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Major Goals: Piezoluminescence (PZL) is a promising energy-conversion phenomena for mechanically driven photon sources, such as displays, lighting, bioimaging, and sensing. However, realization of practical PZL materials is challenging, and currently, none of the available components and devices utilize this effect due to extremely low-light intensity and restricted control of the emission wavelength. This is a new emerging field of research with limited number of publications and even less understanding of the basic physics controlling the coupling of mechanical strain with interband transitions and charge recombination reactions. The scientific approach presented here provides clear direction to systematically elucidate the principles governing the intensity and wavelength of PZL emission.Defect chemistry, band structure, and nanostructured composite architecture will be investigated to improve the light emission intensity. There are many ways to introduce intrinsic effect into a given material system (e.g., gaseous diffusion) which results in new energy levels between its bandgap. Hydrogenation treatment in conjunction with the composition design will be utilized to improve the intensity.

Accomplishments: Direct conversion of mechanical energy into light of specific wavelength provides new direction for design of novel sensing systems, displays and controls. Systematic material design and characterization experiments were conducted to discover the physical principles that lead to controlled piezoluminescence (PZL) in flexible sheets and bulk. PZL implies generation of light of desired wavelength by mechanical action. The effect has been observed in compounds with suitable crystallographic symmetry modified with activator ion. The underlying basis for the effect has been correlated with the presence of local piezoelectricity and energy states below conduction band available from the suitable activator ion. In order to achieve higher PZL intensity, both structural engineering and “defect engineering” were utilized in order to generate the trap states that facilitate the electron transfer under minimal stress magnitudes. The concentration of trapped electrons is predicted to have strong correlation with the PZL performance, and our results show that an optimum electron concentration is necessary to maximize PZL intensity due to adequate electron energy transfer ratio between non-radiative recombination (NRR) and thermal radiative recombination (TRR). Theoretical analysis and extensive experiments provide basic understanding of the effect of various processing parameters that affect the relationship between mechanical strain, band structure and optical properties. Microstructural engineering was utilized to find geometrical arrangements and distributions that provides elastic compatibility in the networked structure. PZL can be utilized in various scenarios where mechanical energy is continuously available such as roadways and pedestrian walkways; high deformation structures such as vehicles and aircrafts, etc. Demonstrations of the new sensing technology for stress, impact, and damage were designed based on the PZL effect. The non-contact part of this system, since light is used for detection and communication, is highly attractive. In this case, stress sensing is passive as PZL sensor responds directly by emitting light in response to the mechanical stimulation.

Training Opportunities: Postdoctoral researcher working on the program was provided training in professional research practices in the context of the research through the regular meetings and discussions. Direction and feedback were provided to the postdoctoral researcher covering (a) the fundamental knowledge needed to support the tasks in the proposed effort, (b) strategies for maintaining depth and breadth in the relevant literature, including active service as a peer reviewer, (c) technical presentation skills, and (d) skills and best practices in technical writing for publications and proposals. PI also actively involved the postdoc in the discussions and decision-making with sponsors. Finally, the postdoctoral scholar was required (and supported) to attend professional meetings and was encouraged to organize and chair invited sessions at these meetings in order to extend the scholar's professional network.

Results Dissemination: Postdoctoral researcher working on the program attended the 2nd annual energy harvesting society meeting and presented the results. A journal paper based upon the experimental and modeling results in being finalized. Some more experiments are required to complete the paper for high impact factor journal. These experiments are currently in progress and we hope to complete them soon.

Honors and Awards: Selected to provide Taylor Lecture at Penn State, 2018

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PARTICIPANTS:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Amin Nozariasbmarz
Person Months Worked: 5.00 **Funding Support:**
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Final Progress Report

1. Statement of the problem studied

There are two commonly utilized stress sensing techniques based on output being either electrical signal or optical signal [1]. Magneto-resistive, piezoelectric or strain sensitive conducting materials and devices are known as typical electrical signal sensors [2,3,4]. However, these sensors need direct physical contact and are restricted in size (less than 5×5 cm), limited to single point measurement and planar surface [5]. Optical sensors can solve these problems. One of the optical methods is based on piezoluminescence (PZL) concept, also known as mechanoluminescence. Piezoluminsecence is the emission of light due to the mechanical force or stress imposed on a material. Mechanical excitation can be in the form of pressure, stretching, rubbing, crushing, impacting, scratching, etc. PZL requires no battery or electrical charge/discharge to generate light.

To increase the application of PZL materials, several criteria needs to be met including, recoverable properties, long lasting life time, high intensity emission of light, different color spectrum, and response to varying AC stress sources. The light is emitted from PZL materials when the trapped electrons are detrapped into the conduction band. Therefore, the intensity of emitted light strongly depends on the defect structure of the materials. In this project we used ZnS powder with different dopants including Cu, Al and co-doping of Cu,Mn, and focused our attending on enhancing the amplitude of emitted light. Secondary focus in the program was on synthesizing PZL materials with different colors and exploring Army related applications based on PZL properties such as health monitoring sensors, force-activated displays and writing pad. The developed flexible PZL materials can respond to compression, stretching, bending, impact, friction, folding and torsion.

2. Summary of the most important results:

2.1. Materials fabrication

PZL materials are typically made of ceramics such as $Ca_2Al_2SiO_7:Ce^{3+}$ (blue) [6], $BaTiO_3$-$CaTiO_3:Pr^{3+}$ (red) [7], $SrAl_2O_4:Ce^{3+}(Ho^{3+})$ (ultraviolet) [8], $CaMgSi_2O_7:Eu^{2+}(Dy^{3+})$ (green) [9], $CaAl_2Si_2O_8:Eu^{2+}$ (blue) [10], $CaYAl_3O_7:Eu^{2+}$ (blue) [11], $SrMg_2(PO_4)_2:Eu^{2+}$ (purple) [12] and $ZnS:Mn^{2+}$ [13], all of which have very small fracture toughness and are not bendable. However, for PZL application it is required to apply uniform or nonuniform mechanical load on the material. Therefore, bulk ceramics are not capable to act as high quality practical PZL materials. Ceramic powders embedded in a flexible matrix can provide desired mechanical strength while at the same time providing higher light emission. In this case, the functionality of the PZL materials improves because the device can respond to all different mechanical loads including compression, stretching, bending, torsion, friction, impact, and folding.

In order to synthesize a flexible PZL, an organic polymer based on polydimethylsiloxane (PDMS) was mixed with ZnS powder with different dopants including Cu, Al and co-doping of Cu and Mn, with the average particle size of ~25 μm, having different aspect ratios. The mixture of powder and PDMS was initially put in a vacuum oven to release embedded air inside the PDMS due to the mixing of PDMS and powder. Then, it was cured at different temperatures to achieve maximum flexibility and PZL performance. Flexible PZL elastomers were synthesized with a range of thickness between 0.1 mm to 8 mm. Lower thickness of the PZL elastomers results in a more uniform sample because the PZL powder in the mixture can settle down during degassing and curing process.

2.2. Piezoluminescent property in ZnS Crystal

The emitted light in PZL materials under mechanical load is related to the transition of electrons from excited state to the ground state of dopants [14]. These electrons are naturally generated by deformation as they become detrapped from trapped charge carriers [15]. For exciting a visible light, a few eV of energy is required. In fact, the average mechanical energy during elastic deformation on an atom (on the order of 10^{-6} eV/atom) is not enough to excite emission of visible light [16]. Dopants or cation/anion vacancies create traps for carriers. Mechanical loading can release the charged carriers from these trap states, that can recombine with luminescent centers to yield PZL characteristics.

Wurtzite ZnS has a hexagonal closed pack arrangement of …ABABAB… structure along (001) planes. Piezoelectricity in this structure is due to the absence of inversion centers [17]. PZL characteristics has been found to exist in Cu, Al, and Cu:Mn doped ZnS which comes from the interaction between piezoelectricity and shallow donor and acceptor levels [18]. PZL properties in ZnS:Cu and ZnS:Cu,Mn materials is generated by the detrapping of electrons due to the piezoelectric field [19]. This mechanism happens in several steps [20]: (1) due to the non-centrosymmetric crystal structure of ZnS, a piezoelectric field is produced [21]; (2) piezoelectric field results in band bending that generates detrapped electrons from occupied electron traps; (3) energy releases during electron-hole recombination, (4) dopants such as Mn^{2+} and Cu^{2+} are excited by the released energy from recombination, and (5) light is emitted during the excitation of Mn^{2+} and Cu^{2+} ions [19]. The intensity of the emitted light from PZL materials is dependent on several factors including magnitude and rate of applied loading. The PZL intensity in ZnS:Cu and ZnS:Mn can be expressed as [19]:

$$I = N_0 \sigma \mu B^2 d_0^2 \tau Z \alpha n_{h0} \dot{P} (P - P_{th})$$

where N_0 is the total number of detrappable traps, σ is the capture cross-section of the electrons moving in the conduction band, μ is the mobility of electrons, B is the correlating factor, d_0 is the piezoelectric constant, τ is the lifetime of electrons in the conduction band, Z=1/kT is the distribution coefficient in which k is the Boltzmann constant and T is the absolute temperature of the phosphor material, α is the decrease in the trap depth per unit electric field, n_{h0} is the initial number of the holes in the sample, $\dot{P}$ is the pressing rate, P is the applied pressure and P_{th} is the threshold pressure. This equation indicates that for micron size powder of ZnS:Cu and ZnS:Mn, after the threshold pressure, the PZL intensity increases linearly with the applied pressure (P) and pressure rate ($\dot{P}$).

It should be noticed that the intensity of the emitted light can only be compared if the samples have the same size and are characterized under similar measurement condition. Therefore, there needs to be a standard method of testing PZL materials which can be widely accepted. In addition, the size and thickness of the sample (shape factors), photodetector type, exposure time and detector slit size (measurement factors) can be effective factors in comparing the PZL intensity measurements. Figure 1(a) and (b) show the setup for periodic stretching-releasing test for measurement of PZL intensity. Room temperature photoluminescence spectra of as-prepared ZnS:Cu,Mn and ZnS:Cu at different curing temperatures and powder to PDMS ratios in the wavelength of 300-800 nm are shown in Figure 1 (c) and (d), respectively. The peak intensity of ZnS:Cu,Mn happens at lower wavelength than ZnS:Cu which results in a more bluish color compared to the green color of ZnS:Cu. The maximum intensity of the light was achieved at optimum weight ratio of the ZnS,Cu,Mn:PDMS=40:100 (Figure 1-c) and ZnS,Cu:PDMS=50:100

(Figure 1(d)). Although the PZL elastomer emitted light in a dark room, the light was not detectable with naked eye under normal lab light condition. Therefore, it was required to further optimize the material composition to enhance the intensity of the light.

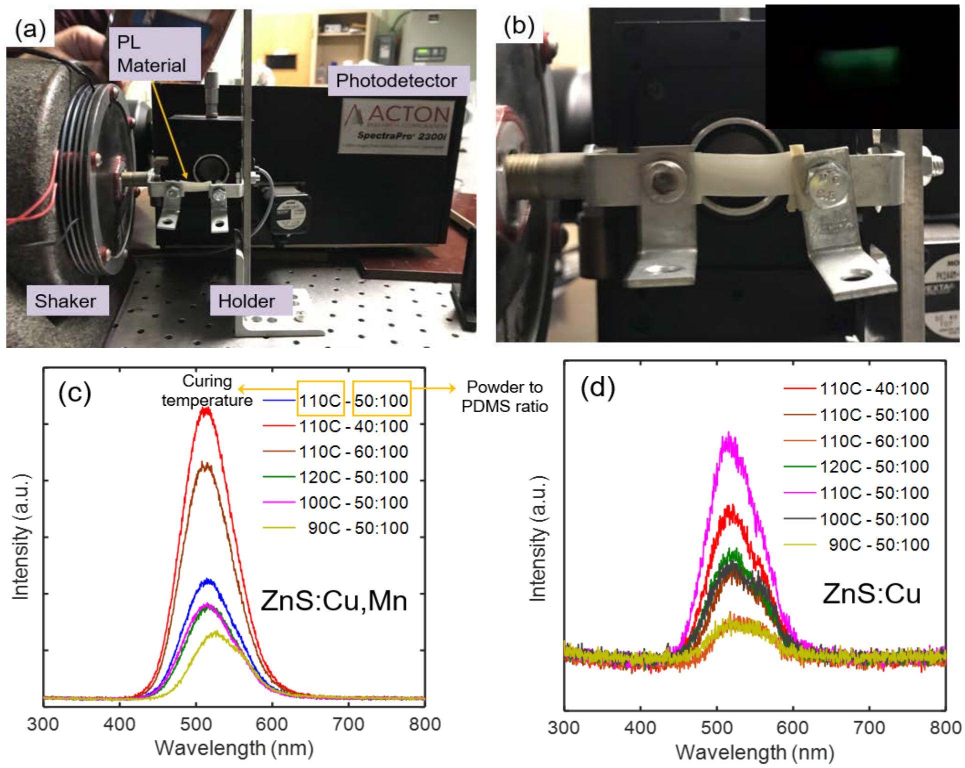

Figure 1. (a) and (b) Setup for periodic stretching-releasing test developed for measuring PZL. Room temperature photoluminescence spectra of as-prepared (c) ZnS:Cu,Mn and (d) ZnS:Cu at different curing temperatures and powder to PDMS ratios.

2.3. Defect Generation

As discussed earlier, the intensity of the emitted light strongly depends on introducing defects in PZL materials. Therefore, two different methods i.e. mechanical milling and hydrogenation were applied to introduce defects in the PZL powder. The mechanical milling was not effective, which might be due to the non-uniform distribution of defects and/or reducing the particle size of PZL powders. However, hydrogenation was an effective way to introduce uniformly distributed defects into the PZL powder. While hydrogeneration at different temperatures can improve PZL properties of Cu-doped ZnS, the improvement in brightness of Al-doped ZnS and Cu,Mn-doped ZnS under similar condition was negligible. The samples were hydrogenated at 200, 250 and 300 °C. Higher intensity light was emitted in the Cu-doped ZnS powder which was hydrogenated at 250 °C. It is expected that hydrogenated powders will have more defects at higher temperature [22], however, 300 °C sample did not exhibit the best PZL properties. From the results of mechanical milling and higher temperature hydrogenation, we hypothesize that there is an optimum defect concentration that can provide maximum emitted light intensity. Generally, there are two light emission categories: near-band-edge emissions (NBE) and deep level (DL) emissions. NBE requires high crystallinity while DL promotes impurities and crystal defects [23]. It seems that in Cu-doped ZnS, the optimum DL emissions occurs at 250 °C.

2.4. Applications

We developed flexible PZL elastomers with different colors using a mixture of PZL powders. As depicted in Figure 2, the PZL elastomers emitted green and white light under the periodic stretch-stress load or under friction of a point force on the surface of the PZL materials. Green and white colors were obtained by mixing ZnS:Cu powder with ZnS:Al in the ratio of 5 to 0 and 4 to 1, respectively. ZnS:Al has an orange color, however, the intensity of its emitted light is very low, while the mixture of ZnS:Al and ZnS:Cu produces a glowing white light. The materials synthesis technique developed in this program is a fast and simple, that can be applied to different PZL materials to get a spectrum of colors for different applications. For example, similar to Figure 2, PZL writing pads can be applied on different surfaces with various shapes.

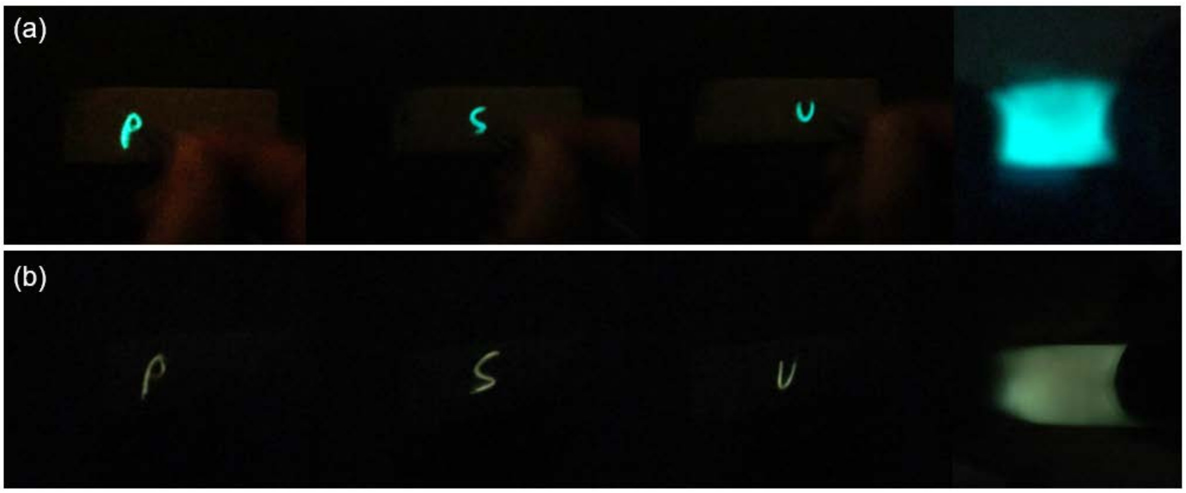

Figure 2. PZL writing pad using different colors (a) green and (b) white color.

The developed flexible PZL devices can respond to compression, stretching, bending, impact, friction, folding and torsion which is the unique characteristics of these materials. For example, several types of forcing function including folding (Figure 3-a), torsion (Figure 3-b), bending (Figure 3-c), and stretching (Figure 3-d) are depicted in Figure 3. Therefore, these PZL elastomers are promising materials for the non-contact strain sensor and motion detection devices.

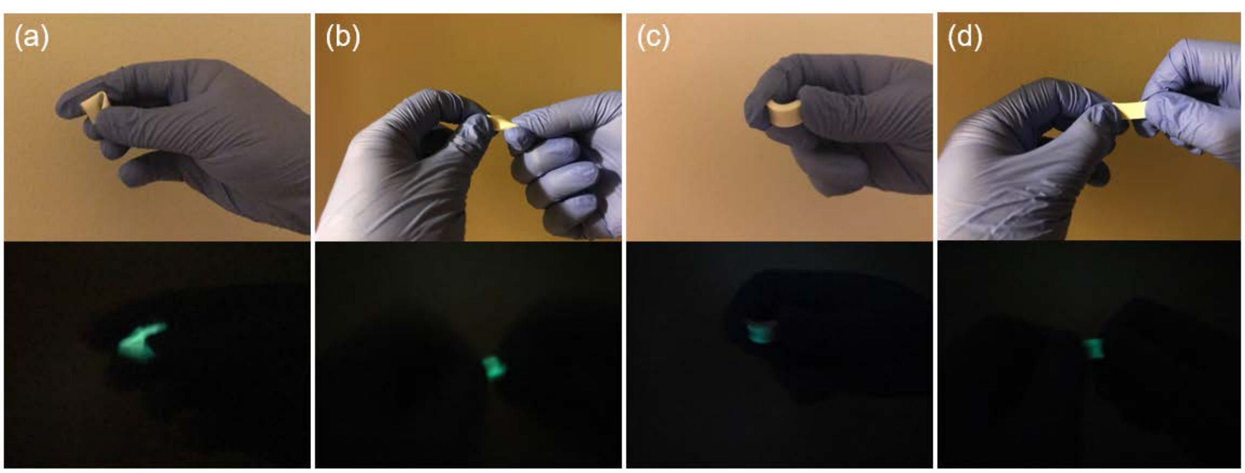

Figure 3. Light emission from synthesized PZL materials under different mechanical loading conditions: (a) folding, (b) torsion, (c) bending, and (d) stretching.

One of the applications of our PZL elastomers can be smart floors that can replace LED floor tiles. The floor glows when a person walk on those floors. Similarly, a pressure sensing matrix or a motion sensitive brick can be attractive for certain purposes. Another application of the PZL elastomers can be pedestrian caution kits (Figure 4-a). These kits can be attached to the body or cloths of pedestrian and they can glow during night during walking or jogging which could avoid probable casualties. These devices in future could be practical substitute to the lights which require batteries to power them. PZL elastomers are cheap and they do not require batteries or electrical charge/discharge to generate light. They glow while a person is moving based on the stretching forces because of body motion. These elastomers can also be used as a smart textile in a fabric with the same functionality.

The PZL materials can also considered as an energy storage material that is able to store light and release it by a mechanical stimulus. Another application of our PZL elastomers is force activated displays as shown in Figure 4-b, where a sign, symbol or writing can glow by applying force. For example, these materials can emit light with the force of wind. Finally, writing pad is a promising application of these PZL elastomers that can be used for safety codes. The PZL writing pad enables tracking and detection of the writing motions. This can be used for signature recording systems where the emitted light can be detected by digital imaging.

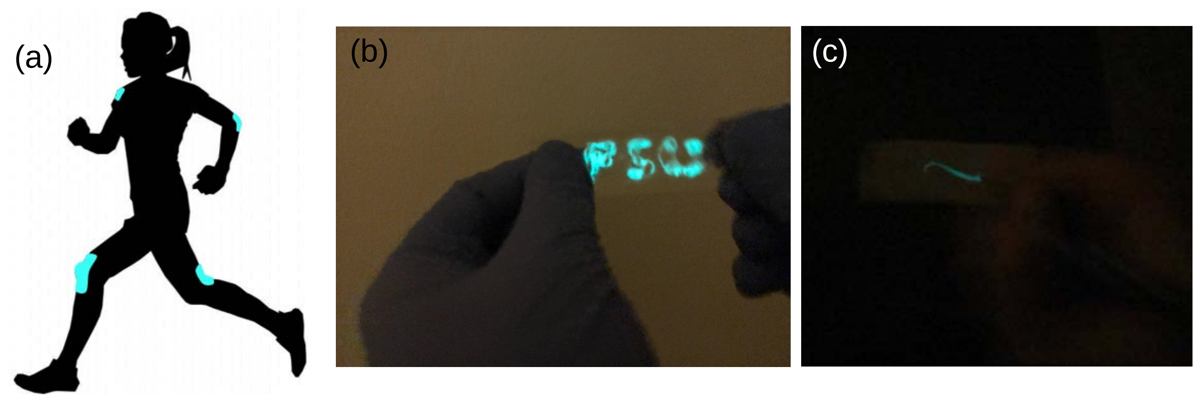

Figure 4. Demonstration of different applications of PZL materials: (a) pedestrian caution kit, (b) Force-activated display and (c) writing pad.

2.5. Future works:

We have synthesized different types of PZL powders including $CaZnOS:Mn^{2+}$ and have studied the effect on PZL characteristics of different dopants and induced defects through hydrogenation treatment. Next, we plan to study the effect of microwave radiation on defect generation in PZL powders and characterize them to optimize the density of the defects for maximum light emission. We believe that in addition to synthesizing new powders with high PZL intensity, finding new applications for PZL materials can rapidly advance the deployment of these materials. Fundamental physics based models are being developed to understand and quantify the light emission as a function of AC stress cycles. In conjunction, a standardized testing methodology is being developed in order facilitate the comparative analysis of the PZL materials being developed world-wide. Combination of improved material composition and synthesis technique based upon the theoretical models will provide further improvement in the properties.

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