Temporal and remote tuning of piezophotonic effect-induced luminescence and color gamut via modulating magnetic field

Man-Chung Wong, Li Chen, Gongxun Bai, *Long-Biao Huang, Jianhua Hao**

M.-C. Wong, L. Chen, Dr. G. X. Bai, Dr. L. B. Huang, Prof. J. H. Hao

Department of Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong, P. R. China

The Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen 518057, P. R. China

Email: jh.hao@polyu.edu.hk

Keywords: piezophotonic effect, metal-ion doped phosphor, mechanoluminescence，magnetic sensor, RGB color

Luminescence materials have been extensively investigated because of their wide range of applications in display, solid state lighting, sensor, memory and bioimaging.[1-8] In these applications, it is highly desirable to achieve tunable luminescence in terms of luminescent intensity and wavelength (e.g, color in visible spectrum (VIS) region). Numerous studies had focused on tuning the properties of luminescence by changing phosphor's chemical compositions, crystal structure, phase, crystal size, and surface groups.[9-12] However, all those approaches are essentially an

ex-situ and irreversible process. Compared to modifying luminescent intensity, it is rare to modify and control the emitting wavelength of luminescence or color gamut in VIS of a phosphor with fixed composition by *in-situ* and dynamic approaches. The development of such a multi-color emitting material may lead to a broad spectrum of novel applications. [1-3, 6, 13-20] Recently, Liu's group realized a temporal full-color tuning through non-steady state upconversion photoluminescence via pulse width modulation of laser interaction with the samples.[21] They demonstrate dynamical fine-tuning emission of core-shell multiphase nanocrystal by controlling the optical excitation dynamics. Up to now, there has been very limited work in which both luminescence intensity and color gamut can be remotely modified, particularly in a single-phase phosphor. In our previous study, we presented a magnetic-induced luminescence (MIL) that light emission can be generated by low magnetic field excitation via strain-medicated coupling with piezophotonic phosphor (piezophosphor).[22, 23] The MIL intensity can be modulated by the magnitude and excitation frequency of magnetic stimuli in a reversible and dynamical manner.

Xu et al. demonstrated pioneering works that strong visible light can be emitted from the mechanoluminescent samples upon stressing.[20] It is noticeable that the significant development of piezophosphors, such as metal ion-doped ZnS have led to the implementation of a platform for achieving multicolor emissions.[7, 19, 24-28] The

piezophosphor has a crystal structure which can create a piezoelectric potential (piezopotential) within the crystal lattice under an external stress.[29] The co-doped multiple metal ions in the piezophosphor feature ladder-like arranged energy levels, producing a set of emission wavelengths. In this work, we present a strategy based on the modulation of magnetic excitation frequency, offering exquisite control over the emission color of metal ion-doped ZnS piezophosphor. The experimental results reported here have provided an evidence of the temporal tuning of emitting wavelength covering three primary colors of red, green, blue (RGB) and white light under the remote modulation of low magnetic field strength. Therefore, our results will not only provide a new insight into tuning luminescence but also expand the applications of light-emitting materials and magnetic sensor.

In our design, polydimethylsiloxane (PDMS) is chosen as a matrix for packaging a flexible laminated composite, and also functions as delivering the generated strain. The composite was fabricated with integration of one layer embedding soft ferromagnetic particles into PDMS, generating magnetostrictive strain under magnetic field. This magnetostrictive strain then triggers the adjacent PDMS layer embedded with various metal ions (e.g., Al, Cu)-doped ZnS piezophosphor to produce light emission, schematically illustrated in **Figure 1a**. The ratio of phosphor and PDMS was optimized at 7:3. Such an optimized value was obtained from numerous

experiment results, which is a compromise between elastic module and luminescence. During the measurement process, when the intensity of magnetic field varies in the range of 2.0~3.5 kOe, the strain and stress from the composite increase monotonically with the applied magnetic field.[22] Since the magnetic elastomer shows a very low conceive field (~9 Oe) under the applied magnetic field strength (2~3.5 kOe), the strain rate should increase with the modulating frequency. The luminescent spectra of the piezophosphor were measured under different modulation frequency (*f*) of magnetic field excitation (**Figure 1b)**. When the excitation frequencies are set at no higher than 50 Hz, the composite produces a dominant green emission band peaked at 503 nm. Intriguingly, when increasing modulation frequency of magnetic field with fixed strength, the emission shows a trend of an intensity increase in the shoulder peak at a range from 460 to 472 nm of blue emission band, while green emission the intensity at 503 nm exhibits a gradual suppression simultaneously. Remarkably, as the modulation frequency further increases, the suppression of emission intensity at 503 nm continues, while the blue emission intensity continuously increases until the main spectrum peaked at around 460 nm ~ 472 nm when f = 470 Hz. Therefore, we can achieve a dynamic and *in-situ* control over the piezophotonic emission wavelength simply by adjusting the modulation frequency of magnetic field excitation. Obviously, such a temporal tuning of emission wavelength differs greatly from conventional

methods where *ex-situ* ways (e.g., changes in chemical compositions of hosts and/or metal ion dopants of phosphors) are routinely employed for tuning emission wavelength.[24] Apart from the change in emitting wavelength, the luminescent intensity is varied with the modulation frequency. **Figure 1c** shows the integrated intensities of overall emissions as a function of *f* when the strength of applied magnetic field was fixed. As seen in the result, the integrated emission intensity increases with increment of excitation frequency. As the excitation frequency increases up to around 300 Hz, the emission intensity reaches its maximum value. The intensity of the luminescence declines afterwards with further *f* increment. We further visualize the frequency dependent emission color and intensity observed from our MIL composite. **Figure 1d** illustrates the photographs presenting the emission color varied from green to blue and intensity variation when *f* was modulated from 50 to 470 Hz, according with the measured data as shown in Fig. 1c, respectively. It is known that color coordinates (x, y) are a measure of color properties in chromaticity diagram. As shown in **Table 1**, it is evident that the emissions in terms of color coordinates, peak wavelength and luminance of the samples can be effectively tuned by modulating the frequency of magnetic field excitation.

In order to study the blue and green components of the emissions, we further characterized the ZnS: Al, Cu emissions at the two characteristic wavelengths (472

nm and 503 nm) selected in this work as shown in **Figure 2**. First, the two characteristic MIL emissions were measured under a sinusoidal modulated magnetic field with a constant magnetic strength of root-mean-square (H_{rms}). The single wavelength transient characteristic of the switchable MIL with different modulated frequencies is shown in **Figure 2a.** When the magnetic field is switched on (i.e., H_{rms}= 3 kOe), the total emission consisted of the emissions at the two selected wavelengths, namely blue component (472 nm) and green component (503 nm), rises until its saturated value, and then begins to fall towards zero as the magnetic field is subsequently switched off (i.e., H_{rms}= 0 Oe). As indicated in Figure 1, the green emission is more intense at low modulation frequency while the emission is peaked in blue spectrum region is gradually enhanced under high modulation frequency. **Figure 2b** shows the rise times of blue/green emission as a function of excitation modulation frequency, where the rise time is defined here as the time duration for the emission intensity reaches its saturated values in response to the magnetic field switching. The result suggests that the rise time for both blue and green components becomes longer with the accretion of excitation frequency. Apart from the changes in rise time with the modulation frequency, the relative intensity of blue and green emissions can be adjusted by the modulation frequency. Since MIL intensity can be solely adjusted by excitation frequency, therefore, we study the relative intensities of the two

characteristic wavelengths to further investigate the excitation frequency depended peak shift. **Figure 2c** shows the relative emission intensities and emission ratio at the two characteristic wavelengths as a function of excitation frequency. The measured result is consistent with Fig. 1(b) that blue emission is enhanced with an increase in the frequency of excitation. Accordingly, the ratio of blue/green emission intensity also increases with the increment of excitation frequency. With this interesting result, one may expect that the emission spectrum and color can be modulated simply by alternating the frequency of magnetic field in an *in-situ* and reversible way. In addition to the frequency dependence of emission, the emission intensity is also affected by H_{rms} under different modulation frequency. Here the H_{rms} was varied by adjusting the separation between the magnet and the measured sample. **Figure 2d** shows the luminescence intensity at the two wavelengths versus the square of H_{rms} applied to the sample. Apparently, the emission intensity of both blue and green components is linearly enhanced when increasing H_{rms}^2, which is similar to our previous observation on the sample applied with the magnetic field of low frequency ($f < 50$ Hz).[22] The results can be understood that an increase in H_{rms} may cause the enhancement in the magnitude of strain, leading to detrapping more charge carriers and hence intensifying electron-hole recombination and luminescence. It is noticeable that such a good linear relationship between the output and input signals as shown in

Fig. 2d is very helpful for sensing application. The obtained results have the potential for developing magnetic-luminescence sensors which are capable of detecting magnetic field with a wide range of modulation frequency. Additionally, there is no observable spectrum shift of MIL as magnetic field strength varies within our measurement range.

Figure 3 presents the proposed excitation temporal tuning mechanism of MIL from ZnS: Al, Cu piezophosphor. Generally, when specific metal ions (Al and Cu) are doped into host lattice of the piezophosphor (ZnS), non-equivalent substitutions take place, resulting in various kinds of defects. These defects generate several kinds of luminescent centers which can give rise to different color emission. Typically, sulfide vacancies (V_S) are attributed to the lattice mismatch in the host crystal, which can form shallow donor state below the conduction band (CB) by acquiring a free electron. In the meantime, Al^{3+} related defects Al_{Zn} create deeper donor levels under the CB which act as trapping centers for electrons, while the Cu^{+} related defects Cu_{Zn} carrying one negative charge act as the acceptor levels which can trap holes above the valence band (VB). These charge traps in different energy levels are bounded together by Coulomb interaction to form various luminescent centers in the form of donor-acceptor (D-A) pairs with discrete spatial intra-pair separation (r).[30] As shown in the left panel of **Figure 3**, $r_1 < r_2$ where r_1 and r_2 represent the spatial

intra-pair-separation r of V_s-Cu_{Zn} and Al_{Zn}-Cu_{Zn} pairs, respectively.[15] The relationship between the emission photon energy and the intra-pair separation can be expressed as [31]

$$E(r) = E_g - (E_A + E_D) + \frac{q^2}{4\pi\varepsilon_r r} \quad (1)$$

where E_g is the energy band gap, E_A and E_D represent the trap depth of acceptor and donor, respectively; q is the electron charge, and ε_r is the permittivity of phosphors.

In our experiment, when modulating magnetic field (H) is applied to the composites, the induced magnetostrictive strain (ε) will generate an inner piezoelectric potential in the ZnS crystals. According to our previous study, the magnetostrictive coefficient λ can be written as,[22]

$$\lambda = \frac{\partial \varepsilon}{\partial H} \quad (2)$$

This is a parameter of the strain change with magnetic field. This piezoelectric potential induces an increase of electrostatic energy of electron in a charge trap, which can be expressed as,[32]

$$\Delta E = \frac{1}{k}\left(\frac{\lambda q H d_0}{\varepsilon_r}\right)^2 \quad (3)$$

where d_0 is the local piezoelectric constant, k is the force constant of host lattice. Since piezophotonic emission is essentially a dynamic process, the relationship between the change rate of the electrostatic energy and the applied magnetic field excitation can be written as

$$\frac{\partial E}{\partial t} = \frac{2H\dot{H}}{k}\left(\frac{\lambda q d_0}{\varepsilon_r}\right)^2 \quad (4)$$

where $\dot{H} = \partial H / \partial t$ is the change rate of magnetic field, which is related to the strain change rate of the sample. When this induced strain sustains for a time *t*, the instantaneous trap depth $E_D^{'}$ of the charge trap would decreases to,[32]

$$E_D^{'} = E_D - \frac{2H\dot{H}}{k}\left(\frac{\lambda q d_0}{\varepsilon_r}\right)^2 t \quad (5)$$

From Eq. (1) and (5), it is conceivable that the binding energy of trapped electron decreases with increasing modulation frequency of magnetic excitation.

Hence, the phenomenon of tunable piezophotonic emission observed in Figure 1 can be interpreted as follows. When applying an alternating magnetic field to the composites, magnetostrictive strain induced piezopotential causes the band structure of ZnS to tilt and detrapping of electrons in the donor states takes place.[1, 15] At low modulation frequency of magnetic field (middle panel of Figure 3), mainly the deep charge traps Al_{Zn} sites are excited, leading to a green emission. As the frequency increases further (right panel of Figure 3), from Eq. 5, the trap depths of these donor states started to decrease. The shallower charge traps V_s therefore could be triggered and ionized even the magnitude of magnetic field remains constant, leading to an increase in the emission intensity at 472 nm. In addition, a small r of the V_s-Cu_{Zn} pair leads to a large overlapping of the pair's wavefunction, resulting a high e^--h^+

recombination rate. Meanwhile, the Al_{Zn}-Cu_{Zn} pairs with a larger r value will be saturated readily due to small overlapping of wavefunction under high excitation modulation frequency.[30, 33] Therefore, the green emission intensity saturates and declines as the excitation frequency increases, while blue emission will subsequently dominates in the luminescence spectrum, as shown in Figure 2c.

The *in-situ* color tunability by excitation frequency provides a convenient approach to implement full-color display. In addition, achieving real-time modulation of color temperature of white emission via reversible physical approach has been an attractive target for both fundamental research and numerous applications.[15, 25] As a proof of concept, we moved forward to combine the MIL composite with other fluorescence phosphors to achieve a real-time tunable white light and multicolor display. Through temporal control of the magnetic excitation, we can generate RGB display and white color with tunable color temperature (**Figure 4a**).

To construct the tunable white MIL emission, Ce doped $Y_3Al_5O_{12}$ (YAG: Ce) was chosen by considering it is an efficient yellow phosphor excited by blue color radiation. The corresponding yellow emission from YAG: Ce is able to complement the blue light which escapes through in order to produce a white light. By combining MIL composite with YAG: Ce fluorescence phosphor, we have achieved white emission with correlated color temperature (CCT) ranging from 3700 to 5700 K via

varying modulation frequency as shown in **Figure 4b**. The mixing YAG: Ce fluorescence phosphors with tunable piezophosphor produces white color possessing a wide range of specific color temperature. The modifying contributions of blue and yellow emissions thereby allow a reliable and continuous tuning of the emission color perceived by the naked eye, ranging from saturated yellow and warm-white to deep blue through cold-white lights. **Figure 4c** shows the change trends in CIE coordinates of the white emissions from the two composites samples with different ratio of YAG: Ce phosphor. These coordinates are close to the Planckian locus, and migrated in accordance to the mixing ratio of the composites and the temporal tuning. For example, in the composite with mixing ratio of 1:1 (ZnS: Al, Cu based composite: YAG:Ce), we observed a shift of CIE coordinate with increasing blue component under high frequency of magnetic field in a direction which was dictated by this weight ratio. As a result, the emission from the sample at f = 300 Hz occurs at the CIE (x, y) = (0.3352; 0.3354), which is approximately standard white point, with an efficiency η of about 0.0018 lm Oe^{-1} (η~light emission output/magnetic field input strength). Therefore, an appealing feature of these white emissions is that the emission color temperature of a fixed sample can be controlled in reversible and *in-situ* route simply by varying the temporal of magnetic excitation alone, providing ground for diverse application opportunities.

It is well known that RGB is essential to achieve a full-color display. To develop a tri-colored *in-situ* tunable MIL with simultaneous persistence luminescence, we studied on coupling the MIL sample with a highly efficient red-emitting phosphorescence phosphor of $(Ca_{1-x}Sr_x)S$: Eu. We explored the possibility via a patterned array of ZnS: Cu based MIL composite combined with this red phosphor. A sinusoidal magnetic field excitation was applied to trigger the composite. The $(Ca_{1-x}Sr_x)S$: Eu phosphorescence was employed to convert the green piezophotonic emission and displays a red colored logo of Hong Kong Polytechnic University (**Figure 4d**). In addition, by incorporating both $(Ca_{1-x}Sr_x)S$: Eu phosphor into two kinds of MIL composite (ZnS: Cu green, and ZnS: Al, Cu blue), we have been able to generate a RGB display capable of converting magnetic energy to luminescence with emission chromaticity modulated in reversible and dynamical manner via controlling the excitation frequency (**Figure 4e**). The RGB composite emission can be seen by the naked eyes.

Figure 4f shows the transient characteristic of the red emission from MIL composite incoroporated with $(Ca_{1-x}Sr_x)S$: Eu persistence phosphor. In this measurement, magnetic field with f = 250 Hz was initially switched on and retained at H_{rms} = 2.0 kOe for 1 min and subsequently switched off. The 640 nm emission rises almost instantaneously when the MIL excitation emission occurs and then begins to decay

exponentially when the magnetic field excitation ceases, resulting in a prolonged reddish persistence luminescence as expected. It is interesting to notice that this colour conversion not only broaden the color expression of MIL, but also prolonged the illumination of our composite after the stoppage of the excitation.

In summary, conventional tuning of the emitting wavelength and color from the materials are traditionally achieved by *ex-situ* and irreversible chemical approaches, namely changing the composition of the samples. In contrast, our novel approach reported in this work is based on a dynamic control of the piezophosphor's energy band structure and the trap depth of charge carriers, subsequently inducing activation or saturation of charge traps via a remote excitation. Experimentally, we have provided an evidence of tuning emission peak wavelength and color of ZnS: Al, Cu phosphors by modulating frequency of magnetic field excitation. Moreover, RGB full-color and white light with tunable color temperature are achieved via photon energy coupling with YAG: Ce and $(Ca_{1-x}Sr_x)S$: Eu persistence phosphor. The study provides a new insight and understanding on the piezophotonic emission mechanism. Our new finding of the luminescent materials with ability to be accessed and modulated remotely will offer opportunities for applications in the fields of magnetic optical sensing, piezophotonics, energy harvester, non-destructive environmental surveillance, novel light sources and displays.

Method

Preparation of color-tunable MIL composites. Metal ions doped ZnS microparticles with the average size of 23 μm (Global Tungsten & Powders) were uniformly mixed into a PDMS matrix. Figure S1 shows the corresponding X-ray diffraction (XRD) pattern. The ratio of phosphor material: PDMS was maintained at 7:3. The cured piezophosphor doped PDMS (5 mm in length, and 1 mm in diameter) was embedded into magnetic elastomer (2 mm in length and 1 mm in diameter) consisted of soft ferromagnetic microparticle (Fe-Co-Ni alloy particle average sizes 100 μm) uncured PDMS in weight ratio 2.5:1. The samples were cured at 120 °C for 45 min. The resultant composite

Fabrication of the phosphor possessing RGB and tunable white MIL composite. The red colored Hong Kong Polytechnic University logo was patterned by screen printing (thickness 200 μm) the (SrS, CaS): Eu phosphor paste onto the top of a ZnS:Cu based MIL composite. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of (SrS, CaS): Eu are shown in Figure S2. This green MIL composite consisted of 16 composite rods, each with a diameter of 1 mm and a depth of 5 mm. For the element of individual multicolor volumetric MIL composite, the red phosphor paste was coated onto ZnS: Cu based MIL composite element rod.

The tunable white MIL composite was fabricated via homogenous mixing YAG: Ce phosphor with ZnS: Al, Cu piezophosphor. Figure S3 shows the PLE and PL spectra of YAG:Ce. Then this mixture was mixed into PDMS to form the tunable white MIL composite.

Optical characterization. The MIL spectra and CIE coordinates of the MIL composites were measured using a CCD camera (Ocean Optics USB4000) and spectroradiometer (PR-655, Photo Research Inc.) with a detection spot of diameter 5.25 mm. The MIL images were captured by a digital camera (Olympus Pen Lite E-PL3).

Measuring of tunable MIL emission. A homemade apparatus was used to generate sinusoidal magnetic field at room temperature. A pulse width modulator (PWM) was used to modulate the frequency of the magnetic field. In detail, an electric motor rotates a magnet with the rotation speed controlled by a pulse width modulation module. The magnet has a strong magnetic field along its radical axis, and it is rotated around the longitudinal axis of the magnet. The applied magnetic field strength on the composite is controlled via changing the distance between the MIL composite and the magnet. The green to blue color displayed was tuned by controlling the modulation frequency of the magnetic field. The magnetic field was set in the range of 2.5 ~ 3.5 kOe, depending on the intensity of emission required.

Acknowledgements

The research was financially supported by the grants from Research Grants Council of Hong Kong (GRF No. PolyU 5005/13P) and National Natural Science Foundation of China (Grant No. 11474241).

References

[1] X. Wang, H. Zhang, R. Yu, L. Dong, D. Peng, A. Zhang, Y. Zhang, H. Liu, C. Pan, Z. L. Wang, Adv. Mater. **2015**, 27, 2324.

[2] Y. Zhang, G. Gao, H. L. Chan, J. Dai, Y. Wang, J. Hao, Adv. Mater. **2012**, 24, 1729.

[3] J. Lee, P. W. Bisso, R. L. Srinivas, J. J. Kim, A. J. Swiston, P. S. Doyle, Nat. Mater **2014**, 13, 524.

[4] S. M. Jeong, S. Song, S. K. Lee, N. Y. Ha, Adv. Mater. **2013**, 25, 6194.

[5] H. Fang, X. Wang, Q. Li, D. Peng, Q. Yan, C. Pan, Advanced Energy Materials **2016**, 6, 1600829.

[6] D. Tu, C.-N. Xu, A. Yoshida, M. Fujihala, J. Hirotsu, X.-G. Zheng, Adv. Mater. **2017**, 29, 1606914.

[7] C. Pan, M. Chen, R. Yu, Q. Yang, Y. Hu, Y. Zhang, Z. L. Wang, Adv. Mater. **2016**, 28, 1535.

[8] D. Peng, B. Chen, F. Wang, ChemPlusChem **2015**, 80, 1209.

[9] G. Bai, M.-K. Tsang, J. Hao, Adv. Opt. Mater. **2015**, 3, 431.

[10] C. Feldmann, T. Jüstel, C. R. Ronda, P. J. Schmidt, Adv. Funct. Mater. **2003**, 13, 511.

[11] T. Dong, X. Chao-Nan, F. Yuki, Y. Akihito, J. Phys. D: Appl. Phys. **2015**, 48, 475105.

[12] H. Li, N. Liu, X. Zhang, J. Su, L. Li, Y. Gao, Z. L. Wang, Nano Energy **2016**, 27, 587.

[13] S. M. Jeong, S. Song, H. Kim, Nano Energy **2016**, 21, 154.

[14] S. M. Jeong, S. Song, K.-I. Joo, J. Kim, S.-H. Hwang, J. Jeong, H. Kim, Energy Environ Sci. **2014**, 7, 3338.

[15] L. Chen, M.-C. Wong, G. Bai, W. Jie, J. Hao, Nano Energy **2015**, 14, 372

[16] Y. Sagara, T. Kato, Nat Chem **2009**, 1, 605.

[17] K. Y. Sasaki, J. B. Talbot, Adv. Mater. **1999**, 11, 91.

[18] W. Wu, Z. L. Wang, Adv. Mater. **2016**, 1, 16031.

[19] X. Han, W. Du, M. Chen, X. Wang, X. Zhang, X. Li, J. Li, Z. Peng, C. Pan, Z. L. Wang, Adv. Mater. **2017**, 29, 1701253.

[20] C. N. Xu, T. Watanabe, M. Akiyama, X. G. Zheng, Appl. Phys. Lett. **1999**, 74, 1236.

[21] R. Deng, F. Qin, R. Chen, W. Huang, M. Hong, X. Liu, Nat. Nanotechnol. **2015**, 10, 237.

[22] M. C. Wong, L. Chen, M. K. Tsang, Y. Zhang, J. H. Hao, Adv. Mater. **2015**, 27, 4488.

[23] O. Graydon, Nat Photon. **2015**, 9, 558.

[24] G. Bai, M.-K. Tsang, J. Hao, Adv. Funct. Mater. **2016**, 26, 6330.

[25] D. Tu, C.-N. Xu, Y. Fujio, A. Yoshida, Light Sci Appl. **2015**, 4, e356.

[26] O. Chen, D. E. Shelby, Y. Yang, J. Zhuang, T. Wang, C. Niu, N. Omenetto, Y. C. Cao, Angew. Chem. Int. Ed. **2010**, 49, 10132.

[27] Y. Chen, Y. Zhang, D. Karnaushenko, L. Chen, J. Hao, F. Ding, O. G. Schmidt, Adv. Mater. **2017**, 29, 1605165.

[28] C.-N. Xu, T. Watanabe, M. Akiyama, X.-G. Zheng, Appl. Phys. Lett. **1999**, 74, 2414.

[29] Z. L. Wang, NANO TODAY **2010**, 5, 540.

[30] D. Vij, *Luminescence of solids*, Springer Science & Business Media, **2012**.

[31] K. Era, S. Shionoya, Y. Washizawa, J. Phys. Chem. Solids **1968**, 29, 1827.

[32] B. P. Chandra, V. K. Chandra, P. Jha, Appl. Phys. Lett. **2014**, 104, 031102.

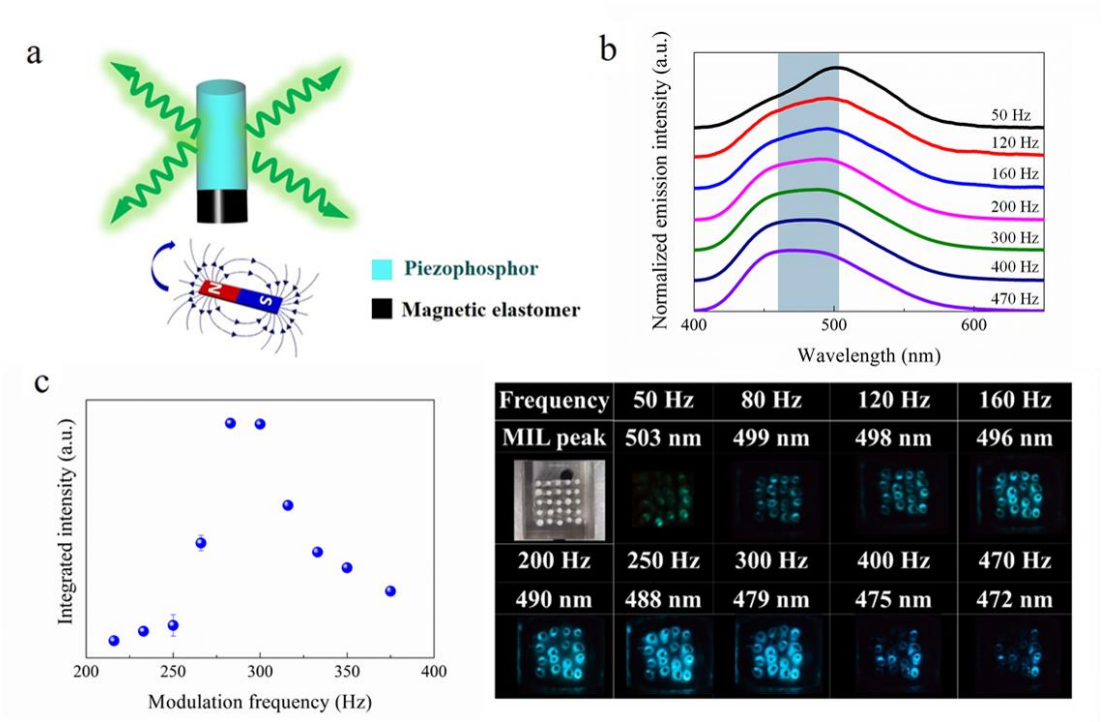

Figure 1 (a) Schematic illustration of metal ions (e.g., Al, Cu)-doped ZnS MIL composite when excited by a modulated magnetic field. (b) Normalized emission intensity of the composite under various frequencies, showing the emission wavelength tuning. (c) Integrated emission intensity as a function of the modulation frequency of magnetic field at fixed strength (2.0 kOe). (d) Photographs showing from green to blue color variation of the sample by changing the modulation frequency of magnetic field.

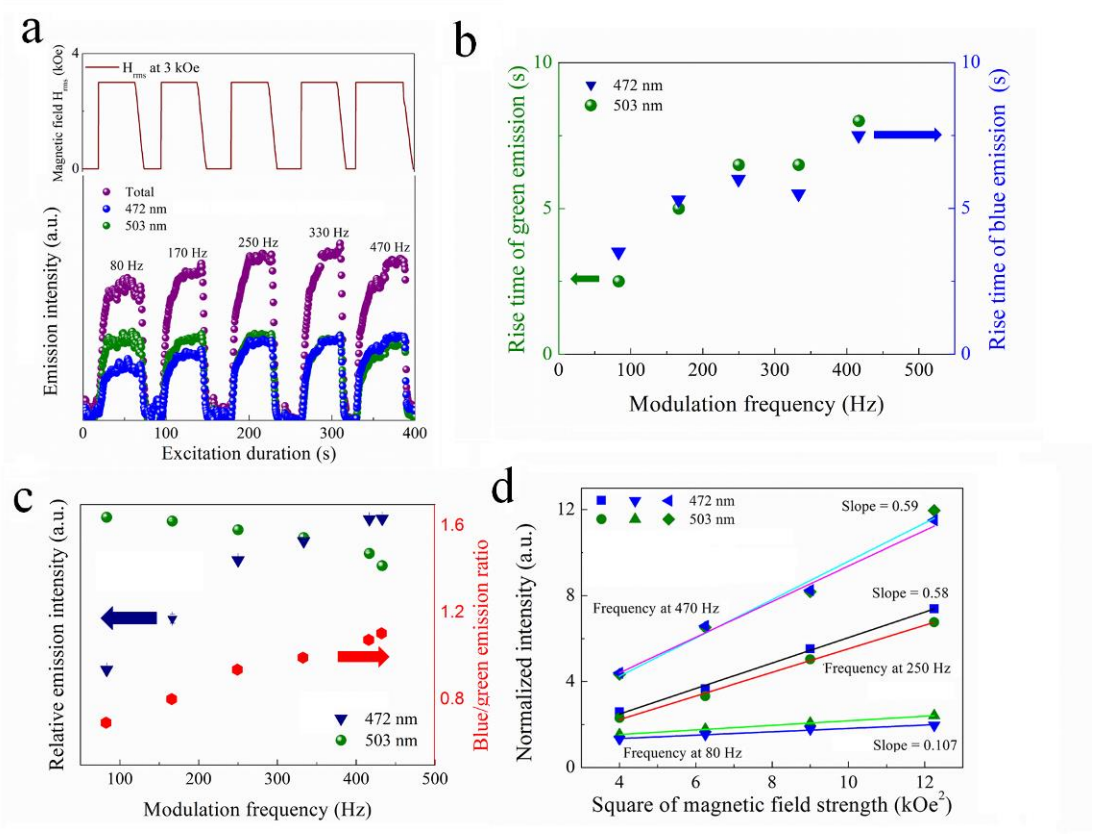

Figure 2 (a) Time dependent luminescence profiles of ZnS: Al, Cu emitting at 472 and 503 nm under sinusoidal magnetic field with various frequencies. (b) The rise time of 472 and 503 nm emission under different excitation modulating frequency. (c) The relative MIL intensity at 472 and 503 nm as a function of excitation frequency. (d) Emission intensity at 472 and 503 nm as a function of the square of magnetic field strength and the corresponding linear fittings.

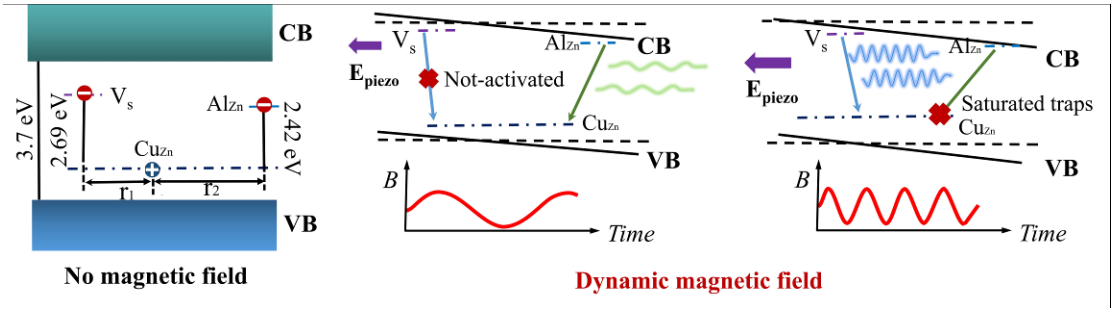

Figure 3 Schematic illustration of the mechanism responsible for temporal color tuning of MIL in ZnS: Al, Cu piezophosphor.

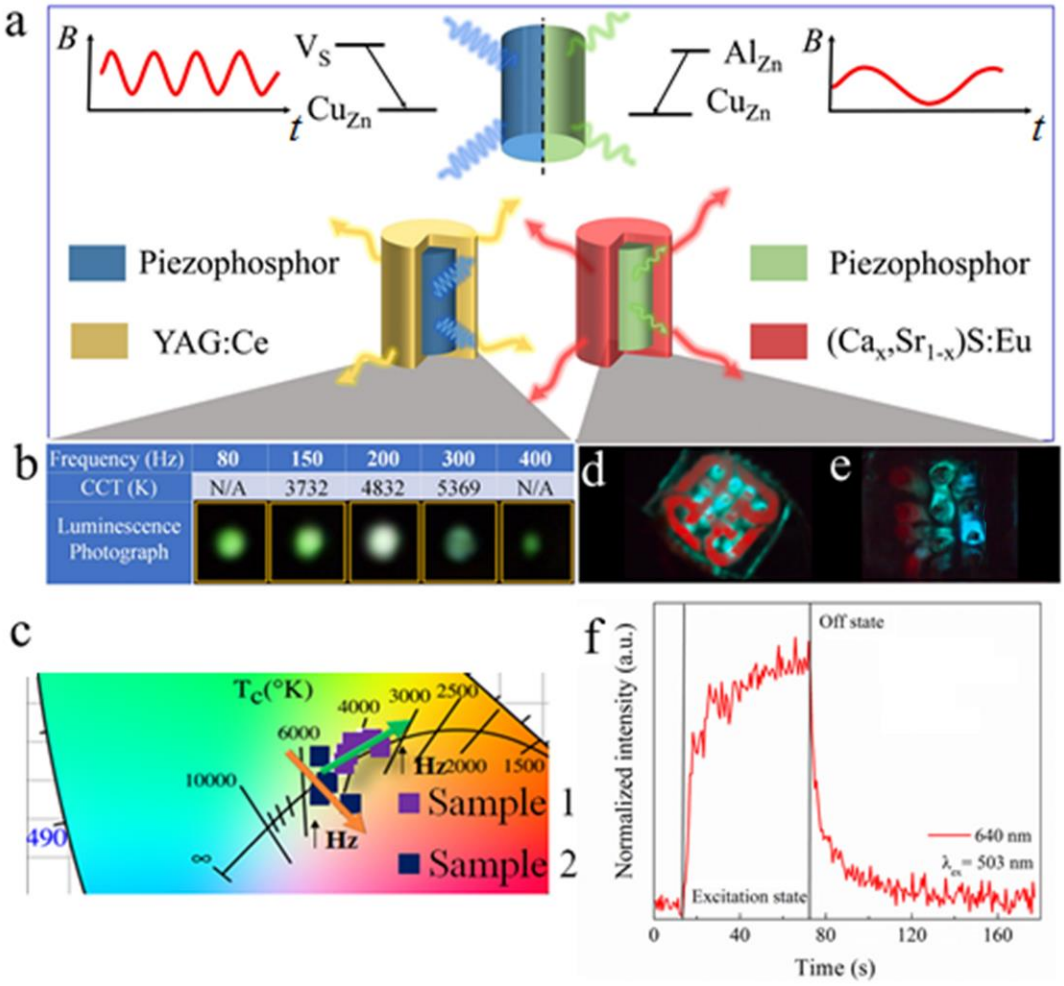

Figure 4 Demonstration of full-color display in MIL composite combined with other fluorescent materials. (a) Schematic of MIL full-color display realized by coupling MIL composite with different fluorescent materials. (b) Photographs of white emission with tunable color temperature under different modulation frequency of magnetic field from MIL composite mixed with YAG: Ce phosphor. (c) Enlarged CIE coordinates of adjustable white MIL emissions. (d) Multicolor MIL flexible composite combined with ($Ca_{x,}$ Sr_{1-x}) S: Eu displaying the logo of the Hong Kong Polytechnic University. (e) Display of RGB and white MIL emissions (f) The excitation and afterglow of red emission intensity at 640 nm as a function of time.

Table 1 CIE coordinates, emission peak wavelength and corresponding light intensity of ZnS:Al, Cu under different modulating frequency of magnetic excitation.

Frequency of excitation (Hz)	CIE (x ,y)	Peak wavelength (nm)	Luminance (cd/m^2)
80	(0.2129, 0.3470)	503	24
120	(0.1975, 0.2996)	496	30
160	(0.2216, 0.2679)	494	59
200	(0.2252, 0.2279)	489	82
300	(0.1841, 0.2239)	488	166
400	(0.1802, 0.2266)	479	64
470	(0.1627, 0.2108)	472	47

The table of contents

We present a strategy of temporal tuning of light-emitting wavelength and color in *in-situ* and reversible way, greatly differing from conventional approach. RGB and tunable white-light are demonstrated by modulating frequency of magnetic excitation. The study provides a new understanding on luminescence mechanism. Our finding will offer opportunities in magnetic-optical sensing, piezophotonics, energy harvester, novel light sources and displays.

M.-C. Wong, L. Chen, Dr. G. X. Bai, Dr. L. B. Huang, Prof. J. H. Hao*

Temporal and remote tuning of piezophotonic effect-induced luminescence and color gamut via modulating magnetic field