 (Fig. 4.51) the medium particle size are almost 2 times bigger than for solutions x = 0.1 (Fig. 4.41) and x = 0.2 (Fig. 4.43). Mostly for the mullite Bi₂Ga₄O₉ and Bi₂Fe₄O₉ are present non-uniform large grains, which are probably due to the agglomeration of the particles during the preparation of the samples as the consequence of the long time of heating or by high angular velocity of milling process. Perhaps for this reason the crystallite size obtained by Williamson-Hall method do not correspond to the mean particle size (Figure 4.52).





Figure 4.36: SEM micrograph of $Bi_2Ga_4O_9$ composition

Although the particle size of our samples does not correspond their crystallite size, observed agglomeration of the particles does not affect the magnetic properties which already have been investigated by Santiago [8] and by Giaguinta [9].







Figure 4.40: SEM micrograph of $Bi_2(Fe_{0.1}Ga_{0.9})_4O_9$ composition



Figure 4.41: Particle size distribution histogram of ${\rm Bi}_2({\rm Fe}_{0.1}{\rm Ga}_{0.9})_4{\rm O}_9$ composition







 $\begin{array}{l} \mbox{Figure 4.44: SEM micrograph} \\ \mbox{ of } Bi_2(Fe_{0.3}Ga_{0.7})_4O_9 \mbox{ composition} \end{array}$



Figure 4.45: Particle size distribution histogram of ${\rm Bi}_2({\rm Fe}_{0.3}{\rm Ga}_{0.7})_4{\rm O}_9$ composition



Figure 4.46: SEM micrograph of $Bi_2(Fe_{0.5}Ga_{0.5})_4O_9$ composition





Figure 4.48: SEM micrograph of $Bi_2(Fe_{0.7}Ga_{0.3})_4O_9$ composition





Figure 4.50: SEM micrograph of $\mathrm{Bi}_2(\mathrm{Fe}_{0.8}\mathrm{Ga}_{0.2})_4\mathrm{O}_9$ composition



Figure 4.51: Particle size distribution histogram of ${\rm Bi}_2({\rm Fe}_{0.8}{\rm Ga}_{0.2})_4{\rm O}_9$ composition



Figure 4.52: Crystallite size and particle size as a function of iron content (x)

Chapter 5

Conclusions and perspectives

5.1 Conclusions

Analyses of the the polycrystalline samples of the mullite-type $Bi_2(Fe_xGa_{1-x})_4O_9$ ($0 \le x \le 1$) bring us interesting results about vibrational, structural and morphological properties.

XRD analyses revealed that mullites synthesized in this work crystallize in an orthorhombic symmetry with space group *Pbam*. The crystallite size estimated by Scherrer and Williamson-Hall method are in the concordance.

With the increasing of iron content, it has been observed a shift in the peaks position towards lower angle in X-ray diffraction and towards lower wavenumber in IR spectroscopy.

Stretching and bending vibrations of the tetrahedral and octahedral sites were observed in the range 850-400 cm⁻¹ for IR spectrum and 750-300 cm⁻¹ for Raman spectrum. IR spectra revealed a preference of iron ions for the octahedral sites. In the x = 0.5 it was found transition point that is the point of concentration where the amount of iron started to be randomly. From the full width at half maximum plots was observed that the lifetime increases with gallium content and decreases with iron content, showing a transition point at x = 0.5.

SEM images of our polycrystals showed non-homogeneity of the particle size and non-homogeneity of the morphology of the particles. The obtained histograms revealed that the mean particle size is increasing with iron doping in the range between 0.38 μ m and 0.83 μ m.

5.2 Perspectives

This work does not answer all questions which are produced in our minds and it gives opportunity for the future works.

It is difficult to make Raman assignment of the polycrystals $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ with a few information of the published literature. Therefore, it can be interesting to make Raman measurements on the mullite-type $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ and $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ and compare it with our results.

The obtained mean particle size does not correspond to the crystallite size as the consequence of the long time of heating or by high angular velocity of milling process during the preparation of the samples. Maybe it can be a good attempt for the future works to reduce the time of heating and high angular velocity.

Appendices



Williamson-Hall method

In this section are shown Williamson-Hall Curves of all samples studied in this work.



Figure A.1: The W-H analysis of the $Bi_2(Fe_{0.1}Ga_{0.9})_4O_9$ composition



Figure A.2: The W-H analysis of the $Bi_2(Fe_{0.2}Ga_{0.8})_4O_9$ composition



Figure A.3: The W-H analysis of the $Bi_2(Fe_{0.3}Ga_{0.7})_4O_9$ composition



Figure A.5: The W-H analysis of the $Bi_2(Fe_{0.7}Ga_{0.3})_4O_9$ composition



Figure A.4: The W-H analysis of the $Bi_2(Fe_{0.5}Ga_{0.5})_4O_9$ composition



Figure A.6: The W-H analysis of the $Bi_2(Fe_{0.8}Ga_{0.2})_4O_9$ composition



Figure A.7: The W-H analysis of the $Bi_2(Fe_{0.9}Ga_{0.1})_4O_9$ composition



FT-IR spectroscopy

This section reveal fitted parameters of our samples used in infrared spectroscopy and also the bond length values of the tetrahedral bond Ga-O-Ga and Fe-O-Fe calculated by FT-IR spectra.

Band notation	Band position (cm^{-1})	Area (a.u.)	FWHM (cm^{-1})
D	851.5	10.0	29.1
${ m E}$	712.0	13.8	62.4
F	698.0	5.5	28.8
\mathbf{F}^*	652.7	20.0	44.7
G^{**}	620.1	6.0	27.4
G	565.1	1.2	13.5
H^{**}	522.3	3.0	21.2
H^*	502.0	7.5	31.2
Н	475.4	8.0	31.6
I	458.0	3.0	28.3

Table B.1: Band notation, band positions, area and full width at half maximum (FWHM) of the mullite-type $Bi_2Ga_4O_9$ compositions

Band notation	Band position (cm^{-1})	Area (a.u.)	FWHM (cm^{-1})
D	851.2	8.7	26.4
D^*	835.7	2.0	29.4
${ m E}$	712.6	13.9	62.4
\mathbf{F}	695.9	5.5	28.0
F^*	647.6	28.0	54.2
G^{**}	611.7	5.7	27.4
G	562.1	1.5	15.3
H**	524.5	3.0	21.2
H^*	501.3	8.0	32.4
Н	475.6	5.9	34.7
Ι	460.4	3.0	28.3

Table B.2: Band notation, band positions, area and full width at half maximum (FWHM) of the mullite-type $Bi_2(Fe_{0.1}Ga_{0.9})_4O_9$ compositions

Table B.3: Band notation, band positions, area and full width at half maximum (FWHM) of the mullite-type $Bi_2(Fe_{0.2}Ga_{0.8})_4O_9$ compositions

Band notation	Band position (cm^{-1})	Area (a.u.)	$FWHM (cm^{-1})$
D	850.9	6.0	20.0
D^*	834.3	4.0	22.4
${ m E}$	716.8	9.0	58.9
\mathbf{F}	687.0	15.0	47.1
F^*	642.6	22.0	44.5
G^{**}	614.0	6.0	26.0
G	558.9	1.0	14.1
H**	522.2	3.5	24.7
H^*	498.8	7.0	29.0
Н	473.4	7.0	29.9
Ι	454.0	2.5	23.5

Band notation	Band position (cm^{-1})	Area (a.u.)	FWHM (cm^{-1})
D	850.5	5.0	17.9
D^*	833.3	5.0	19.1
${ m E}$	715.1	9.0	58.9
\mathbf{F}	685.3	15.0	44.7
F^*	639.4	22.0	42.9
G^{**}	610.8	6.0	26.0
G	552.8	1.0	15.0
H^{**}	519.2	3.5	24.7
H^*	496.7	6.5	28.3
Н	472.3	6.0	27.1
Ι	453.8	2.5	17.7

Table B.4: Band notation, band positions, area and full width at half maximum (FWHM) of the mullite-type $Bi_2(Fe_{0.3}Ga_{0.7})_4O_9$ compositions

Table B.5: Band notation, band positions, area and full width at half maximum (FWHM) of the mullite-type $Bi_2(Fe_{0.5}Ga_{0.5})_4O_9$ compositions

Band notation	Band position (cm^{-1})	Area (a.u.)	FWHM (cm^{-1})
D	849.3	6.0	20.3
D^*	831.5	4.0	17.3
D^{**}	814.3	1.0	20.0
${ m E}$	708.2	11.0	58.9
\mathbf{F}	682.4	13.0	45.9
F^*	638.5	24.0	47.4
G^{**}	607.8	6.0	28.3
G	552.8	1.4	20.6
H**	518.3	4.5	29.4
H^*	494.8	6.5	29.4
Н	469.4	6.5	28.8
I	449.7	2.0	17.7
Band notation	Band position (cm^{-1})	Area (a.u.)	FWHM (cm^{-1})
----------------	---------------------------	-------------	------------------
D	846.1	2.0	18.8
D^*	828.4	5.5	22.1
D**	812.4	6.0	22.4
${ m E}$	699.1	9.1	59.9
\mathbf{F}	660.9	17.1	52.8
F^*	616.4	22.8	51.4
G^{**}	581.4	5.3	28.0
G	534.5	0.4	14.1
H^{**}	503.0	4.0	49.5
H^*	485.0	6.0	47.1
Н	455.0	4.1	28.3
Ι	435.0	1.4	22.4

 $\label{eq:table B.6: Band notation, band positions, area and full width at half maximum (FWHM) of the mullite-type Bi_2(Fe_{0.7}Ga_{0.3})_4O_9 \ compositions$

Table B.7: Band notation, band positions, area and full width at half maximum (FWHM) of the mullite-type $Bi_2(Fe_{0.8}Ga_{0.2})_4O_9$ compositions

Band notation	Band position (cm^{-1})	Area (a.u.)	FWHM (cm^{-1})
D	844.3	1.0	21.2
D^*	826.5	4.0	24.1
D^{**}	811.4	6.5	25.0
${ m E}$	694.0	7.0	47.1
\mathbf{F}	654.3	15.0	46.7
F^*	617.8	13.9	39.1
G^{**}	588.4	8.1	33.3
G	531.4	0.7	16.5
H^{**}	499.0	4.0	29.4
H^*	475.6	3.0	27.1
Н	453.0	4.1	26.8
Ι	435.5	1.4	22.4

Band notation	Band position (cm^{-1})	Area (a.u.)	FWHM (cm^{-1})
D*	824.4	3.0	33.0
D**	810.7	8.5	30.0
${ m E}$	690.5	6.0	42.4
\mathbf{F}	650.5	15.0	48.3
F^*	610.0	14.2	41.8
G^{**}	576.2	6.0	32.4
G	528.3	0.4	17.7
H^{**}	488.1	2.6	23.3
H^*	468.4	2.3	23.5
Н	446.9	4.1	28.3
Ι	430.0	1.4	22.4

Table B.8: Band notation, band positions, area and full width at half maximum (FWHM) of the mullite-type $Bi_2(Fe_{0.9}Ga_{0.1})_4O_9$ compositions

Table B.9: Band notation, band positions, area and full width at half maximum (FWHM) of the mullite-type $Bi_2Fe_4O_9$ compositions

Band notation	Band position (cm^{-1})	Area (a.u.)	FWHM (cm^{-1})
D**	810.0	8.0	31.8
${ m E}$	688.0	4.0	46.5
F	643.0	15.0	48.9
\mathbf{F}^*	602.0	11.0	40.0
G^{**}	571.0	5.0	35.3
G	527.0	0.7	23.5
H^{**}	489.0	1.5	24.3
H^*	470.2	1.3	29.4
Н	458.7	0.8	30.6
I	438.0	5.0	32.4

 $\mathbf{x} = 0.5$

x = 0.7

 $\mathbf{x} = 0.8$

849.35

846.14

844.32

uth Rietve	eld			
Conc.	$W(cm^{-1})$	μ (10 ⁻²⁶ kg)	K(N/cm)	$\mathbf{B}_L(\mathbf{\dot{A}})(\mathrm{FTIR})$
$\mathbf{x} = 0$	851.52	1.820	4.6853	1.5366
$\mathbf{x} = 0.1$	851.20	1.789	4.6008	1.5460
$\mathbf{x} = 0.2$	850.90	1.730	4.4455	1.5638
$\mathrm{x}=0.3$	850.45	1.665	4.2738	1.5845

1.510

1.208

0.943

3.8671

3.0685

2.3870

1.6381

1.7695

1.9240

Table B.10: Tetrahedral Ga-O-Ga bond lenght values B_L calculated by FTIR using wavenumber (W), effective mass (μ), force constant (K) compared with Rietveld

Table B.11: Tetrahedral Fe-O-Fe bond lenght values B_L calculated by FTIR using wavenumber (W), effective mass (μ), force constant (K) compared with Rietveld

Conc.	$W(cm^{-1})$	μ (10 ⁻²⁶ kg)	K(N/cm)	$\mathbf{B}_L(\mathbf{\dot{A}})(\mathrm{FTIR})$
x = 0.5	814.30	1.084	2.5534	1.8812
x = 0.7	812.34	1.378	3.2267	1.7401
x = 0.8	811.36	1.503	3.5125	1.6915
x = 0.9	810.70	1.604	3.7407	1.6564
$\mathbf{x} = 1$	810.00	1.688	3.9321	1.6291

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