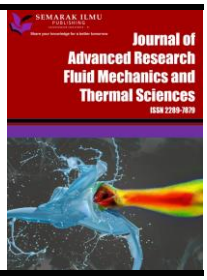
SEMARAK ILMU PUBLISHING

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage:
https://semarakilmu.com.my/journals/index.php/fluid_mechanics_thermal_sciences/index
ISSN: 2289-7879



Synthesisation of Photo-Mechanoluminescence Crystal of Europium Dibenzoylmethide Triethylamine (EuD_4TEA) with Different Solvent

Ng Kim Seng[1], Mohd Khairul Ahmad[1,*], Noor Kamalia Abd Hamed[1], Faridah Abu Bakar[2], Mohamad Hafiz Mamat[3], Suriani Abu Bakar[4], Azmi Mohamed[4], Masaru Shimomura[5]

[1] Microelectronics and Nanotechnology - Shamsuddin Research Centre (MiNT-SRC), Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat, Johor, Malaysia
[2] Faculty of Applied Sciences and Technology, Pagoh Campus, Universiti Tun Hussein Onn Malaysia, 84600 Muar, Johor, Malaysia
[3] Nano-Electronic Centre, Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[4] Nanotechnology Research Centre, Department of Physic, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjung Malim, Perak, Malaysia
[5] Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University, 432-8011Hamamatsu, Shizuoka, Japan

ARTICLE INFO

Article history:
Received 10 October 2023
Received in revised form 5 March 2024
Accepted 14 March 2024
Available online 30 March 2024

Keywords:
Photoluminescence;
Mechanoluminescece; EuD_4TEA

ABSTRACT

EuD_4TEA crystals have a few fascinating properties, such as photoluminescence and mechanoluminescence. Both phenomena occur when external excitation is performed on EuD_4TEA crystals. Photoluminescence is excited by external light radiation, whereas mechanoluminescence is stimulated by an external mechanical force applied to it. EuD_4TEA has easily been prepared only by standard crystallisation using dibenzoylmethane, europium nitrate hexahydrate, and triethylamine. This research mainly focused on the solvent for the synthesis of EuD_4TEA crystals. The solvents used were ethanol and acetone. Acetone has the main credit for producing much higher-quality EuD_4TEA crystals in certain aspects. Acetone-based end products are larger and have higher light emission under excitation.

1. Introduction

Luminescence is defined as the emission of cold light caused by any form of excitation source for certain materials and is in contrast to the light emitted from incandescent bodies, such as the burning of coal or wood [1]. Luminescence is one of the primary research methods and characterisation techniques in studies of semiconductor materials [2,3]. Besides providing information about crystalline quality, it also identifies and quantifies defects and impurities in semiconductors [4]. The excitation sources can be either stress that is applied to crystals, subatomic motions, electrical energy, or chemical reactions.

Photoluminescence, an optical radiation system that emits as a result of being excited by light irradiation [5], has attracted a lot of attention for many years [4]. PL can play a role in tackling defects

* *Corresponding author.*
E-mail address: akhairul@uthm.edu.my

https://doi.org/10.37934/arfmts.115.2.233241

in semiconductors because of their high photoluminescence quantum yield (PLQY), narrow and tuneable PL covering a broad visible spectral range (400−700 nm), and high stability towards moisture and heat, among others [4,5].

Mechanoluminescence (ML) is the phenomenon of mechanical-induced luminescence in which the materials absorb the energy from the actions, and the energy is re-emitted in the form of visible light [8]. ML can be categorized as Plastico-Mechanoluminescence (PML), Elastico-Mechanoluminescence (EML) [9,10] and Fracto-Mechanoluminescence (FML) [11,12] in a narrower sense. Elastic deformation induces luminescence without damage to samples, which is termed EML [9], where FML and PML are the luminescence induced by the fracture of solids and plastic deformation respectively [5-7]. So, ML materials can be used to detect mechanical strain or stress and are extensively employed for the potential applications of stress sensing of structural components and active crack monitoring due to their properties of converting mechanical energy into visible light [5-7,15].

According to Chandra, B.P., the PL and ML phenomenon is present in between about one-fourth and one-third of all organic solids and in half of all inorganic solids [16], which comprise both crystalline and non-crystalline materials [11,13]. Among the PL and ML solids, there are six types of solids, consisting of composite [4,11-12], crystalline, amorphous, tribo-mechanoluminophors, ceramic, and polymeric [8]. ML has been reported to be induced by either deformation plastically or elastically and fracture of the solid materials, whereas PL is induced by excitation irradiation. Nearly half of all inorganic and organic solids [6,13] have been discovered to exhibit ML phenomena during solid material fracture, whereas only a few solids exhibit ML phenomena during plastic and elastic deformation [9].

There were a number of mechanoluminescent solid-state compounds with high photoluminescent quantum yields. According to the findings of Bourhill *et al.,* research, there are a large number of organic and inorganic substances [19]. It was discovered that among all of these compounds, the following materials have nearly optimal solid-state photoluminescent quantum yields: Europium tetrakis (dibenzoylmethide) triethylammonium (EuD4TEA), Europium tris (2-thenoyltrifluoroacetone) solid-state compound – phenanthroline, Tris (1,3-di-terl-butyl-β-propanedione) terbium-p-dimethylaminopyridine and Mn: ZnS with the quantum yields reported to be 0.75, 0.85, 0.71, and 1.00, respectively [19]. Among all solid-state compounds reported for photoluminescence in earlier studies, the highest. Except for Mn:ZnS, the reported compounds with better quantum yield were made of inorganic components [9,12].

Hurt *et al.,* discovered EuD_4TEA [20], commonly known as Europium tetrakis, for the first time. From the study [21], EuD_4TEA is an organic material that reported the ML phenomenon that can be detected during daylight [22]. Hurt *et al.,* synthesised europium tetrakis dibenzoylmethide triethylammonium (EuD_4TEA) in 1966. The ML spectrum obtained in Hurt *et al.*'s study on EuD_4TEA is red-orange. $EuD_4TstimEA$ with the optical properties of triboluminescence (TL) [12] was visible in daylight under room conditions. EuD_4TEA's red-orange ML spectrum originates from the properties of Eu(III) fluorescence, which developed from the transition of $^5D_0/^7F_2$ (613 nm) with a decay duration of 0.5 ms [21].

In this paper, solvents are one of the factors that enhance the production of EuD_4TEA. The synthesis of EuD_4TEA needs organic solvents due to the organic materials used to synthesise EuD4TEA. Ethanol and acetone are the solvents that are used for synthesis of EuD_4TEA.

2. Methodology

2.1 Synthesis of Europium Dibenzoylmethide Triethylamine

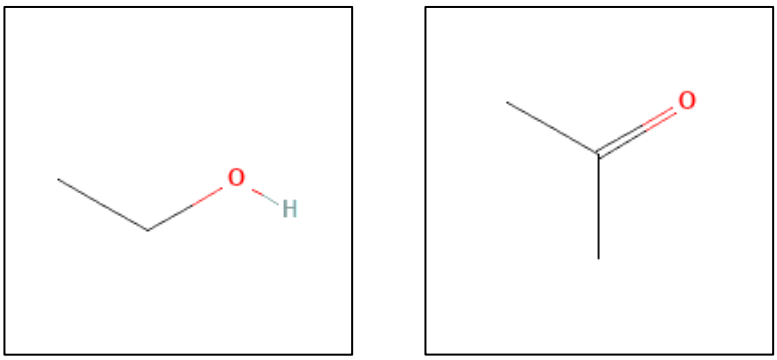
The mechanoluminescent powder, EuD_4TEA, is used to induce the FML through rubbing motion on the composites. Firstly, 80 ml of the HmbG chemicals brand ethanol was heated to 70 °C followed by 0.8 mmol of 1,3-diphenyl-1,3-propanedione which is also known as dibenzoylmethane (DBM) from Merck added to the hot solution mixture and dissolved for the synthesis of EuD4TEA. 0.3 mmol of europium nitrate hexahydrate from PubChem was added to the mixture after the solution was completely dissolved. N, N-diethylethanamine or triethylamine (TEA) R&M chemicals were added, and the solution was maintained at 70 °C for 20 minutes. The solution is then tightly capped and placed in a thermos overnight. For optimal crystal formation, regulating slow cooling in the thermos was important. The solution vessel was then taken out for solution removal after the cooling process. Europium dibenzoylmethide triethylammonium, EuD_4TEA compound crystals were extracted by filtration after excluding the leftover solution. Sample 1 was obtained.

Sample 2 was prepared using the same process and material. The only difference was that the solvent was changed into 30 ml of acetone. The solvent temperature was heated to 60 °C, which is the boiling point of acetone. Both of these experiments were run using carbonyl-containing solvents. Later, surface morphology on EuD4TEA samples was examined by Jeol FESEM and EDS. And lastly, record the colour intensity of mechanoluminescence and photoluminescence properties by using OES spectroscopy with the assistance of a self-made device.

3. Results

The results were focused on the EuD_4TEA crystal synthesised by using dibenzoylmethane, europium nitrate hexahydrate, and lastly, triethylamine. The only difference is the usage of solvents, which were ethanol (C_2H_5OH) and acetone ($(CH_3)_2CO$). The samples were divided into two categories: samples crystallised in ethanol and samples crystallised in acetone.

Figure 1 shows the 2D structure of the solvent's ethanol and acetone. The chemical formulae for ethanol are C_2H_5OH and $(CH_3)_2CO$ for acetone, respectively. By comparing both of the solvents, the oxygen atom in ethanol was bonded with one hydrogen atom (-OH), while acetone possessed a double bond with the carbon atom (=O). The stability of a chemical bond depends on the energy required to break the bond and the energy released when the bond forms. In the context of double bonding, which comprises double covalent bonds, two atoms share two pairs of electrons. When two atoms share two pairs of electrons, a double bond is produced. A double line (=) between the atoms represents them [23]. A double bond's atoms generally have accessible orbitals to accept the extra electrons necessary for the bond. A double bond's stability is not fundamentally lower than that of a single bond. In reality, double bonds are stronger than single bonds in general because they entail greater electron sharing and are shorter in length, resulting in larger attractive forces between the nuclei and the shared electrons. However, in terms of reactivity, double bonds have the potential to be more reactive than single bonds. Because there are numerous electrons in the shared orbital, the bond is more vulnerable to assault by other atoms or molecules, resulting in chemical reactions. In some chemical conditions, this reactivity might make the double bond less stable [24].

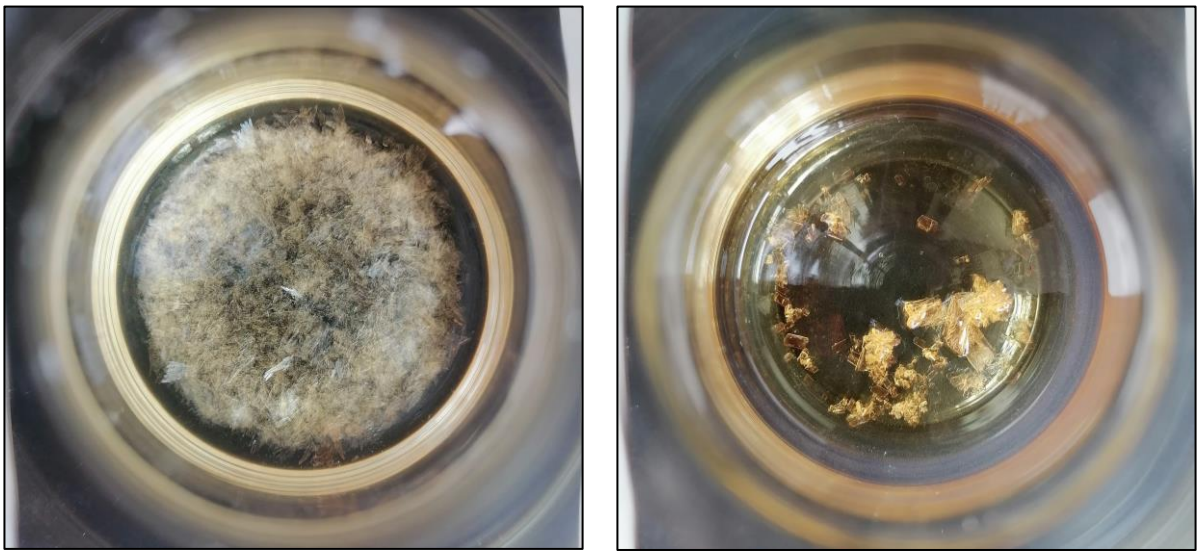


Ethanol Acetone

Fig. 1. 2D structure for ethanol and acetone

3.1 Actual View on EuD_4TEA Crystals Before Filter

EuD_4TEA crystals were formed using the crystallisation method at low dropping rate temperatures. Figure 2 shows the photo taken before filtration from a conical flask. Sample (a) was synthesised using the base chemicals and ethanol. While sample (b) was composed using acetone as the base solvent. The samples were collected from the precursor after slow crystallisation for 24 hours. Based on Figure 2, crystals from sample (a) were flaky, whereas crystals from sample (b) were solid. From the size of the naked eye, the size of crystals has a big difference. The crystals produced by using ethanol were a lot smaller and flaky, around mm in size. Acetone product end crystals were a lot bigger than the average size, which can reach several cm in size. It can be said that acetone could have the ability to gather the crystal into a stronger form. The double bond from acetone might be the main reason that it gathered more EuD_4TEA crystals compared to ethanol.



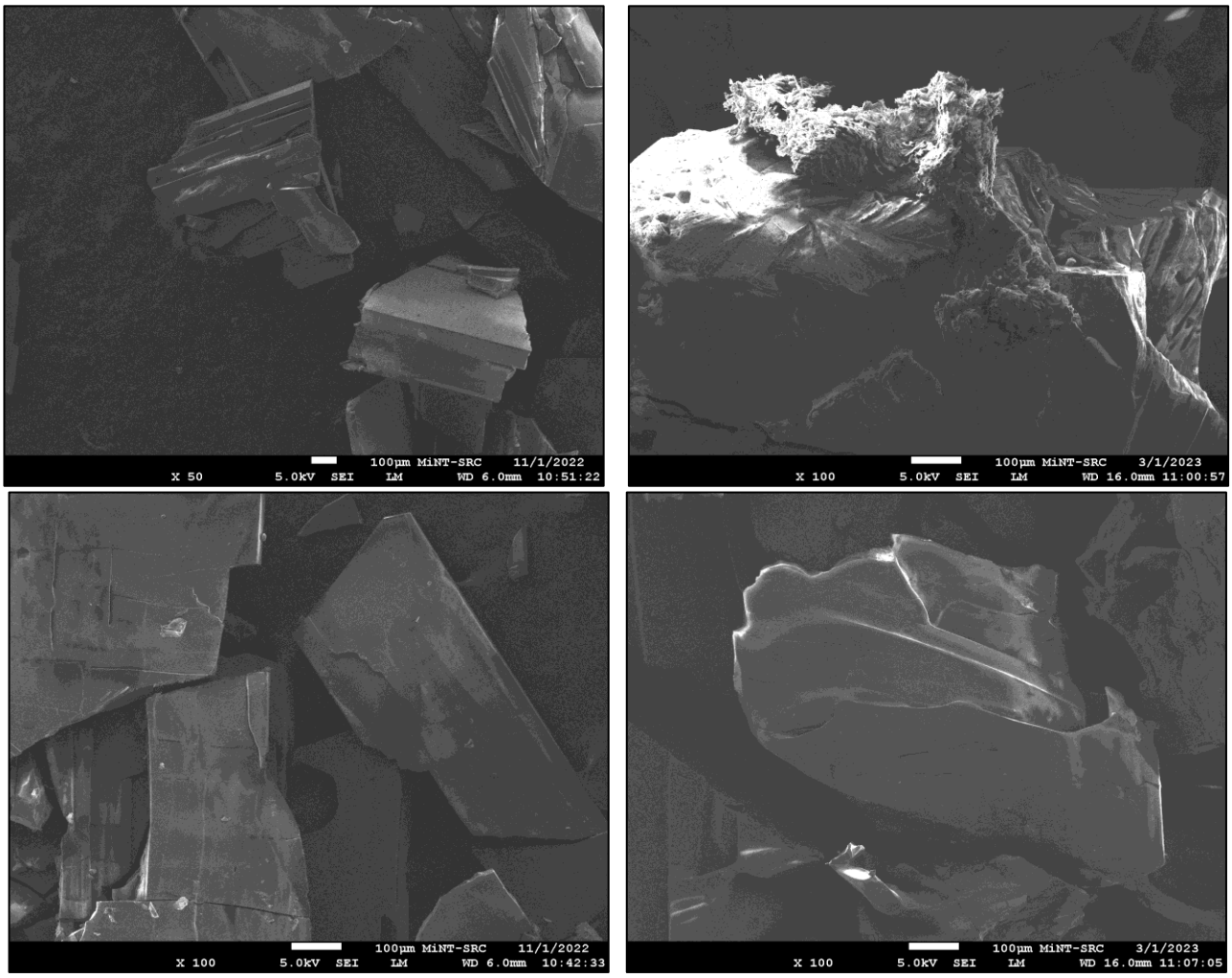
(a) (b)

Fig. 2. Actual sample photo capture by camera before filtration with preparation in the solvent of (a) ethanol and (b) acetone

3.2 Surface Morphology on EuD_4TEA Crystals

EuD4TEA crystals were successfully formed by using ethanol and acetone as crystallisation solvents. Surface morphology on EuD_4TEA crystals was taken on sample (a) and sample (b) in FESEM, respectively. Figure 3 shows the FESEM images on sample (a) and sample (b). As mentioned earlier,

sample (a) was synthesised using ethanol as solvent, whereas sample (b) was synthesised using acetone as solvent. Crystal size differences can be seen by comparing the four images below. Sample (b) was a lot larger compared to sample (a). This is also one of the proofs that showed acetone was capable of attracting more EuD_4TEA compared to ethanol.



(a) (b)

Fig. 3. Surface morphology image taken from FESEM with the samples crystallised in solvent (a) ethanol and (b) acetone and different locations on samples with the magnification of 100 µm

3.3 EDS Results on EuD_4TEA Crystals

Energy Dispersive Spectroscopy (EDS) is a technique used to analyse the elemental composition of materials. It works by detecting characteristic X-rays emitted by elements in the material being analysed. Table 1 shows the weight percentage and atomic percentage for EuD_4TEA synthesised by using ethanol and acetone obtained by EDS. As mentioned before, sample (a) was synthesised in ethanol, and sample (b) was synthesised in acetone. As indicated in the table below, the weight percentage from sample (b) is much higher than sample (a), which is almost three times higher than sample (a). The hypothesis that the solvent acetone manages to gather Eu atoms was much more verified.

Table 1
Weight percentage and atomic percentage for EuD_4TEA synthesised by using ethanol and acetone obtained by EDS

Solvent	Ethanol (a)		Acetone (b)	
Element	Weight %	Atomic %	Weight %	Atomic %
Carbon (C)	76.36	82.79	67.69	77.39
Oxygen (O)	20.85	16.97	25.65	22. 01
Europium (Eu)	2.79	0.24	6.66	0.60
Totals	100	100	100	100

3.4 Colour Emission from EuD_4TEA Crystals

3.4.1 Colour emission when UV light applied on EuD_4TEA crystals

Figure 4 shows the graph obtained from Ocean OES, a spectrometer that is used for recording the colour of EuD_4TEA crystals with the support of a self-made device, in the condition of ultraviolet (UV) light radiation. The wavelength shown on the graph, from 450 nm to 700 nm, was the wavelength of the visible light spectrum. The data obtained showed that a high peak was expressed at 610 nm in wavelength. The wavelength of 610 nm in the visible light spectrum is between orange and red. Therefore, this concludes that the light emission from the EuD_4TEA is orange-red. From the graph again, the light intensity peaks from EuD_4TEA crystals emission were 6699 and 9082 from the crystals using the solvents ethanol and acetone. The light emission given out by the crystals synthesised by using acetone was much higher than the one synthesised by using ethanol. The main reason for the peak presentation difference was that the percentage Eu atom attraction in the sample synthesised by using acetone was much higher than in ethanol-based solvent crystallisation of EuD_4TEA crystals.

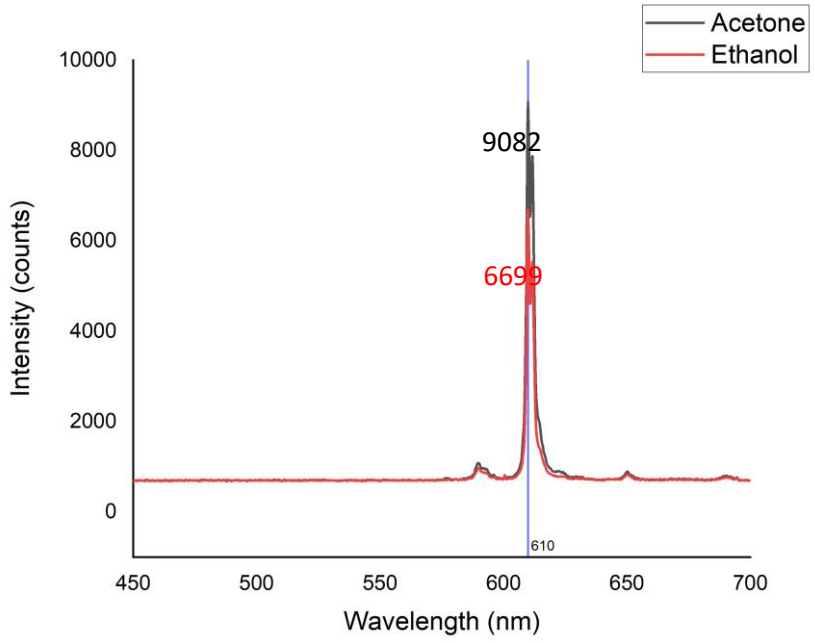


Fig. 4. Wavelength vs Intensity graph for crystal synthesised in ethanol and acetone when external excitation light irradiated on the samples

3.4.2 Colour emission when force applied on EuD_4TEA crystals

Figure 5 shows the graph obtained from Ocean OES, a spectrometer that is used for recording the colour of EuD_4TEA crystals with the support of a self-made device, in the condition of grinding the crystals for performing mechanoluminescence light emission. The visible light spectrum's wavelength ranged from 450 nm to 700 nm, as seen on the graph. The results demonstrated that a strong peak was expressed at 610 nm in wavelength. Between the orange and red colours of the visible light spectrum is the wavelength 610 nm. Therefore, this leads to the conclusion that the light emitted by the EuD_4TEA is orange-red in hue. Relative to the graph, the light intensity peaks from the emission from EuD_4TEA crystals using ethanol and acetone were 965 and 1080, respectively. The acetone-produced crystals had significantly higher light emissions than the ethanol-produced crystals. The percentage of Eu atom attraction in the sample synthesised using acetone was significantly larger than that of ethanol-based solvent crystallisation EuD_4TEA crystals, which was the primary cause of the peaks' differing presentations.

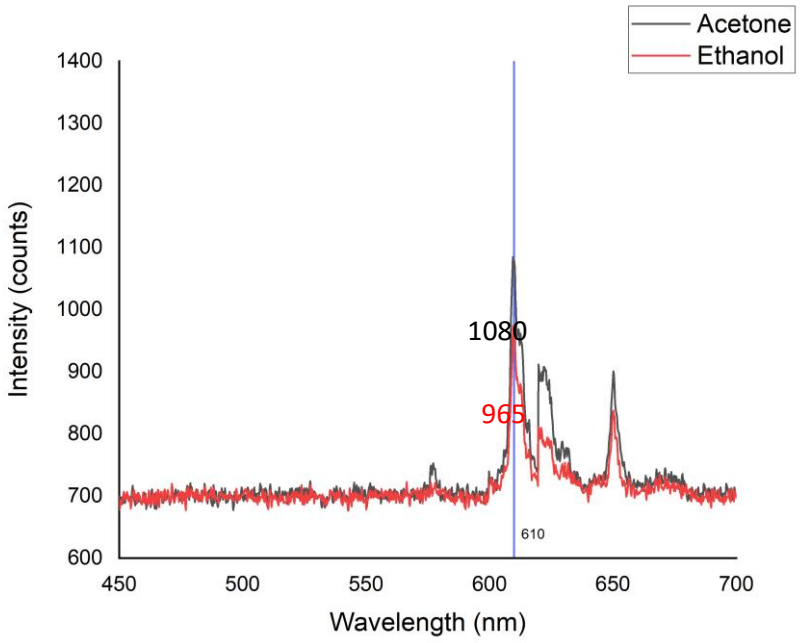


Fig. 5. Wavelength vs Intensity graph for crystal synthesised in ethanol and acetone when the external force applied to the samples

4. Conclusions

As an overall outcome, crystals obtained by using ethanol and acetone as solvents have a high difference from synthesised EuD_4TEA crystals. In comparison, acetone produced EuD_4TEA in multiple aspects, which was much higher as compared to the crystals synthesised by using ethanol as a solvent. In visual and FESEM images, EuD_4TEA formed in acetone, the size was much bigger and more focused. From EDS statistics, Eu atom concentration was higher in acetone solvent synthesis. Light emission from the crystals by either photoexcitation or force excitation was also much higher compared to the ethanol solvent product. These concluded that EuD_4TEA synthesised by using acetone has a higher ability in comparison with EuD4TEA synthesised by using ethanol as a solvent in several aspects.

Acknowledgement

The authors would like to acknowledge Universiti Tun Hussein Onn Malaysia (Geran GRA vot H023) and the Ministry of Education Malaysia for financially supporting this work.

References

[1] Murthy, K. V. R., and Hardev Singh Virk. "Luminescence phenomena: an introduction." *Defect and diffusion fórum* 347 (2014): 1-34. https://doi.org/10.4028/www.scientific.net/DDF.347.1

[2] Xingwang, L. I. U., Jiadong Jiang, Y. O. N. G. Shengli, G. U. O. Yuwei, Y. A. N. G. Kun, and W. A. N. G. Li. "Synthesis and fluorescence properties of Eu (III), Tb (III) and Sm (III) with β-diketone and 2, 2′-bipyridine." *Journal of rare earths* 30, no. 6 (2012): 520-523. https://doi.org/10.1016/S1002-0721(12)60083-0

[3] Ho, Quoc Duy, Thomas Frauenheim, and Peter Deak. "Origin of photoluminescence in ss-Ga2O3." *PHYSICAL REVIEW B* 97, no. 11 (2018). https://doi.org/10.1103/PhysRevB.97.115163

[4] Reshchikov, Michael A. "Measurement and analysis of photoluminescence in GaN." *Journal of Applied Physics* 129, no. 12 (2021). https://doi.org/10.1063/5.0041608

[5] Bebb, H. Barry, and E. W. Williams. "Photoluminescence I: theory." In *Semiconductors and semimetals*, vol. 8, pp. 181-320. Elsevier, 1972. https://doi.org/10.1016/S0080-8784(08)62345-5

[6] Protesescu, Loredana, Sergii Yakunin, Maryna I. Bodnarchuk, Franziska Krieg, Riccarda Caputo, Christopher H. Hendon, Ruo Xi Yang, Aron Walsh, and Maksym V. Kovalenko. "Nanocrystals of cesium lead halide perovskites (CsPbX3, X= Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut." *Nano letters* 15, no. 6 (2015): 3692-3696. https://doi.org/10.1021/nl5048779

[7] Dutta, Anirban, Rakesh Kumar Behera, Sumit Kumar Dutta, Samrat Das Adhikari, and Narayan Pradhan. "Annealing CsPbX3 (X= Cl and Br) perovskite nanocrystals at high reaction temperatures: phase change and its prevention." *The journal of physical chemistry letters* 9, no. 22 (2018): 6599-6604. https://doi.org/10.1021/acs.jpclett.8b02825

[8] Feng, Ang, and Philippe F. Smet. "A review of mechanoluminescence in inorganic solids: compounds, mechanisms, models and applications." *Materials* 11, no. 4 (2018): 484. https://doi.org/10.3390/ma11040484

[9] Chandra, V. K., and B. P. Chandra. "Suitable materials for elastico mechanoluminescence-based stress sensors." *Optical Materials* 34, no. 1 (2011): 194-200. https://doi.org/10.1016/j.optmat.2011.08.003

[10] Chandra, B. P., C. N. Xu, H. Yamada, and X. G. Zheng. "Luminescence induced by elastic deformation of ZnS: Mn nanoparticles." *Journal of Luminescence* 130, no. 3 (2010): 442-450. https://doi.org/10.1016/j.jlumin.2009.10.010

[11] Chandra, B. P., V. K. Chandra, and Piyush Jha. "Modelling of fracto-mechanoluminescence damage sensor for structures." *Sensors and Actuators A: Physical* 230 (2015): 83-93. https://doi.org/10.1016/j.sna.2015.04.005

[12] Chandra, B. P., V. K. Chandra, and Piyush Jha. "Models for intrinsic and extrinsic fracto-mechanoluminescence of solids." *Journal of Luminescence* 135 (2013): 139-153. https://doi.org/10.1016/j.jlumin.2012.10.009

[13] Agyeman, O., C. N. Xu, M. Suzuki, and X. G. Zheng. "Upgrading the triboluminescence of ZnS: Mn film by optimization of sputtering and thermal annealing conditions." *Journal of materials research* 17, no. 5 (2002): 959-963. https://doi.org/10.1557/JMR.2002.0143

[14] Aich, Nirupam, Aditya Appalla, Navid B. Saleh, and Paul Ziehl. "Triboluminescence for distributed damage assessment in cement-based materials." *Journal of intelligent material systems and structures* 24, no. 14 (2013): 1714-1721. https://doi.org/10.1177/1045389X13484100

[15] Ilatovskii, Daniil A., Nikita A. Tyutkov, Vladimir V. Vinogradov, and Alexandr V. Vinogradov. "Stimuli-responsive mechanoluminescence in different matrices." *ACS omega* 3, no. 12 (2018): 18803-18810. https://doi.org/10.1021/acsomega.8b02696

[16] Timilsina, Suman, Ji Sik Kim, Jaehwan Kim, and Gi-Woo Kim. "Review of state-of-the-art sensor applications using mechanoluminescence microparticles." *International Journal of Precision Engineering and Manufacturing* 17 (2016): 1237-1247. https://doi.org/10.1007/s12541-016-0149-y

[17] Chandra, B. P., and J. I. Zink. "Triboluminescence and the dynamics of crystal fracture." *Physical Review B* 21, no. 2 (1980): 816. https://doi.org/10.1103/PhysRevB.21.816

[18] Dickens, Tarik J., David Olawale, Garrett Sullivan, Jolie Breaux, Okenwa OI Okoli, and Ben Wang. "Toward triboluminescent sensor realization for SHM: statistical modeling of triboluminescent composites." In *Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2011*, vol. 7981, pp. 172-184. SPIE, 2011. https://doi.org/10.1117/12.880536

[19] Sage, Ian, and Grant Bourhill. "Triboluminescent materials for structural damage monitoring© British Crown Copyright 2000/DERA. Published with the permission of the Controller of Her Britannic Majesty's Stationery Office." *Journal of Materials Chemistry* 11, no. 2 (2001): 231-245. https://doi.org/10.1039/b007029g

[20] Fontenot, Ross S., William A. Hollerman, Kamala N. Bhat, Stephen W. Allison, and Mohan D. Aggarwal. "Luminescent properties of lanthanide dibenzoylmethide triethylammonium compounds." *Journal of Theoretical and Applied Physics* 7 (2013): 1-10. https://doi.org/10.1186/2251-7235-7-30
[21] Fontenot, R. S., K. N. Bhat, W. A. Hollerman, M. D. Aggarwal, and K. M. Nguyen. "Comparison of the triboluminescent yield and decay time for europium dibenzoylmethide triethylammonium synthesized using different solvents." *CrystEngComm* 14, no. 4 (2012): 1382-1386. https://doi.org/10.1039/C2CE06277A
[22] Wang, Jian, Jingru Wang, Yang Li, Min Jiang, Lingwen Zhang, and Pengyan Wu. "A europium (III)-based metal–organic framework as a naked-eye and fast response luminescence sensor for acetone and ferric iron." *New Journal of Chemistry* 40, no. 10 (2016): 8600-8606. https://doi.org/10.1039/C6NJ02163H
[23] Clayden, Jonathan, Nick Greeves, and Stuart Warren. *Organic chemistry*. Oxford University Press, USA, 2012. https://doi.org/10.1093/hesc/9780199270293.001.0001
[24] Tojo, Gabriel, and Marcos Fernández. "Selective Oxidations of Secondary Alcohols in Presence of Primary Alcohols." *Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice* (2006): 339-349.