Studies of phosphor material have witnessed a rapid growth in research and development of luminescence phenomenon due to their diverse applications. Calcium titanate (CaTiO$_3$) compound based phosphor doped with praseodymium provides a subject for fundamental structural studies aiming at exploring a new functional material. The effect of calcium concentration on structural properties of CaTiO$_3$ phosphor was investigated by Fourier transform infrared (FTIR) spectroscopy and Fourier transform Raman spectroscopy (FT-Raman). FTIR studies confirmed the presence of the functional groups modes of vibrations. The bands in the region of 416-460 cm$^{-1}$ were assigned to Ti-O-Ti bending modes. Meanwhile, the band in the region of 515-570 cm$^{-1}$ was attributed to Ti-O stretching vibration. Only 6 Raman active modes of CaTiO$_3$ were detected in the samples by FT-Raman spectroscopy.

**Keywords**: phosphor, calcium titanate, Fourier transform infrared (FTIR) spectroscopy

**1.0 INTRODUCTION**

Luminescence in solid is the phenomenon in which electronic states of solid is excited by an external source and this excitation energy is released as light. When the energy comes from short-wavelength light, usually ultraviolet light, the phenomenon is called photoluminescence [1]. There are two basic kinds of luminescence materials recognized as inorganic (phosphor) and organic (organoluminophosphors) luminescence. Substances containing of solid luminescence materials are called as phosphors. Usually, inorganic phosphor consist of a crystalline “host material” added with small amount of certain impurities that are called the “activators”. Perovskite-type prasedodymium doped CaTiO$_3$: Pr$^{3+}$ is potential red phosphor for various display application such as for safety and emergency marking.

Philippe Boutinaud et al. [2] reports on luminescence properties of praseodymium doping in titanate host material show high luminescence efficiency and attract much attention. From previous studies, a lot of report have been published focus on luminescent properties compare to local structure of titania based phosphor or another phosphor...
material. Nowadays, studies on the structure of phosphor material and their relations to luminescence properties are less conducted by researchers. From literature review, Kong Li et. al. [3] was reported that the structure of the sample are related to the luminescence properties. In addition, effect of doping material and percentage of host concentration were effected the structural and luminescence behavior.

In these work, structural studies of $x$CaO-(100-$x$)TiO$_2$:1%Pr$^{3+}$, where $10 \leq x$(mol%) $\leq 40$ phosphor was investigated by solid state reaction method. Optimum percentage of CaO content in TiO$_2$ host lattice and their effect on structural behaviour of vibration was studied in calcium titanate host phosphor. The samples were characterize by Fourier Transform Infrared (FTIR) spectroscopy and Fourier Transform Raman (FT-Raman) spectroscopy.

2.0 EXPERIMENTAL

Calcium oxide (99% CaO: Riedel-de Haen), titanium dioxide (99% TiO$_2$: Fluka Alrich were employed as the raw materials. Praseodymium oxide (99% P$_2$O$_3$: Acros) was incorporated as a doped material in appropriate amounts for charge compensation purposes.

The calcium titanate phosphor doped with praseodymium are synthesized using solid state reaction method using high temperature. Starting material were mixed and homogenized through grinding process using ball milling for 1hour. Then, the sample were sintered at 1000°C for 6 hours. Lastly, the furnace shall be set to room temperature to let the mixture to cool down. After the reactions, the samples will be characterized by Fourier Transform infrared spectroscopy (FTIR) and Fourier Transform Raman spectroscopy (FT-Raman).

The samples were prepared using potassium bromide method (KBr) pellet on powder samples by infrared excitation scan. The IR spectra were recorded using 10 scans and resolution at 4cm$^{-1}$. The IR spectra of samples were recorded in range of 400–2000 cm$^{-1}$. The Raman spectra were measured by Jobin Yvon HR 800 UV in the spectral range of 100–1200 cm$^{-1}$. The sample was excited with an argon ion laser ($\lambda = 514.5$nm) with power of about 20mW. The digital intensity data were recorded at intervals of 4 cm$^{-1}$ and the spectral resolution was about 4 cm$^{-1}$.

3.0 RESULTS AND DISCUSSION

3.1 The effect of calcium concentration on host structure by FT-Infrared spectroscopy

Infrared spectroscopy analysis was carried out to study the effect of different concentration of Ca atom to the properties of CaTiO$_3$ crystal structure. The infrared spectra different concentration of CaO in $x$CaO-(100-$x$)TiO$_2$, where $10 \leq x$(mol%) $\leq 40$ doped with 1 mol% Pr$^{3+}$ with are shown in Figure 1. The infrared spectra of these samples, which were sintered at 1000°C, showed main bands around 710, 570, 527, 460 and 415 cm$^{-1}$. The broad bands in the region 710 cm$^{-1}$ and 570 cm$^{-1}$ band were assigned to Ti-O stretching vibrations of TiO$_6$. The absorption band at 527 cm$^{-1}$ could be assigned to the Ti-O stretching vibration [4]. While the vibration at 460 and 415 cm$^{-1}$ attributed to the vibration of Ti-O-Ti bending mode [5]. FTIR band and their assignment of CaTiO$_3$ structure were list on Table 1.

From Figure 1, the wavenumber of the transmittance peaks of Ti-O bonds corresponds to vibration at 710 cm$^{-1}$ shift to smaller value when the concentration of Ca increased. The wavenumber of transmittance peaks in 10Ca-90TiO$_2$ (mol %) was near 710 cm$^{-1}$ while in 40Ca-60TiO$_2$ (mol %) was shift near to 675 cm$^{-1}$. According to the study, when the concentration of Ca in the sample increases, it is shifted to smaller wavenumbers. Shifted to smaller wavenumber showed less energy is needed by titanium (Ti) and oxygen (O) atoms of Ti-O bond in the molecule for all samples to vibrate with their certain wavenumber. Hence, reduction in energy has defined that the bonding of Ti-O bond length becomes increasingly elongated in cell size [6].

The infrared-active mode Ti-O-Ti bending vibrations ($\delta$(Ti-O-Ti)) at 460 cm$^{-1}$ became clearly determined in infrared spectra and slightly shifted to lower value when $x$ was increased. The addition of higher CaO (x CaO mol% are increase) content will enhance the formation of Ti-O-Ti bonding. The spectrum are shifted to lower wavenumber, hence, higher energy are given to the samples in addition of xCaO mol%. The peaks at this region have higher energy to break the bond and easily determine at $x = 30$ CaO mol% and $x = 40$ CaO mol%. All the bands (710, 570, 527, 460 and 415 cm$^{-1}$) were vibrate in the TiO$_6$ octahedra lattice.
Table 1: FTIR band and their assignment of CaTiO₃ structure

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Modes of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>710</td>
<td>Ti-O stretching vibration of TiO₆</td>
</tr>
<tr>
<td>570</td>
<td>Ti-O stretching vibration of TiO₆</td>
</tr>
<tr>
<td>527</td>
<td>Ti-O stretching vibration</td>
</tr>
<tr>
<td>460</td>
<td>Ti-O-Ti bending</td>
</tr>
<tr>
<td>415</td>
<td>Ti-O-Ti bending</td>
</tr>
</tbody>
</table>

Figure 1: FTIR spectrum of \(x\)CaO-(100-x)TiO₂:1%Pr³⁺, different concentration of CaO 10 ≤ x (mol%) ≤ 40

3.2 The effect of percentage of Ca on host lattice by FT-Raman spectroscopy

Figure 2 shows the Raman spectra of \(x\)CaO-(100-x)TiO₂:Pr³⁺ in series of 0 ≤ x (mol%) ≤ 40 where Pr³⁺ ions were constant at 1mol %. The Raman spectra of CaTiO₃ shown a number of sharp peaks superimposed on a broad feature between 150 cm⁻¹ and 700 cm⁻¹ region. Raman-active modes were detected for the powder of \(x\)CaO-(1-x)TiO₂:Pr³⁺ when \(x\) was in the range of 10 to 40 mol%. As \(x\) increased, several peaks diverged and new Raman-active modes appeared. Therefore, the percentage of Ca²⁺ ion was able to increase or decrease the structural organization in perovskite structure. As a result, the percentage of Ca in CaTiO₃ promoted a different coordination of interaction
between the ions, which mainly aroused from the stretching, torsional and bending vibrations of the shorter metal-oxygen bonds, contributing to the observation of the Raman-active modes.

There were a total of 24 Raman-active modes for orthorhombic CaTiO$_3$. Factor group analysis gave the Raman active vibration modes as $7A_g+7B_{1g}+5B_{2g}+5B_{3g}$. Although 24 Raman active modes were expected, several of these modes could not be detected because of their low polarizabilities [7]. Hence, only six Raman active modes were commonly observed.

The Raman spectra of $x$CaO-$(100-x)$TiO$_2$: Pr$^{3+}$ where $10 \leq x$(mol%) $\leq 40$ had only six Raman active mode which were observed at $\sim 150$, $\sim 260$, $\sim 415$, $\sim 450$, $\sim 517$ and $\sim 630$ cm$^{-1}$. It was found that the Raman active modes for these samples were in good agreement with Sanjay et al. [8]. According to Marques et. al., [9] band at $\sim 150$ cm$^{-1}$ was related to the vibration of Ca bonded to a TiO$_3$ group (Ca–TiO$_3$) lattice mode. The band observed at $\sim 260$ cm$^{-1}$ could be assigned to the O-Ti-O bending vibration mode or caused by the tilting phenomenon between the [TiO6]-[TiO6] clusters. The bands at $\sim 415$ cm$^{-1}$, $\sim 450$ cm$^{-1}$ and $\sim 517$ cm$^{-1}$ were assigned to Ti-O$_3$ torsional (bending or internal vibration of oxygen cage) modes. Particularly, the $\sim 620$ cm$^{-1}$ mode of CaTiO$_3$ was assigned to Ti-O symmetric stretching vibration mode [10,11]. The Raman bands and their assignment are listed in Table 2.

### Table 2: Raman band and their assignment of CaTiO$_3$ structure

<table>
<thead>
<tr>
<th>Raman Bands (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>(Ca–TiO$_3$)</td>
</tr>
<tr>
<td>260</td>
<td>$\delta$(O-Ti-O)</td>
</tr>
<tr>
<td>415</td>
<td>$\delta$(Ti-O$_3$)</td>
</tr>
<tr>
<td>450</td>
<td>$\delta$(Ti-O$_3$)</td>
</tr>
<tr>
<td>517</td>
<td>$\delta$(Ti-O$_3$)</td>
</tr>
<tr>
<td>620</td>
<td>$\nu_s$(Ti-O)</td>
</tr>
</tbody>
</table>
An analysis of Figure 2 reports that no drastic spectral changes and only slight shifts were observed on the characteristic position of Raman active modes when $x$ increased from 10 to 40 mol%. Even though Raman spectra shown in Figure 2 was similar in pattern, but their vibration (peak position and width) were different in $10 \leq x \text{ mol\%} \leq 40$ in CaTiO$_3$ crystals, which were related to the effect of different percentage on the calcium titanate network. As $x$ increased, the band at 434 cm$^{-1}$ diminished and slightly shifted due to a reduction in the degree of Ti-site order. The intensity 251 cm$^{-1}$ bands decreased with an increasing $x$. Thus, it is suggested that these band was related to the rotation of the oxygen octahedral cage associated with the orthorhombic distortion. At lower percentage of $x$ ($x=10$ mol%) stronger interactions between Ti-O bonds occurred, suggesting an increase of [TiO$_6$]-[TiO$_6$] clusters vibration at around 250 cm$^{-1}$ in perovskite structure. When $x=30$, a narrow peak at 510 cm$^{-1}$ started to appear. Therefore, the intensity of this peak increased with increasing $x$, implying a stronger distortion in high CaTiO$_3$ compounds as reported by Zheng et al., (12). When the Ca$^{2+}$ and Ti$^{4+}$ varied at a fixed Pr quantity, the bands at ~600 cm$^{-1}$ diminished presumably due to the Ca-rich. As shown in the figure, the crystallinity was poor in excess Ca. Since the Ca-rich ($x=40$ mol%), the Ti-O vibration due to this band could not be detected because of low polarizabilities of Ti$^{4+}$ ions. As a result, this band would diminish due to a reduction in the degree of Ti-site order (13).
4.0 CONCLUSION

Structural characteristic of calcium titanate, CaTiO₃ phosphor doped with Pr-ion synthesize via solid state reaction have been investigated. Phase crystallinity of CaTiO₃ can be obtained at 1000°C for 6 hours by conventional solid state reaction method via using CaO and TiO₂ as raw materials. As low as CaO concentration (x=10 mol%), the phase of CaTiO₃ are obtained in the samples. Therefore, in order to compose a CaTiO₃ phase, minimum nominal composition could be used by this method.

Infrared bands have been analyzed for identifying the functional groups of CaTiO₃. The bands at around 570 cm⁻¹ and 710 cm⁻¹ are due to the vibration of Ti-O stretching vibration of TiO₆ cluster. The band at 527 cm⁻¹ is due to the Ti-O stretching vibrations. Furthermore, the bands near 460 cm⁻¹ and 415 cm⁻¹ is attributed to the Ti-O-Ti bending mode.

There are 24 Raman active modes for the orthorhombic structure of CaTiO₃ and can be ascribed by 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}. However, only 6 Raman active modes are detected in the samples. The bands at ~150 cm⁻¹ are attributed to the Ca-TiO₃ lattice vibration mode. Near 260 cm⁻¹ are ascribes to O-Ti-O bending mode and the bands at ~415 cm⁻¹, ~435 cm⁻¹, and ~520 cm⁻¹ are assigned to the Ti-O₃ torsional mode. In addition, Ti-O symmetric stretching is detected at around 620 cm⁻¹. When the sample are doped with praseodymium, the slight shift observed on the characteristic position of Raman modes which can be related to the degree of crystallization, interaction force between ions, structural defects and influence of doping.

ACKNOWLEDGEMENT

This research was support financially by Ministry of Science Technology and Innovation (MOSTI) under Science Fund research grant Project Number: 03-01-06-SF0053.

REFERENCES

