SYNTHESIS, CHARACTERIZATION AND APPLICATION STUDIES OF MIXED METAL TITANATES PREPARED VIA THERMAL DECOMPOSITION OF OXALATE PRECURSORS
5.1 Introduction

The perovskite family mainly various titanates (metal oxide) used in a wide range of applications in electronic, electro-optical, and electromechanical modelling of ceramics. Perovskite compounds become one of the hottest topics in Materials science due to their special properties and potential applications. Precursors for metal oxide have been continuously studied because they can often be tailored structurally; certain precursors are known to transform into the corresponding nano metal oxides with high degrees of shape retention or similarity. BaTiO$_3$ with a perovskite structure, show exceptional dielectric, piezoelectric, electrostrictive, and electrooptic properties with corresponding electronic applications [1–3]. Barium titanate with a high dielectric constant, widely utilized to manufacture electronic components as multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers, and a variety of electro-optic devices [4]. The ferroelectricity observed in barium titanate is utilized in memory applications, i.e., in RAM. The pyroelectricity and piezoelectricity are also used in the passive infrared detectors and Sonars (Sound Navigation and Ranging). Besides PTCR properties, semiconductor barium titanate is used for sensor applications [5]. Pure barium titanate is an insulator whereas upon doping it transforms into a semiconductor [6].

Various studies have been performed to obtain BaTiO$_3$ of better electronic properties by doping different elements [7–10]. In order to obtain BaTiO$_3$ of low resistivity, Zhao et al. [11] prepared Ag$^+$ doped into BaTiO$_3$. Wu et al. [12] studied the influences on conductivity of
doping different rare-earth elements into BaTiO$_3$. Hao et al. prepared BaTiO$_3$ ceramics doped with Nb$_2$O$_3$ [13], Sm$_2$O$_3$ [14], Gd$_2$O$_3$ [15] and La$^{3+}$ [16] by gaseous penetration method and resistivity was explained. There are lots of reports on the structural, dielectric and ferroelectric properties of modified BaTiO$_3$ ceramics via doping [17-20].

Recently many potential antibacterial agents, nanometer sized metal oxides have been identified [21]. Some of these agents were found to be cytotoxic against bacteria but not against human cells thus, possible for many medical applications. The use of inorganic nanoparticles has attracted lots of interest mostly because of their reliable antimicrobial activity found to be effective at low concentrations [22]. This is due to their high specific surface area which allows a broad range of reactions with the bacterial surface. Barium titanate nanoparticles exhibit bacteriocidal activity which is highly dependent on the particle size and concentration and to act against both Gram-positive and Gram-negative bacteria [23]. These nanoparticles are considered as a promising novel antibacterial agent, being harmless to human cells and the environment [24]. Gupta et al. [25] investigated the antimicrobial activity of TiO$_2$ and Ag-doped TiO$_2$ nanoparticles against Gram-positive (S. aureus) and Gram-negative (P. aeruginosa, E. coli) bacteria and were found to be effective [26]. Raja et al. [27] synthesized and discussed the remedial aspect of BaTiO$_3$ nanoparticles against bacteria. Therefore, in the present study the characterization of the hydrated and dehydrated products of the prepared barium-potassium mixed titanyl oxalates and also the
nanosized products were tested for conductance behaviour as well as anti bacterial efficiency.

5.2 Experimental

5.2.1 Materials

AnalaR grade barium nitrate (Ba(NO$_3$)$_2$) (Merck, India; assay ≥ 99.9 %), potassium titanyl oxalate (K$_2$TiO(C$_2$O$_4$)$_2$) (BHO Laboratory England; assay ≥ 99.9 %), Luria Bertani (LB) broth and agar plates, glass speader, Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa and Staphylococcus pneumonia culture were used in the present investigation.

5.2.1.1 Sample preparation for conductance study

The K$^+$-doped BaTiO$_3$ powders were prepared by precipitation method well explained in Chapter 3. The samples were prepared at different concentrations, viz. $10^{-4}$, $10^{-3}$, $10^{-2}$, $10^{-1}$ and $10^{0}$ mol % are named as a, b, c, d and e respectively and control compound as BT. The prepared sample powders were calcined at 773 K for 1 h. The samples were formed as pellets with 15 mm in diameter and 1 mm in thickness. Finally, the pellets were sintered at 723 K for 2 h.

5.2.1.2 Sample preparation for anti bacterial study

Barium titanyl oxalate is prepared from Ba(NO$_3$)$_2$ and K$_2$TiO(C$_2$O$_4$)$_2$. The precipitate obtained was filtered, washed with ethanol and water repeatedly and air-dried in an oven at 333 K for 24 h. Both barium titanyl oxalate (BTO) and potassium titanyl oxalate (KTO) were powderied in an agate mortar and sieved through the mesh
and fixed the particle size in the range 95-105 µm. The samples are prepared by physical mixing of potassium and barium titanyl oxalate.

Different compositions: 100 m/m (%) barium titanyl oxalate (AS₁), 99 m/m (%) barium titanyl oxalate (AS₂), 98 m/m (%) barium titanyl oxalate (AS₃), 95 m/m (%) barium titanyl oxalate (AS₄), 93 m/m (%) barium titanyl oxalate (AS₅), 90 m/m (%) barium titanyl oxalate (AS₆), 80 m/m (%) barium titanyl oxalate (AS₇) and 100 m/m (%) potassium titanyl oxalate (AS₈), were prepared each by thorough mechanical mixing in an agate mortar. The samples were decomposed by keeping in a muffle furnace at about 1023 K for 1 h.

5.2.2 Methods

The resistivity of the prepared pallets was determined by using a standard four-probe method (Keithley’s source meter, model 2400, America). In vitro antibacterial activity of mixed barium titanate nano particles was studied by agar disc diffusion assay method. The structures of the calcined materials were determined by measurement of XRD. The XRD analysis was carried out on a Rigaku-Dmax 2000 diffractometer with Cu Kα radiation (40kV, 30mA, λ = 1.5405Å). Fourier Transform Infrared spectroscopic measurements were performed by using an IR spectrophotometer (Nicolet AVATAR 320, America) ranging from 400 to 4000 cm⁻¹. Absorption spectra were scanned by using a UV-Vis spectrophotometer (Shimadzu, UV-2450) with a deuterium lamp. SEM analyses of the samples studied were performed with FE-SEM-EDS combination using Carl Zeiss Gemini SEM 300.
5.3 Results and Discussion

5.3.1 Conductance study

5.3.1.1 XRD Analysis

Fig. 5.1 shows the XRD patterns; K\(^+\) doped BaTiO\(_3\) possesses the same perovskite structure as that of the pure BaTiO\(_3\) material. It can be concluded that no new substance was formed during the doping and calcination process other than BaTiO\(_3\) which implies that the dopants have entirely entered the unit-cell maintaining the perovskite structure of the solid. During doping K\(^+\) entered into crystal lattices of BaTiO\(_3\) leading to the increase of the conductivity of the samples [28]. The particle size of samples was calculated using Scherrer formula. The particle size of the sample (a) is calculated and found to be 11.81 nm, while the particle sizes of sample (b), (c), (d), (e) and (f) are in the range 20.31-18.29 nm.

![XRD patterns](image)

**Fig. 5.1** XRD patterns of the BaTiO\(_3\) powders (BT) doped with 10\(^4\) (a), 10\(^{-3}\) (b), 10\(^{-2}\) (c), 10\(^{-1}\) (d) and 1mol % K (e), after the calcination at 1023 K for 1 h.
5.3.1.2 FTIR Spectra Analysis

The FTIR spectra of samples are shown in Fig. 5.3. The characteristic absorption at 3410 cm\(^{-1}\) is assigned to –OH stretching vibration, due to the water brought by KBr or absorbed on the powder surface. The characteristic absorption at 1440 cm\(^{-1}\) is assigned to the stretching vibrations of carboxylate [29]. All the three samples exhibit strong absorptions around 550 and 450 cm\(^{-1}\), which can be assigned to the stretching and bending vibrations of the Ti-O bond in [TiO\(_6\)]\(^{2-}\) octahedron. But the strongest absorption observed around 550 cm\(^{-1}\) varied slightly for all the five samples: 559.1, 552.2, 545.7, 553.1, and 621.7 cm\(^{-1}\) respectively for samples a, b, c, d, & e. Since the wave number increases when infrared light of higher frequency and thus stronger energy is absorbed, it can be concluded that the Ti-O bond was strengthened after the doping and further strengthened after calcination [30].

![FTIR Spectra](image)

**Fig. 5.2** FTIR spectrum of samples: undoped BaTiO\(_3\) (BT),\(10^{-4}\) (a) \(10^{-3}\) (b), \(10^{-2}\) (c), \(10^{-1}\) (d) and 1 mol % K (e), after the calcination at 373 K for 1 h.
5.3.1.3 Four probe method

The electrical characteristics of any material can be analyzed on electrical resistivity and based on this, materials are classified as conductors, semiconductors and insulators. The resistivity of the conductors (metals) is very low because of the large number of free electrons. In the case of semiconductors usually the sheet or surface resistance of the thin layers are be considered. In any direct resistance measurement the metal terminals when come into contact with the layer, then there is a contact resistance similar to a rectifier due to metal semiconductor interface. There is another resistance also involved due to the spreading of charges into the semiconductor material apart from the surface called spreading resistance. The resistance observed in the direct measurement is the sum of actual surface resistance, contact resistance, spreading resistance and the resistance between the probes [31].

In order to eliminate the contact resistance as well as spreading resistance [32], while taking the resistance measurement, the four probe method is used to measure sheet resistivity. Here we are used four probe measuring set up using Keithley’s source meter, model 2400. Along with four probe set up, each probe separated by a distance of 0.6 cm and constant current (1 μA) is applied. The samples are prepared as bare sample and five number of K⁺ doped at various concentrations in BaTiO₃ and pelletized and then sintered at 723 K for 2 h. The measured sheet resistance and the conductance of different samples are given in the Table 5.1.
5.3.1.4 Electric Properties of samples.

During the calcination process $K_2TiO(C_2O_4)_2$ decomposes into $K_2O$, which entered BaTiO$_3$ lattice. Since K$^+$ possesses only one positive charge and Ba$^{2+}$ possesses two, the substitution must be charge-compensated to maintain charge neutrality by using defect theory [33]. According to the defect theory the incorporation of K$^+$ as an acceptor dopant can be written as in equation (5.1):

$$K_2O \xrightarrow{BaTiO_3} 2K_{Ba} + V_0^{**} + O_0$$  \hspace{1cm} (5.1)

The formation of oxygen vacancy is responsible for conducting properties of the samples. Here the strength of Ti-O bond in the $[\text{TiO}_6]^{2-}$ octahedron is stronger in the sample doped with K$^+$ than the undoped BaTiO$_3$ sample. Since the $O^{2-}$ leaving the cell, the $[\text{TiO}_6]^{2-}$ octahedron was distorted and Ti$^{4+}$ gains a stronger attraction of the $O^{2-}$ left, rendering the Ti-O bond stronger [33].

The oxygen vacancy formed was in equilibrium with the formation of hole:

$$V_0^{**} \rightarrow V_0 + 2h$$  \hspace{1cm} (5.2)

So that the ultimate result, when doping with $K_2TiO(C_2O_4)_2$, would render BaTiO$_3$ semi conductive. The electric resistivity of BaTiO$_3$ at different K$^+$ concentrations is measured. In Fig. 5a, while increasing the concentration of $K_2TiO(C_2O_4)_2$ the resistivity decreases since the conductivity is proportional to the concentration of oxygen vacancy.
However, we should also be aware that a high concentration of defect would distort the crystal structure thus undermining conductivity.

**Fig. 5.3** The variations of the conductance of BaTiO₃ powders (BT) doped with 10⁻⁴, 10⁻³, 10⁻², 10⁻¹ and 1 mol % K⁺ after the sintered at 723 K for 2 h.

**Fig. 5.4** The comparison of the conductance of BaTiO₃ powders (BT) doped with 10⁻⁴ (A), 10⁻³ (B), 10⁻² (C), 10⁻¹ (D) and 1 mol % K (E), after the sintered at 723 K for 2 h.
Fig. 5.4 shows comparison of conductance calculated by four probe method by column graph. It shows that, during doping the conductance of the sample BT increases while the resistivity decreases which is proportional to the concentration of the dopant (Table 5.1).

5.3.1.5 UV- Visible spectroscopic studies

For UV/VIS absorption analysis was carried out on a Shimadzu, UV-2450 spectrometer capable of taking measurement in the range 200-1100 nm. Analysis of samples in different forms, viz., film, solution and powder are possible with this spectrometer. For the determination of optical properties, the band gap the UV–Vis diffuse reflectance spectrum of BaTiO$_3$ and K doped BaTiO$_3$ samples was measured (Fig. 5.5). It absorbs the UV light below 400 nm. Fig. 5.6a shows the UV–Vis diffuse reflectance spectrum of BaTiO$_3$ and K$^+$ doped BaTiO$_3$ samples and it show noticeable shift towards higher wavelength, i.e., red shift, due to the presence of K$^+$ ions.

![Absorption Spectra](image)

**Fig. 5.5** UV-Vis absorption spectra of BaTiO$_3$ + x mol % K (x = $10^{-4}$, $10^{-3}$, $10^{-2}$, $10^{-1}$ and 1).
The concentration increased in K$^+$ doped BaTiO$_3$ when UV-Vis absorption shifted to long wave region in K$^+$ doped samples. The red shift of UV-Vis absorption was observed, the red shift effect was enhances with increase of the concentration of K$^+$ shown in Fig. 5.6a. Absorption is expressed in terms of a coefficient $\alpha(h\nu)$, which is related to the energy gap $E_g$ according to Tauc-equation

$$\alpha h\nu = A(h\nu - E_g)^n$$

(5.3)

Where $A$ is a constant, $h$ is Plank’s constant; $\nu$ the frequency of the incident beam and $n$ is equal to $\frac{1}{2}$ for a direct gap and 2 for an indirect gap [34]. Band gap measurements are mainly carried out by this technique on the basis of Tauc plot as the intercept value of the plot of $(\alpha h\nu)^2$ against light energy $(h\nu)$. The optical band gap $(E_g)$ is estimated by the extrapolation of the linear portion to $(\alpha h\nu)^2=0$ in the $h\nu$ versus $(\alpha h\nu)^2$ curve (Tauc-plot) is shown in Fig. 5.6b, and band gap was found and tabulated (Table 5.1), which reveals that the band gap decreases from 2.97 to 2.78 eV supporting the red shift. The reported value of $E_g$ corresponding to BaTiO$_3$ is 3.1 eV [35]. The decrease in the value of $E_g$ of a material reflects the increase of conducting properties. It has been reported that electron donors accelerate thermal process and electron acceptors retard the thermal process [36]. Therefore, the presence of K$^+$ along with BaTiO$_3$ causes an increase in the conducting properties of BaTiO$_3$. 

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Fig. 5.6 UV-vis reflectance spectra (A) and Tauc-plot (B) of BaTiO$_3$ + x mol % K ($x = 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}$ and 1) within the range of wavelength.

The conductance increases with increase of K$^+$ concentration in the system, it was seen that the dopant decreases the band-gap energy between the valence band and conduction band so that electrons could jump from the valence band to the conduction band easily. The understanding about the experimental results is helpful to reveal the mechanism of doping. Moreover, it provides a possible way to modify the optical property and the conductive property of the materials that are potential candidate in electronic industry.

Table 5.1 Parameters obtained from Four probe method and UV-Vis. spectroscopy.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conductance (Ω$^{-1}$m$^{-1}$)</th>
<th>Band gap (eV)</th>
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<tbody>
<tr>
<td>BT</td>
<td>0.549</td>
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</tr>
<tr>
<td>BT+10$^{-4}$ mol % K</td>
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<td>2.91</td>
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<tr>
<td>BT+10$^{-3}$ mol % K</td>
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<tr>
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<tr>
<td>BT+10$^{-1}$ mol % K</td>
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<td>2.73</td>
</tr>
<tr>
<td>BT+1 mol % K</td>
<td>5.649</td>
<td>2.68</td>
</tr>
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</table>
5.3.2 Anti bacterial Study

5.3.2.1 XRD analysis

XRD analysis was employed to affirm the composition of as prepared oxide nanoparticles. Fig. 5.7 shows the structural characteristics of pure barium titanyl oxalate, potassium titanyl oxalate and their mixtures when heated to 973 K for 1h investigated by XRD. The XRD results of the hydrated samples AS$_1$ and AS$_8$ show significant amount of amorphous phase and the dehydrated mixed samples AS$_2$, AS$_3$, AS$_4$, AS$_5$, AS$_6$ and AS$_7$, the peak positions with 2θ values of 31.84, 39.17, 45.5, 51.21, 60.04 and 75.25$^0$ can be assigned to (002), (111), (202), (020), (202) and (311) planes which matches well with the values of tetragonal phase of BaTiO$_3$ reported with the JCPDS file no. 05-0626 [37]. The relative crystallite sizes determined from the XRD line broadening using the Scherrer equation: $d = \frac{0.9\lambda}{\beta \cos \theta}$, where $d$ is the crystallite size, $\lambda$ is the wavelength used in XRD (1.5418 Å$^0$), $\theta$ is the Bragg angle, $\beta$ is the pure diffraction broadening of a peak at half height, i.e., broadening due to crystallite dimensions. The crystallite size of the mixed oxides ranges from 28-35 nm and hydrated AS$_1$ and AS$_8$ obtained as 45 & 50 nm according to the Scherrer equation [38]
Fig. 5.7 XRD pattern of barium titanyl oxalate tetrahydrate (AS₁), potassium titanyl oxalate dehydrate (AS₈) and the different mixtures AS₂, AS₃, AS₄, AS₅, AS₆, AS₇ heated to 973 K for 1 h.

5.3.2.2 SEM Analysis

Fig. 5.8 shows the FE-SEM images of AS₁, AS₂, AS₃, AS₄ and AS₅ respectively. From the images it is evident that all the mixed BTNPs are highly porous, in addition to which, agglomeration of the particles is also clear. Similar trend was observed for all other mixed samples. SEM images reveals different morphology such as spherical and rod shape particles with temperature of calcination.
Energy dispersive X-ray spectroscopic analysis (EDS) carried out to identify the purity of the mixed BTNPs synthesized by calcining at a temperature of 750 K. From the EDS analysis, it is found that mixed BTNPs did not contain any impurities (Fig. 5.9). The high intensity peaks observed in the EDS patterns of the nanoparticles, in Fig. 5.9, corresponds to Ba, K, O and Ti elements [39].
5.3.2.3 Agar- well diffusion method

The microbial toxicity of mixed metal oxide nanoparticles was demonstrated using Gram-positive (G+) and Gram-negative (G–) bacteria. The antibacterial activity of mixed metal oxide nanostructures was evaluated by well diffusion method using four pathogenic bacteria
Escherichia coli (G−), Staphylococcus aureus (G+), Pseudomonas aeruginosa (G−) and Staphylococcus pneumonia (G+).

5.3.2.3.1 Antibacterial activity test

In order to investigate the antibacterial activity, mixed BaTiO$_3$ nanoparticles along with standard antibiotic [Gentamicin (G)] were tested against four bacterial strains: Escherichia coli (Gram-negative), Pseudomonas aeruginosa (Gram-negative), Staphylococcus pneumonia (Gram-positive) and Staphylococcus aureus (Gram-positive) by disc diffusion methods.

Luria Bertani (LB) medium was prepared in distilled water and sterilized. Sterile LB agar was poured into Petri dishes and allowed to set in a laminar air flow cabinet. The plates were then stored in a refrigerator for further use. A 24 h exponentially grown bacterial culture further inoculated into LB broth and shake well in 310 K incubator shaker till it reaches 0.5 Macfarlane’s turbidity. The culture was then spread on LB agar plates already prepared, with sterile glass spreader. On drying of the spreader layer, small wells were dug in the plates according to the number of samples to be screened particles in 1 mg/ml concentration was pipette out into the respective wells and incubated for 16 h at 310 K. The obtained zone of inhibition of bacterial growth was then analyzed by measuring it and recorded in mm.
5.3.2.3.2 Observations

The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the well. The mixed barium titanate nanoparticles exerted a fairly significant antibacterial properties against four pathogens investigated when compared to control (Fig. 5.10). The diameter of inhibition zones increased for the test mixed metal oxide nanoparticles. The negative controls (N) indicated the microbial growth profile in the absence of nanoparticles.

The inhibition data is tabulated in Table 5.2 and zone of inhibition is shown in Fig. 5.11. The well diffusion test was conducted as a qualitative test only and no inference of dosage details is mentioned. The mixed metal oxides show remarkable antibacterial activity against the four studied bacterial stains. The presence of different concentration ratios increases the antibacterial activity of barium titanate nanoparticles significantly. It can be hypothesised that these nanoparticles form stable complexes with vital enzymes inside the cells which hamper cellular functioning resulting in their death.

![Fig. 5.10](image)

**Fig. 5.10** The zones of inhibition against Escherichia coli (a), Staphylococcus aureus (b), Pseudomonas aeruginosa (c) and Staphylococcus pneumonia (d), when treated with Gentamicin.
Fig. 5.11 The zones of inhibition against Escherichia coli (a), Staphylococcus aureus (b), Pseudomonas aeruginosa (c) and Staphylococcus pneumonia (d), when treated with the prepared mixed metal oxides.

Table 5.2 Comparision of activities of samples on Gram-negative and Gram-positive bacteria

<table>
<thead>
<tr>
<th>Bacterias</th>
<th>AS₁</th>
<th>AS₂</th>
<th>AS₃</th>
<th>AS₄</th>
<th>AS₅</th>
<th>AS₆</th>
<th>AS₇</th>
<th>AS₈</th>
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<th>G</th>
</tr>
</thead>
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<td>30</td>
<td>28</td>
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<tr>
<td>Staphylococcus aureus</td>
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<td>28</td>
<td>26</td>
<td>31</td>
<td>23</td>
<td>12</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Pseudomonas aeruginosa</td>
<td>26</td>
<td>29</td>
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<td>19</td>
<td>13</td>
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<td>20</td>
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5.4 Conclusion

- In conductance study, the addition of K⁺ in BaTiO₃ system increases the conductance. UV-Vis spectra reveal that it was
attributed to the decrease of the energy gap. The red shift of absorption edge observed in the K$^+$ doped BaTiO$_3$, confirms that electrons possess a larger possibility for jumping from the valence band to the conductance band. The decrease of resistance was approving for the materials to assemble the demand of electronic circuit. The red shift of absorption edge made the materials available in a wider range of wavelength. The information is important for the material to be applied in a certain range of wavelength. The understanding about the correlation between the conductivity and UV-Vis spectra in this kind of functional material is helpful to improve performances of related devices in electronic industry. The prepared samples were characterized using XRD and FT-IR.

- The microbial toxicity of mixed metal oxides was demonstrated using Gram-positive (G+) and Gram-negative (G−) bacteria. The antibacterial activity of mixed metal oxides nanostructures was evaluated by well diffusion method using four pathogenic bacteria Escherichia coli (G−), Staphylococcus aureus (G+), Pseudomonas aeruginosa (G−), Staphylococcus pneumonia (G+). The mixed metal oxides showed remarkable antibacterial activity against the four studied bacterial strains. The synthesized BTO, KTO and the series of mixtures of barium-potassium titanyl oxalate were decomposed and characterized using XRD and FE-SEM.
5.5 References


30. Miguel G, Juan H, Leticia B, Joaquin N, Mario ERG. Characterization of calcium carbonate, calcium oxide and calcium hydroxide as starting point to the improvement of lime


