

STRUCTURAL STUDIES ON MAGNESIUM CALCIUM TELLURITE DOPED WITH Eu²⁺ AND Dy³⁺

Nur Shahira Alias, Rosli Hussin, Musdalilah Ahmad Salim, Siti Aisyah Ahmad Fuzi, Mutia Suhaibah Abdullah, Suhailah Abdullah and Mohd Nor Md Yusof.

*Phosphor Research Group, Jabatan Fizik, Fakulti Sains,
Universiti Teknologi Malaysia, 81310 Skudai, Johor.*

ABSTRACT

The samples of phosphor material based on alkali earth tellurite, doped with rare earth have been prepared using solid state reaction method. The samples are with the composition in mol %: $x\text{MgO}-(30-x)\text{CaO}-70\text{TeO}_2$ with $0 \leq x \leq 30$ mol%, and have been doped with Eu_2O_3 (2mol%) and Dy_2O_3 (1mol%). The structure of the samples have been investigated by means of X-Ray Diffraction, Raman and Infrared spectroscopy. The x-ray diffraction results show that two phase are observed in the samples, which is MgTe_2O_5 and CaTe_2O_5 phase. Raman spectroscopy studies show that the vibrations of the samples are identical with the $\alpha\text{-TeO}_2$ vibrations, with a shift about $40\text{-}50\text{cm}^{-1}$. Strong bands are observed located at around 435, 616, 689, 785, and 807cm^{-1} . As the concentration of the modifier, MgO and CaO increased, the coordination of TeO_4 are transform from the corner sharing, $\alpha\text{-TeO}_2$ structure to the edge sharing, $\beta\text{-TeO}_2$ structure. It is also indicated that the increasing of MgO contribute to the increasing of symmetry vibration of TeO_4 molecule, $\nu_s(\text{TeO}_4)$, while the addition of CaO increased the asymmetry vibration of TeO_4 molecule, $\nu_{as}(\text{TeO}_4)$. The comparison between Raman and IR spectra is also include to identify the mode vibration of the samples.

INTRODUCTION

Phosphor material is a kind of pigments that absorbs energy and then releases the stored energy in the form of light after being excited. The release luminescent light can last several hours [1]. This phosphor has been studied for long time. The properties of chemical stability, great brightness, long duration, no radiation and environmental capability result in their wide applications in many fields such as safety indication, lighting in emergency, instrument in automobile, luminous paint and optical devices.

The host material used for rare earth doping play important role for obtaining highly efficient luminescent properties. This is because host material with low phonon energy can reduce the non-radiative loss due to the multiphonon relaxations and thus achieve strong luminescence [2]. In this study, tellurite oxide based has been used because of their desirable physical properties, such as high refractive index, excellent infrared transmittance and high dielectric constant, good chemical durability and low melting temperature. This oxide based have been studied from several different points of view attracting interest not only because of their physical properties, but also for their fundamental interest [3, 4]. Another way to achieve this may be by addition of certain

heavy metal oxide like CaO, MgO, BaO as network modifier. In this study, MgO and CaO have been employed since the use of both modifier doped with tellurite based were rarely reported. The study particularly combines the properties of both modifiers and it is expected to bring the interesting properties of the final sample. The formation of these host may also be accompanied by a change in the local TeO₂ structure. For example, the addition of alkali metal ions in tellurite glasses can result in the transformation of some TeO₄ trigonal bipyramid (tbp) structural units into TeO₃ trigonal pyramid (tp) with non-bridging oxygen.

In this study, the system has been doped with rare earth ions, Eu²⁺ and Dy³⁺ as the dopant. Eu²⁺ doped phosphors usually show intense broad band photoluminescence (PL) with a short decay time of the order of tens of nanoseconds. The emission of Eu²⁺ is very strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electro-magnetic spectrum. This is because the 5d \leftrightarrow 4f transition is associated with the change in electric dipole and the 5d excited state is affected by crystal field effects. It is well known that the valence state of the activator dictates the emission wavelength [5].

The aim of this work is to report the structure present in magnesium calcium tellurite based phosphor material by means of x-ray diffraction (XRD), infrared (IR) and Raman spectroscopic studies. However, in this study, the concentration of Eu²⁺ and Dy³⁺ will remain constant and is not focusing about the effect of the different dopant concentration.

EXPERIMENTAL PROCEDURE

Sample preparation

Alkali earth tellurite based phosphor material were prepared by using reagent grade, TeO₂ (Fluka), MgO (Merck) and CaO (Riedel-de-Hean) as starting materials. The samples with the composition in mol %: xMgO-(30-x)CaO-70TeO₂ with 0 \leq x \leq 30 mol%, doped with Eu₂O₃(2mol%) and Dy₂O₃(1mol%) have been prepared using solid state reaction method. All stoichiometric compositions of batch materials (15g) were thoroughly mixed and milled in an agate mortar. The samples are calcined in a alumina crucible at 200°C for 1hour, then cooled to room temperature, grounded, and sintered at 500°C and 900°C for an hour. The samples are then cooled to room temperature.

Characterization

The structure of the prepared samples was analyzed using analytical tools such as X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy. The XRD measurements were carried out with CuK α radiation at room temperature using Siemens Diffractometer D5000, equipped with diffraction software analysis. The diffraction spectral data were collected at constant (2 θ) steps of 0.04°, where 2 θ from 10 to 80°, and dwell of 4s. The d-spacings obtained were compared with those in the literature in an attempt to identify the crystal phases formed. As reference the latest database of ICDD (International Center for Diffraction Data, ICDD) was also used.

The infrared (IR) spectra have been recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer from 2000 to 400 cm^{-1} at intervals of 4 cm^{-1} . Measurements were carried out on dispersed in pressed KBr pellets containing the same weight of the powder samples to enable us to roughly compare the relative intensities of the bands.

The Raman spectra were measured with a Perkin-Elmer Spectrum GX spectrometer in the spectral range 100–1200 cm^{-1} . The sample was excited with an argon ion laser with power of about 200 mW. The spectrum was observed in the quasi-back scattered mode. The digital intensity data were recorded at intervals of 4 cm^{-1} and the spectral resolution was about 4 cm^{-1} .

RESULTS & DISCUSSION

X-Ray Diffraction Patterns

Figure 1 shows the XRD patterns from all of the samples as formed in $x\text{MgO}-(30-x)\text{CaO}-70\text{TeO}_2$ system doped with Eu^{2+} and Dy^{3+} . All the obtained samples were fully crystalline. There are two main phases exist in the powder sample which is MgTe_2O_5 (ICDD: 70-1835) and CaTe_2O_5 (ICDD: 36-0882).

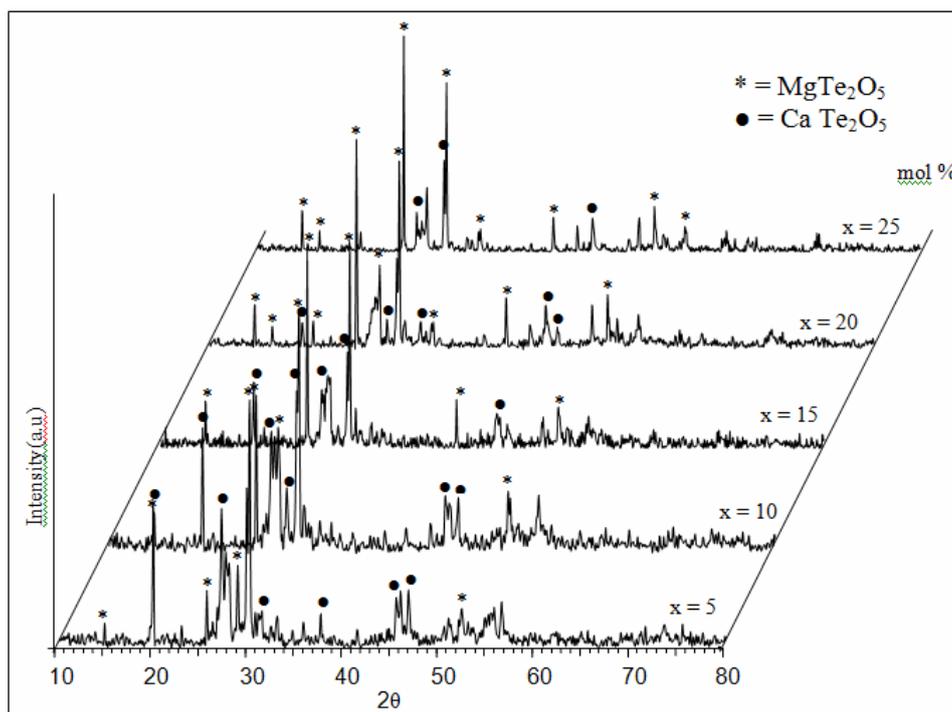


Figure 1: X-ray diffraction (XRD) patterns of $x\text{MgO}-(30-x)\text{CaO}-70\text{TeO}_2$ system, with $5 \leq x \leq 25$.

From the XRD pattern, the phase of MgTe_2O_5 is increase with the increasing of MgO

concentration and the CaTe_2O_5 phase is increasing when the concentration of CaO (30-x) is increased, which provide evident that the modifiers, MgO and CaO contribute to the formation of the phase. The percentage of the crystalline phase can be estimated using the comparison of the highest peak height. The percentages of the crystalline phases are summarized in the Table 1 below:

Table 1: The estimation of percentage of the crystalline phase in $x\text{MgO}-(30-x)\text{CaO}-70\text{TeO}_2$ samples.

x(mol %)	CaTe_2O_5 phase (%)		MgTe_2O_5 phase (%)	
5	60	Increase 10%	40	Decrease 10%
10	50	Increase 15%	50	Decrease 15%
15	35	-	65	-
20	29	Decrease 6%	71	Increase 6%
25	28	Decrease 1%	72	Increase 1%

From the estimation above, it can be conclude that the MgTe_2O_5 phase is the dominant phase. However, when we increase the concentration of MgO or CaO at the equal percentage, the CaTe_2O_5 phase is seem easier to form rather than MgTe_2O_5 phase.

Raman Spectra

Raman spectra of the $x\text{MgO}-(30-x)\text{CaO}-70\text{TeO}_2$ are presented in the Figure 2 and divided into two range which is the range of $1500-4000\text{cm}^{-1}$ (Figure 2(a)) and the range of $100-1500\text{cm}^{-1}$ (Figure 2(b)). The spectra of $\alpha\text{-TeO}_2$ and $\beta\text{-TeO}_2$ are also including as a reference. The assignment of the $x\text{MgO}-(30-x)\text{CaO}-70\text{TeO}_2$ vibration are based on $\alpha\text{-TeO}_2$ vibrations. The vibration of $\alpha\text{-TeO}_2$ consist of the mode of $\delta(\text{Te-O-Te})$, $\nu_s(\text{Te-O-Te})$, $\nu_{as}(\text{TeO}_4)$, $\nu_s(\text{TeO}_4)$ and $\nu_s(\text{Te-O}^-)$, and the structure of $\alpha\text{-TeO}_2$, along with $\beta\text{-TeO}_2$ structure are shown in Figure 3. The assignment of the Raman and IR frequencies are summarized in Table 2.

In the case of $\alpha\text{-TeO}_2$ structure, the concept of the TeO_4 disphenoids as its basic units suggests that the paratellurite lattice is the 3D-framework, made of the bent Te-O-Te bridges considered as homologues to the Si-O-Si bridges in the quartz lattice. If atom X is much harder than oxygen, the middle frequency and the higher-frequency parts of the spectra are associated with the displacement of the oxygen atoms, and can be described in terms of localized stretching vibrations of the X-O-X bridges. The Raman intensity of the asymmetric X-O-X stretching vibrations (occupying the higher frequency range) is related to the difference in the electronic polarizability properties of the two bands involved on the X-O-X bridge [6, 7]. If a given Raman spectrum has strong bands in the middle-frequency range and in the high-frequency range simultaneously, both terminal X-O bonds and X-O-X bridges would be present in the relevant structure, as the independent structural fragments.

It was found that [6], the high-frequency vibration ($\omega > 500\text{cm}^{-1}$) represent the intramolecular Te-O_{eq} stretching motion, and the number of those vibrations always corresponds to the number of Te-O_{eq} bonds. The frequency intervals below 400cm^{-1} are describing the intermolecular forces, which built up of Te-O_{ax} potential.

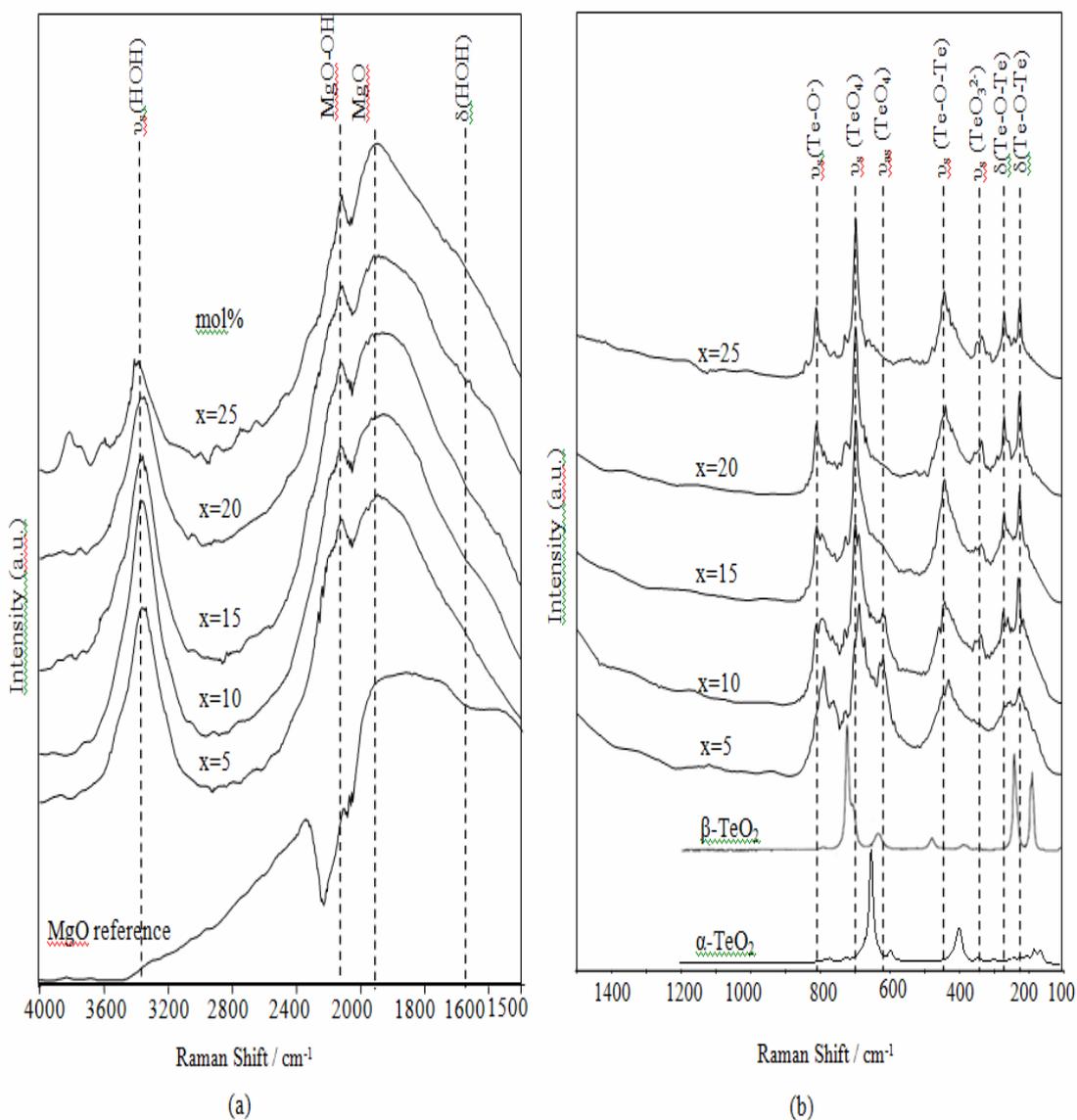
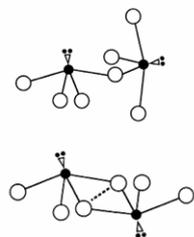


Figure 2: Raman spectra of $x\text{MgO}-(30-x)\text{CaO}-70\text{TeO}_2$ doped with $\text{Eu}_2\text{O}_3(2\text{mol}\%)$ and $\text{Dy}_2\text{O}_3(1\text{mol}\%)$ for (a) Raman spectra in the range $100-1400\text{cm}^{-1}$, (b) Raman spectra in the range $1500-4000\text{cm}^{-1}$.

(a) TeO₄ type



α -TeO₂

- corner sharing
- TeO₃²⁻ ion
- trigonal bipyramid (tbp)

β -TeO₂

- edge sharing

Figure 3: Illustration of the structural models of α -TeO₂ and β -TeO₂ [8].

Table 2: The Raman and IR vibration frequencies of crystalline TeO₂ and xMgO-(30-x)CaO-70TeO₂ with 5 ≤ x ≤ 25 mol% doped with Eu₂O₃(2mol%) and Dy₂O₃(1mol%)

	$\delta(\text{Te-O-Te})$	$\nu_s(\text{TeO}_3^{2-})$		$\nu_s(\text{Te-O-Te})$		$\nu_{as}(\text{TeO}_4)$		$\nu_s(\text{TeO}_4)$		$\nu_s(\text{Te-O})$		$\nu_2(\text{TeO}_4)$		$\delta(\text{HOH})$		<u>MgO</u>		<u>MgO-OH</u>		$\nu_s(\text{HOH})$		
		Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR			
α -TeO ₂	158, 175, 339		-	392		591		647		721		767										
β -TeO ₂	234, 336		-	450		595		673		740												
x=5	222, 264	352	-	425	461	616	613	689	687	785	775	804	825	1721	-	1941	-	2118	-	3363	-	
x=10	220, 264	330	-	435	458	618	616	692	700	787	776	807	824	1707	-	1949	-	2117	-	3358	-	
x=15	222, 266	330	-	435	452	616	615	692	707	790	779	807	826	1743	-	1946	-	2123	-	3358	-	
x=20	220, 264	330	-	435	453		615	694	711	785	781	807	825	1640	-	1917	-	2123	-	3358	-	
x=25	220, 266	330	-	437	455		615	694	711	794	786	807	824	1704	-	1917	-	2123	-	3358	-	

The Raman spectrum shows that two crystalline phase exist in the structure which indicated from two close peaks for each assignment of the band. This is equivalent to the X-ray diffraction result. The vibration frequencies are seemed to shift to higher frequency for 40-50cm⁻¹ from the vibration frequencies of α -TeO₂, which may due to the edge sharing of the TeO₄ structure. It can say that the TeO₄ coordination has distortion from corner sharing (α -TeO₂) to edge sharing which constitute the β -TeO₂ structure. At x=15, the concentration of the modifiers, MgO and CaO are equal. As the concentration of MgO increase, the vibration $\nu_s(\text{TeO}_4)$ is increased, while the vibration of $\nu_{as}(\text{TeO}_4)$ is increase with the concentration of CaO. This signify that Mg²⁺ ion are easy to vibrate compare to Ca²⁺ ions, due to the ionic radius of Ca²⁺ which larger than Mg²⁺.

Figure 2(a) shows the Raman spectra of the xMgO-(30-x)CaO-70TeO₂ in the range of 1500-4000cm⁻¹. The spectra of the MgO are also included as a reference. A broad band is observed at around 1721, 1900, 2118 3358cm⁻¹ which assigned to the vibration of $\delta(\text{HOH})$, MgO, MgO-OH and $\nu_s(\text{HOH})$, respectively.

Infrared Spectra

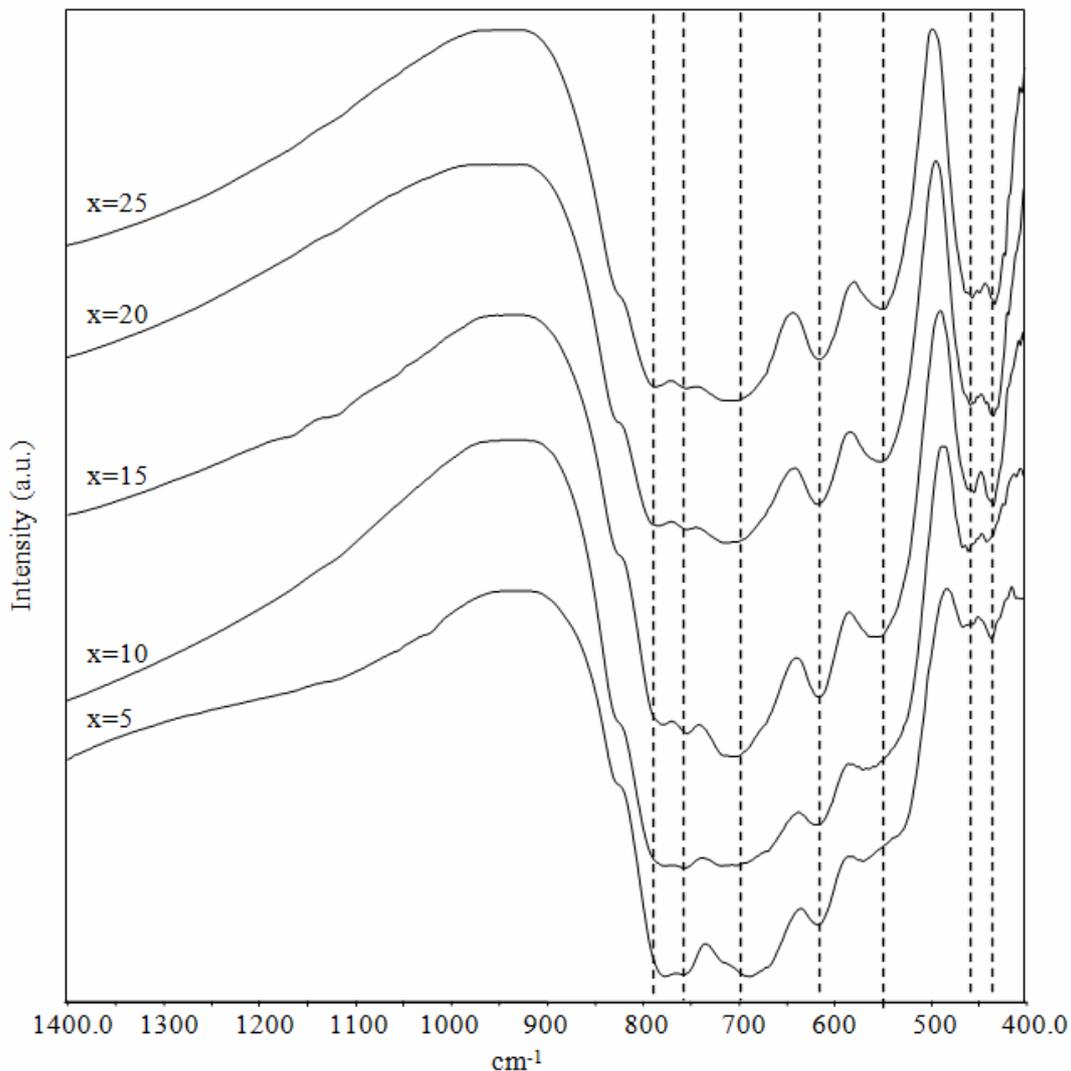


Figure 4: IR spectra of $x\text{MgO}-(30-x)\text{CaO}-70\text{TeO}_2$ doped with $\text{Eu}_2\text{O}_3(2\text{mol}\%)$ and $\text{Dy}_2\text{O}_3(1\text{mol}\%)$.

Figure 4 shows the IR spectra of $x\text{MgO}-(30-x)\text{CaO}-70\text{TeO}_2$ doped with 1mol% of Eu_2O_3 and Dy_2O_3 . The infrared transmission spectrum of the crystalline $\text{MgO}-\text{CaO}-\text{TeO}_2$ system exhibit vibrational bands in the range $400-800\text{cm}^{-1}$. This region may also consist of bands due to anti-symmetrical and symmetrical vibration of TeO_2 . The assignment of the IR bands is compare with the Raman assignment as show in Figure 5.

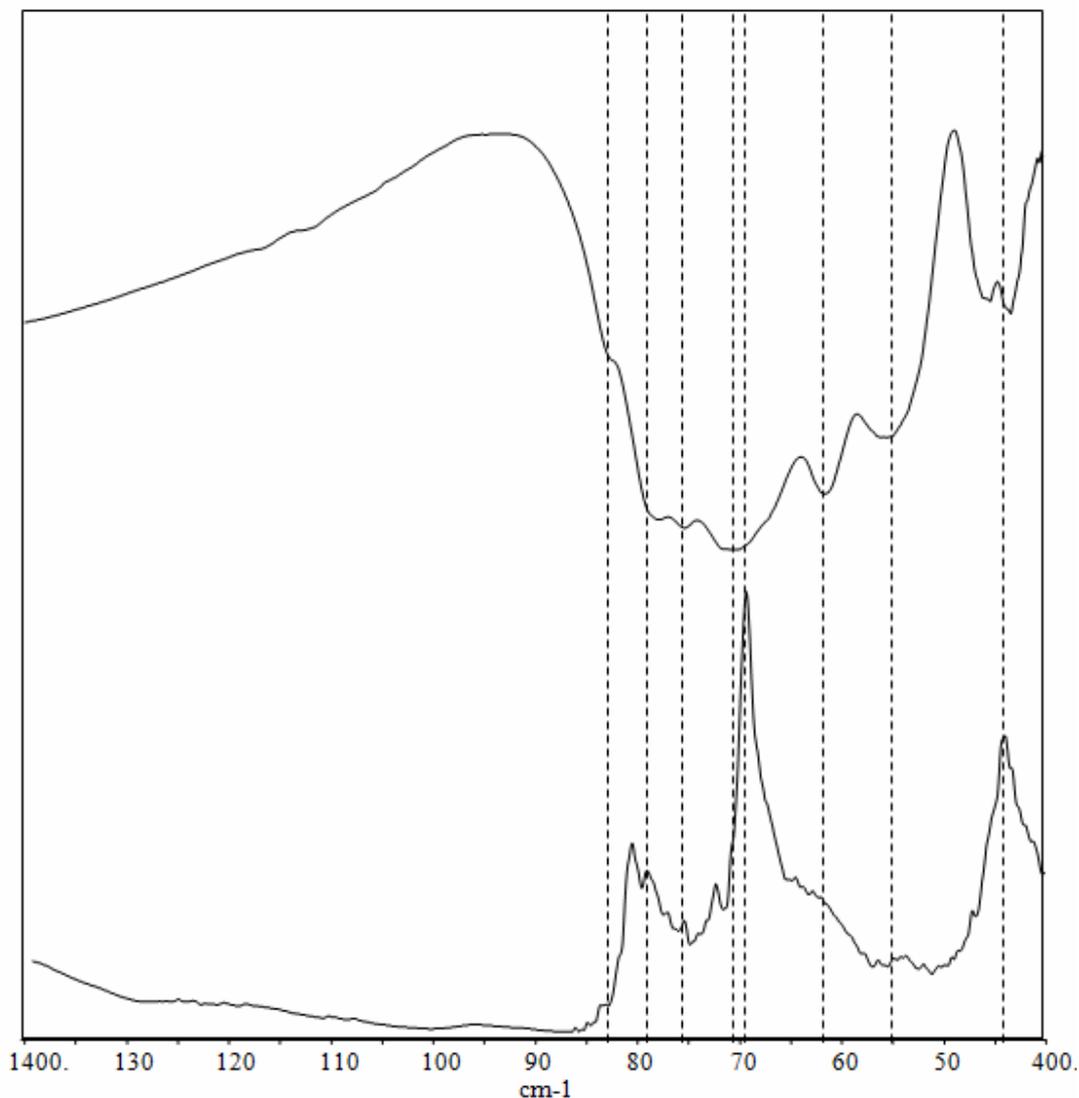


Figure 5: The Raman and IR spectra of $70\text{TeO}_2\text{-}15\text{MgO}\text{-}15\text{CaO}$ doped with $\text{Eu}_2\text{O}_3(2\text{mol}\%)$ and $\text{Dy}_2\text{O}_3(1\text{mol}\%)$

From the comparison, it is observed that there are two crystalline phases exist in the powder samples. There are a shift occur between the IR and Raman spectra, due to the difference of basic interaction with the molecule. IR bands arise from a change in the dipole moment of a molecule while Raman bands arise from a change in the polarizability.

CONCLUSION

The samples of $x\text{MgO}\text{-}(30\text{-}x)\text{CaO}\text{-}70\text{TeO}_2$ with $0 \leq x \leq 30$ mol%, doped with $\text{Eu}^{2+}(2\text{mol}\%)$ and $\text{Dy}^{3+}(1\text{mol}\%)$ have been prepared using solid state reaction method.

The structural studies of the samples have been investigated using X-Ray Diffraction, Infrared and Raman Spectroscopy. X-Ray diffraction pattern shows that there are two main phases exist in the sample which is MgTe_2O_5 and CaTe_2O_5 phase. Raman and Infrared spectroscopy also confirm the existence of the phases indicated from the two close peaks observed in the spectrum. The vibrations of the samples are identical with the $\alpha\text{-TeO}_2$ vibration with a shift about $40\text{-}50\text{cm}^{-1}$ to the higher frequency. As the modifiers, MgO and CaO are added to the tellurite based, the TeO_4 coordination transform from the structure of $\alpha\text{-TeO}_2$ to $\beta\text{-TeO}_2$ structure. The comparison between Raman and Infrared spectra illustrate that the Raman spectra is more functional and informative as its peaks is well-defined rather than more broad peak in Infrared spectra.

ACKNOWLEDGEMENT

We would like to acknowledge the financial supports from Ministry of Science Technology and Inovation (MOSTI) under research grant Project Number: 03-01-06-SF0053, and the authors thank Ibnu Sina Institute, Department of Chemistry, Faculty of Science UTM and Faculty of Mechanical UTM for providing the Raman, FT-IR spectroscopies and XRD measurement facilities.

REFERENCES

- [1]. Luo, X., W. Cao, and Z. Xiao. *Journal of Alloys and Compounds*, (2006). **416**(1-2): p. 250-255.
- [2]. Kumar, K., S.B. Rai, and D.K. Rai. (2007). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **66**(4-5): p. 1052-1057.
- [3]. C. Duverger, M.B., S. Turrell. (1997). *Journal of Non-Crystalline Solids*, **220**: p. 169-177.
- [4]. M.A.P Silva, et al.. (2001). *Journal of Physics and Chemistry of Solids*, **62**: p. 1055-1060.
- [5]. Sang-Do Han, et al.. (2008). *Journal of Luminescence*, **128**: p. 301-305.
- [6]. Noguera, O., et al.. (2003). *Journal of Non-Crystalline Solids*, **330**(1-3): p. 50-60.
- [7]. Takao Sekiya, N.M., Atsushi Ohtsuka, Mamoru Tonokawa. (1992). *Journal of Non-Crystalline Solids*, **144**: p. 128-144.
- [8]. El-Mallawany, R.A.H.. (2002), Menofia, Egypt: University of Menofia.