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Modulating Trap Distribution of Persistent Phosphors upon Simple Microwave-assisted Solid-state Reactions

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Abstract: The trap distribution due to defects in persistent luminescent materials plays a significant role in their scope of applications. However, it is a big challenge to manipulate or modulate this trap distribution. In this work, the trap distribution of green emitting persistent phosphor Li$_2$ZnGeO$_4$:Mn$^{2+}$ is modulated upon a facile microwave-assisted solid-state reaction. A series of systematic temperature dependent trapping, de-trapping and re-trapping measurements are designed to shed light on trap information. An appealing feature of the present synthesis approach is that the trap distribution is modulated towards shallow traps, which offers great promise in low-temperature glow-in-the-dark applications. More importantly, trap re-shuffling can be achieved towards two directions, both lower energy level (shallow
traps) and higher energy levels (deep traps) upon light stimulation. These findings indicate there are optically active trapping defects with photo-stimulated re-trapping behavior in this persistent phosphor. This work not only provides a fundamental advance in revealing re-trapping behavior, but also offers a guidance for the modulation of trap distribution in persistent phosphors upon a facile approach.

1. Introduction
Persistent phosphors, or glow-in-the-dark compounds, relate to a fascinating optical phenomenon in which light emission persists for seconds to hours after switching off the excitation light. Due to their large storage capability upon incident irradiation and controllable photon release under external stimulation, phosphors featuring long-lasting luminescence have been widely applied as self-sustained emitters in the fields of safety signage, road marking, in vivo bio-imaging and optical information storage\(^1,2,3,4,5\). Since the report of the long-lasting green emission SrAl\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) phosphor by Matsuzawa et al.\(^6\), a large number of persistent phosphors (mainly based on trivalent rare-earth ions and transition metal ions) in various host matrices have been developed. In general, luminescent centers and traps are involved in such materials. Appropriate luminescent centers can emit light in the wavelength range of interest, whereas traps store the incident energy and transfer it slowly to the luminescent center with light emission (afterglow)\(^5\). Ultraviolet (UV) light or even high-energy X-ray is generally employed to fill in traps in the form of trapped charge carriers (e.g., electrons). Subsequently, these captured charge carriers can be gradually released upon ambient temperature, commonly at room temperature (RT). Furthermore, these captured charge carriers can be rapidly released via thermal stimulation (for example, by heating), optical stimulation (low-energy illumination, such as visible or near-infrared (NIR) light), or even mechanical
stimulation (e.g., stretching, bending, scratching or grinding). Such light emissions during different external stimulation are named as thermally stimulated luminescence (TSL or thermoluminescence, TL), photo-stimulated luminescence (or optically stimulated luminescence) and mechanoluminescence (ML), respectively. The past decade has witnessed great progress in the development of persistent phosphors covering a broad wavelength range of persistent luminescence. Although most authors have reached an agreement on the general idea that charge carriers are trapped by defect energy levels within the band gap, more details of the nature of traps or the interaction between traps are still needed. Trap re-distributions have been observed in several defect-involving luminescent materials. For instance, Xu and co-workers found the re-distribution of trapped electrons from the deep traps to the shallow ones by light simulation with a 660 nm LED. Persistent phosphor $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}:\text{Er}^{3+}, \text{Cr}^{3+}$ can be recharged in situ by a 660 nm LED by utilizing two different traps with different trap depths thanks to such trap re-distribution. Zhuang et al. investigated the charge carrier transitions in some deep-trap mechanoluminescent materials and the force-induced trap re-distribution or the so-called force-induced charge carrier storage (FICS) effect was confirmed in $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}, \text{Dy}^{3+}$, $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}, \text{Dy}^{3+}$, $(\text{Sr}0.5\text{Ba}0.5)\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}, \text{Dy}^{3+}$, $\text{ZnS}:\text{Cu}$, and $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Yb}^{2+}, \text{Dy}^{3+}$ phosphors. The FICS effect enabled the conversion of part of the applied mechanical energy into deep-trap-related states, which could be stored at RT and released as light emission at higher temperatures. Moreover, in the $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ phosphor with a broad trap depth distribution, Smet et al. first demonstrated that the mechanical stimulation can not only lead to direct light emission, but also result in re-shuffling of trap occupation. Such trap re-distribution effect helps add memory to pressure-sensitive phosphors and contribute to new pressure sensing applications.
Widespread utilization of such defect-controlled materials at various conditions relies on the temperature-dependent persistent luminescence performance at variable ambient temperatures\(^{[20, 21, 22]}\). However, the large variations of afterglow performance at different temperatures are impeding their wide applications. For instance, even the most popular persistent phosphor \(\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}\), is currently not perfectly suited for glow-in-the-dark traffic markings due to the inferior performance upon the overnight temperature drop at various outdoor conditions\(^{[23, 24, 25]}\). Recently, the concept of the optimum working temperature, \(T_{\text{optimum}}\), has been proposed as a criterion for the evaluation of a persistent phosphor\(^{[20]}\). The value of \(T_{\text{optimum}}\) represents the temperature at which the maximum amount of afterglow output is given within a reasonable time frame. \(T_{\text{optimum}}\) of a certain persistent phosphor is largely determined by the distribution of trap depths with multiple trap occupations\(^{[24]}\).

To manipulate or modulate the distribution of these trap energy levels in persistent phosphors, band gap engineering, as one of material design strategies, has been employed in solid-solution compounds\(^{[4, 26, 27, 28]}\). The regulation of the crystalline host lattice by chemical substitution leads to the variation of the relative locations of valence band and conduction band\(^{[27]}\). In addition, co-doping has been an effective method to tailor the trap structure. For example, Poelman et al. investigated \(\text{LiGa}_5\text{O}_{8}:\text{Cr}^{3+}\) with co-dopant \(\text{Si}^{4+}\) or \(\text{Ge}^{4+}\) ions and the formation of deep-lying traps was identified\(^{[29]}\). On the other hand, with the aid of host-referred binding energy and vacuum-referred binding energy schemes, trap depth engineering provides a good example of manipulation of the trapping energy levels within a certain phosphor by appropriately screening trivalent lanthanide co-dopants\(^{[30, 31, 32]}\), although the predictive power of the semi-empirical energy level models is limited\(^{[33]}\). Despite enormous efforts, modulation of traps is difficult and time-consuming. It is still a challenge to manipulate or modulate the trap distribution using a facile approach.
In this work, we demonstrate the modulation of the trap distribution in the Li\textsubscript{2}ZnGeO\textsubscript{4}:Mn\textsuperscript{2+} persistent phosphor as an example, using a facile microwave-assisted solid-state (MASS) approach. The preparation method is strongly associated with properties of luminescent materials, especially the trap-involved materials. An appealing feature of the present MASS synthesis approach is that the trap distribution is modulated into the shallow trap range, and green emitting persistent luminescence at extremely low temperature is achieved, which offers a great promise in low-temperature glow-in-the-dark applications. Moreover, a series of temperature dependent trapping, de-trapping and re-trapping measurements are designed to shed light on trap information. More importantly, trap re-shuffling can be achieved towards both lower energy level (shallow traps) and higher energy levels (deep traps) upon 420 nm light stimulation. These findings indicate there are optically active trapping defects with photo-stimulated re-trapping behavior in Li\textsubscript{2}ZnGeO\textsubscript{4}:Mn\textsuperscript{3+} persistent phosphor. This work not only provides a new insight into re-trapping behavior, but also offers a guidance for the modulation of trap distribution in persistent phosphor using a simple approach.

2. Experimental Section

2.1. Materials Preparation

Mn-substituted Li\textsubscript{2}ZnGeO\textsubscript{4} phosphors (Li\textsubscript{2}ZnGeO\textsubscript{4}:Mn\textsuperscript{2+}) were prepared starting from stoichiometric amounts of the precursors Li\textsubscript{2}CO\textsubscript{3} (Sigma Aldrich, 99.99%), ZnO (Alfa Aesar, 99.99%), GeO\textsubscript{2} (Alfa Aesar, 99.999%), and MnCO\textsubscript{3} (Sigma Aldrich, 99.99%). The amount of Mn dopant was chosen as 0.3% and the molar % is defined with respect to one mole of a host phosphor to make the composition with chemical formula of Li\textsubscript{2}ZnGeO\textsubscript{4}:0.3%Mn\textsuperscript{3+}. The appropriate stoichiometric amounts of the precursors were weighed and manually ground in an agate mortar. Subsequently, the powders were mixed with ethanol and put in a ZrO\textsubscript{2} grinding jar. Grinding was performed in a Retsch PM 100 Planetary ball mill for 8 hours and the ground
samples were dried in an oven at 60 °C. After evaporating the remaining ethanol, thorough grinding was performed again, followed by microwave-assisted solid-state (MASS) synthesis or conventional solid-state reaction (SSR).

For MASS reaction, 10 g of powdered activated charcoal was used as the microwave susceptor\textsuperscript{34, 35, 36}. Two alumina crucibles were used, including a bigger volume crucible (30 mL) to hold charcoal and a smaller one (5 mL) to place 0.4 g of the starting mixed precursors. This inner and smaller crucible was surrounded with a sufficient amount of activated charcoal in order to allow the reaction to fully proceed to completion. The bigger crucible was partially covered with an alumina disk to hold the reaction temperature. Subsequently, the two crucibles were put into a cavity of aluminosilicate thermal insulation bricks. Materials were irradiated in a domestic microwave oven (frequency: 2.45 GHz; power level: 1000 W). The duration of microwaves irradiation was selected from 24 min to 36 min for these germanates\textsuperscript{37, 38}. Finally, the samples were retrieved and no thermal treatment was made afterwards. The temperature profile of the microwave heating process follows a rapid temperature increase in a short period of time\textsuperscript{36}. These parameters were found to be highly reproducible from a number of trials. The detailed MASS procedure above followed the previous work of Miranda de Carvalho et al.\textsuperscript{34, 39}.

For comparison, the samples were also prepared by conventional high-temperature solid-state reaction (SSR). The samples were obtained using a two-step high-temperature calcination, employing a heating rate of 300 °C/h in a tube furnace (ETF30-50/18-S furnace, ENTECH, Sweden). The initial calcination temperature was 600 °C for 5 h and the secondary calcination temperature was 1250 °C for 8 h in air. The prepared samples were allowed to cool down naturally to room temperature inside the tube furnace and they were well ground for further characterization.
2.2. Structural Characterization

Crystallographic phases of the obtained samples were verified with powder X-ray diffraction (XRD) measurements using a Siemens D5000 diffractometer (40 kV, 40 mA) with Cu Kα1 radiation (λ = 0.154 nm). The XRD data were collected with a 0.02° step size and 1.5 s integration step time in the range 2θ from 10° to 80°. A fast XRD scanning was also made to check the samples with excess amount of ZnO.

2.3. Luminescence Characterization

Photoluminescence excitation and emission spectra were obtained with a FS920 Edinburgh fluorescence spectrometer using a monochromated 450 W Xe-arc lamp as the excitation source. Persistent luminescence excitation spectrum was measured by monitoring at 536 nm after 3-min excitation with monochromatic light ranging from 230 to 500 nm. Persistent luminescence decay profiles were collected by using a ProEM1600EMCCD camera equipped with an Acton SP2300 monochromator or a FS920 Edinburgh fluorescence spectrometer above mentioned. Several irradiation sources were employed for sample excitation, such as a 420 nm LED, monochromatic light at different wavelengths, or 254 nm emission line of a 3W germicidal Hg-lamp, or even X-rays from a Siemens D5000 X-ray diffractometer (Cu anode, not filtered, operated at 40 kV, 40 mA).

Thermoluminescence measurements were performed in a lab-built vacuum chamber with a well-characterized cooling and heating stage. Identical size thin pellet samples (thickness ca. 2.0 mm, diameter 5.0 mm) were used and thermally conductive adhesive was added to assure good thermal contact with the heat exchanger. Prior to each experiment, a thermal cleaning of the traps was conducted by heating up to 225 °C to assure all relevant traps were empty at the start of the experiment. After each charging by excitation sources above mentioned, the sample
was kept in the dark for a certain fading period with a controlled ambient temperature. A constant heating rate of 1 K s\(^{-1}\) was employed for the heating stage. A full emission spectrum with spectral shapes and intensities was recorded at each temperature by using a ProEM1600EMCCD camera connected to a 300 mm monochromator (Princeton Instruments). TL intensity was recorded by integrating the TL emission spectra from 500 nm to 600 nm. The maximum temperature of 220 °C was fixed and no higher temperature was applied to restrain the deleterious thermal quenching effects. Furthermore, the activation energy of trap (trap depth) was calculated by simulating the TL glow curves, following the Randall-Wilkins method with the equation\(^{[40, 41]}\).

\[
I(T) = \int_0^\infty \frac{s}{\beta} N(E) f_0(T) \exp \left\{ -\frac{E}{kT} \right\} \times \exp \left\{ -\frac{s}{\beta} \int_{T_0}^{T'} \exp \left\{ -\frac{E}{kT'} \right\} dT' \right\} dE
\]  

(1)

The obtained trap parameters from the TL glow curves were also utilized as input values for the simulation of the persistent luminescence decay profiles\(^{[42]}\).

\[
I(t) = \int_0^\infty s N(E) f_0(T) e^{-E/kT} \exp \left\{ -st e^{-E/kT} \right\} dE
\]  

(2)

The simulation of the afterglow was made for various ambient temperatures (from \(-100\) °C to 100 °C).

2.4. Glow-in-the-dark applications

20 mL commercial printing ink was mixed with 0.4 g fine powder of Li\(_2\)ZnGeO\(_4\):Mn\(^{2+}\) prepared by MASS method. The mixture was mechanical stirring for 30 minutes, and the as-obtained homogeneously dispersing suspension was employed as luminescent ink for screen-printing. Patterns was printed using the luminescent ink on a piece of A4 paper by a brush. A commercial flat printing screen with designed patterns was applied and the printed paper was dried overnight at room temperature. The temperature was fixed at \(-18\) °C in freezer and photographs of printed patterns were taken using a mobile phone (Huawei).
3. Results and Discussion

3.1. Crystalline Phase and Luminescence Properties

X-ray diffraction (XRD) patterns of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphors prepared upon different durations of MASS reaction are shown in Figure S1. All diffraction peaks match well with the standard XRD reference of Li$_2$ZnGeO$_4$ except several Li$_2$GeO$_3$ impurities (marked by violet asterisks) in each XRD pattern. Li$_2$ZnGeO$_4$ crystalizes into the monoclinic crystal system with space group $P2_1/n$[43]. The Li$_2$ZnGeO$_4$ host lattice is built up by three tetrahedral units of [LiO$_4$], [ZnO$_4$], and [GeO$_4$], as illustrated in Figure S2(a). Zn$^{2+}$ is surrounded with four oxygen ions forming the tetrahedron unit. Dopants of Mn$^{2+}$ are expected to occupy Zn$^{2+}$ sites since they have the same valence state and similar ionic radii ($R_{\text{Mn}^{2+}}$ = 0.66 Å, CN = 4; $R_{\text{Zn}^{2+}}$ = 0.6 Å, CN = 4)[44]. The incorporation of Mn$^{2+}$ dopants has no significant change on the host lattice. To improve the purity of the Li$_2$ZnGeO$_4$ crystalline phase, excess amounts of ZnO precursors were used for MASS synthesis. However, the Li$_2$GeO$_3$ phases (see crystal structure in Figure S2(b)) were still present in XRD patterns of the samples with excess ZnO (in Figure S3). In contrast, Li$_2$GeO$_3$ phases were not detected in samples obtained by conventional solid-state reaction (SSR) at 1200 °C, as seen in Figure S4. For MASS synthesis, the small amount of Li$_2$GeO$_3$ phases companied the formation of the Li$_2$ZnGeO$_4$ host lattice, even by employing long-time microwave irradiation (up to 36 min). Usually, a 30-min MASS reaction in our lab-built setup could reach a temperature up to 1250 °C[47]. Therefore, the presence of secondary phases can be attributed to the fast MASS reaction process, rather than an insufficient reaction temperature. In fact, a 24-min MASS reaction was sufficient for the formation of Li$_2$ZnGeO$_4$ as shown in Figure S1.
Figure 1. (a) Photoluminescence and photoluminescence excitation spectra of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared using the MASS method; (b) Persistent luminescence excitation spectrum by monitoring 536 nm; (c) Persistent luminescence decay profile as a function of time.

Figure 1(a) presents the room-temperature (RT) photoluminescence (PL) and photoluminescence excitation (PLE) spectra of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by the MASS method. In this work, the sample obtained by a 30-min MASS reaction was taken as a benchmark. Monitored emission at 536 nm, the PLE spectrum consists of a broad band with a maximum at 278 nm, which is slightly shifted to longer wavelength compared to the excitation...
peak at 270 nm from sample prepared by SSR (in Figure S5). These excitation bands are usually attributed to the charge-transfer transition of Mn$^{2+}$ ions in Li$_2$ZnGeO$_4$ host from previous literature$^{[43, 45]}$. However, transitions of $^6$A$_1$ to excited states of Mn$^{2+}$ were not observed in samples prepared by MASS or SSR method, which may be ascribed to the instrument resolution and insufficiently low temperature. Upon 278 nm excitation, the emission spectrum shows a broad-band profile centered at 536 nm. The strong green emission is typical for Mn$^{2+}$ ions due to the spin forbidden $d$–$d$ transition ($^4$T$_1$ → $^6$A$_1$)$^{[46]}$. It is worth noting that green emission is usually found in Mn$^{2+}$-activated phosphors if Mn$^{2+}$ ions are situated in tetrahedral environment, whereas octahedrally coordinated Mn$^{2+}$ ions present orange to red emissions due to the larger energy splitting of the excited state and the lower energy of Mn$^{2+}$ emission in octahedral crystal fields$^{[46, 47]}$. There are only tetrahedral units in the case of Li$_2$ZnGeO$_4$ host (see Figure S2). As discussed above, Mn$^{2+}$ dopants are expected to occupy the tetrahedrally-coordinated Zn$^{2+}$ sites, consistent with the observed green emission. After excitation with a 254 nm UV lamp, green persistent luminescence can be observed. The persistent luminescence excitation spectrum of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor is given in Figure 1(b), and it provides the effective wavelength range for charging green persistent luminescence. It is seen, by comparing Figures 1(a) and 1(b), that the PL excitation spectrum and the excitation spectrum for persistent luminescence are identical within the limits of accuracy. Decay profiles were monitored at 536 nm after 3-min excitation with monochromatic light ranging from 230 to 500 nm. The persistent luminescence intensity was plotted as a function of the excitation wavelength by integrating the decay profiles during the first 2 minutes of afterglow, for instance, as illustrated in excitation-wavelength dependent persistent luminescence decay profiles of Figure S6. The excitation of commonly used 365 nm UV lamp cannot induce green persistent luminescence from Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor. Furthermore, persistent luminescence decay profile of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor after 10-min charging at the wavelength of 270 nm excitation were recorded at room temperature, as given in Figure 1(c). The afterglow intensity decreases quickly in the first
several minutes and then decays slowly. The shape of the 1-hour persistent luminescence decay curve can be analyzed with multi-exponential components, indicating different decay processes due to the presence of multiple traps. Traps information of samples prepared by MASS or SSR method is discussed in detail later. It is interesting to mention that the emission peak shows a slight redshift when employing a longer excitation wavelength (see the emission spectra of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor in Figure S7 and S8). Moreover, the thermal quenching behavior of the Li$_2$ZnGeO$_4$:Mn$^{2+}$ emission was investigated. The emission intensity was normalized and plotted by integrating the temperature-dependent emission spectra from 500 nm to 600 nm in the temperature range of RT to 220 °C (see Figure S9). At 150 °C, the integrated emission intensity of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor remained about 80% of that at RT. As expected, the emission intensity decreases along with increasing ambient temperature, mainly due to the delocalization of excited electrons from the excited state to the ionized state in Mn$^{2+}$ doped phosphors at high temperature$^{[48, 49]}$.

### 3.2. Trap Distribution upon SSR and MASS Synthesis

Traps information of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor by SSR method was investigated in this part. Charging duration dependent TL glow curves are shown in Figure 2(a). The number of filled traps increased with a longer charging duration (for example, a 10-min UV charging). A broad TL intensity profile covering from −30 °C to 100 °C, was measured with a maximum around 55 °C, a shoulder around 35 °C and continuous TL signals below RT. The obtained TL profile is in consistent with previously reported TL results of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphors, but with more traps distributed below RT due to the different starting temperatures of TL measurements$^{[42]}$. These shallow traps, distributed below RT, could not be observed when Li$_2$ZnGeO$_4$:Mn$^{2+}$ was charged at RT. The temperature dependent afterglow output was studied
via a series of TL measurements (without fading or with 20 min fading between UV charging and heating stage) at different ambient temperatures. It is clear that a 20-min fading at each temperature can lead to the thermal release of previously captured charge carriers, mainly from the lower trap occupation energy levels, as shown in Figure 2(b) and (c). The total amounts of charge carriers trapped before fading (TL1) and after 20-min fading (TL2) were obtained by integrating TL glow curves in Figure 2(b) and (c), respectively. Thus, the temperature dependent afterglow output was extracted from TL1 and TL2 by subtracting the areas under both curves, as illustrated in Figure 2(d). The maximum afterglow output or the optimum working temperature, $T_{optimum}$, of Li$_2$ZnGeO$_4$:Mn$^{2+}$ prepared by SSR, was confirmed to be around 20 °C, indicating a great promise for room-temperature glow-in-the-dark applications[15]. Although the value of $T_{optimum}$ of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by SSR is located at around RT, the afterglow output at lower temperatures is not be negligible, due to the presence of traps occupied at lower energy levels. Figure S10 presents TL glow curves of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor (without fading or with 30-min fading) after charging at 25 °C and −45 °C, and their total afterglow outputs at −45 °C and 25 °C are also given in the insert. The afterglow output at −45 °C is more than half of that at RT, indicating a broad trap distribution of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor made by SSR method and potential of the material for low temperature persistent luminescence applications.
Figure 2. Trap information of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by SSR. (a) TL glow curves upon different UV charging durations (from 1 min to 10 min); (b) TL glow curves at different charging temperatures without fading; (c) TL glow curves at different charging temperatures with 20-min fading (fading temperature corresponded to each charging temperature); (d) Charge carriers trapped before (TL1) and after 20-min fading (TL2) as a function of charging temperature. Total afterglow output (TL1-TL2) within 20 minutes as a function of charging temperature was obtained from the difference between TL1 and TL2.

More importantly, trap re-distribution upon light stimulation was identified by employing the following experimental TL procedure. As shown in Figure 3(a), three experimental stages were involved in the trap re-distribution experiment. Charging of the Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor (Stage-I, $T_{charge} = 0 ^\circ C$), was followed by a rapid cooling to light stimulation temperature (here, $T_{stimuli} = -60 ^\circ C$). The sample was held at $T_{stimuli}$ for 2 minutes with 420 nm LED on and LED off, respectively (Stage-II). Subsequently, a TL profile was recorded by heating up to 220 $^\circ C$
with a fixed heating rate of 60 °C/min (Stage-III). It should be mentioned that two different light sources were used, a 254 nm UV lamp for charging, and a 420 nm light emitting diode (LED) for light stimulation. Here, the 420 nm LED cannot fill traps, as seen from the persistent luminescence excitation spectrum. Figure 3(b) presents a comparison of the trap distributions of the sample before (red curve, TL\textit{LED OFF}) and after 420 nm light stimulation (blue curve, TL\textit{LED ON}). It is clear that charge carriers were transferred from green to orange region, and they were re-distributed upon light stimulation.

Furthermore, the TL glow curve of the Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by MASS was recorded and compared with that of sample made by the SSR method (see Figure S11). For the sample prepared by MASS, traps were distributed at lower energy levels. Although the same TL parameters were employed (UV charging at −40 °C, no fading time, and a constant heating rate of 60 °C/min), the traps in samples prepared by SSR and MASS exhibited a big difference. Moreover, a series of TL measurements at different charging temperatures and their fading experiments were performed for the sample made by MASS, as shown in Figure 4. The difference between solid lines (without fading) and dotted lines (after 20-min fading) indicates a large amount of charge carriers were released, even at very low temperatures, such as -60 °C. As presented from the insert of Figure 4, the value of $T_{optimum}$ of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by MASS is confirmed to be at −60 °C, rather than 20 °C (the value of $T_{optimum}$ of Li$_2$ZnGeO$_4$:Mn$^{2+}$ prepared by SSR is 20 °C). In addition, the presence of strong signals at the starting points of TL glow curves (without fading, solid lines in Figure 4) also indicates considerable afterglow at low temperatures.
Figure 3. (a) A schematic outline of the experimental TL procedure containing three stages for a trap re-distribution experiment. UV charging of the Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor (Stage-I, $T_{charge} = 0 \, ^{\circ}\text{C}$), was followed by a rapid cooling to light stimulation temperature ($T_{stimuli} = -60 ^{\circ}\text{C}$). The sample was held at $T_{stimuli}$ for 2 minutes with 420 nm LED on and LED off, respectively (Stage-II). After Stage-II, TL profile was recorded by heating up to 220 $^{\circ}\text{C}$ with a fixed heating rate of 60 $^{\circ}\text{C}$/min (Stage-III); (b) Trap distributions of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor before (red curve, TL$_{LED \, OFF}$) or after light stimulation (blue curve, TL$_{LED \, ON}$). Traps were re-distributed upon light stimulation, and the two regions involved were filled in green and orange.
Figure 4. Traps information of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by MASS. Charging temperature dependent TL glow curves were plotted in solid lines (without fading) or dotted lines (after 20-min fading). The ambient temperatures for charging and fading were fixed at −60 °C, −40 °C, −20 °C and 20 °C, respectively. The insert presents the afterglow output within 20 minutes as a function of ambient temperature.

3.3. Persistent Luminescence at extremely low temperatures

Low-temperature green persistent luminescence from Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by MASS is discussed in this part. Luminescent inks containing the samples were used for low-temperature glow-in-the-dark application, as demonstrated in Figure 5. A piece of A4 paper was printed with bamboo patterns (see Experimental Section). Images of bamboo patterns were given under daylight without UV charging, or glowing in-the-dark after cessation of UV irradiation in Figure 5 (a) and (b). The patterns were fully charged and kept at low temperature in freezer, in which the temperature was fixed at −18 °C in Figure 5(c). Bright light emissions
were observed within an hour, and clear images of bamboo patterns were recorded during de-trapping processes at low temperature in Figure 5(d). Similarly, afterglow images of emergency sign at low temperature were also demonstrated (see Figure 5(e)). Importantly, such excellent low-temperature persistent luminescence performance offers great promise for outdoor glow-in-the-dark applications, especially at cold night in winter. Efficient charging at low temperatures and a broad distribution of shallow traps (see Figure 6) determine its excellent low-temperature persistent luminescence performance (as demonstrated in Figure 5). In general, insufficient charging of persistent phosphor happens at extremely low temperature, for instance, Eu$^{2+}$ and Dy$^{3+}$ co-doped Sr$_2$MgSi$_2$O$_7$ blue-emitting persistent phosphor$^{[50]}$, provides an indication of a thermal barrier for trapping in this case. In contrast, there is an efficient charge-trapping process of Li$_2$ZnGeO$_4$:Mn$^{2+}$ without occurrence of thermal barriers, as presented in Figure 6(a). UV charging at −80 °C provides the strongest TL glow curve due to the completely trap filling over a wide temperature range. The difference between TL glow curves with 30-min fading (blue curve) and no fading (red curve) is only apparent at the low temperature side (in Figure 6(b)), suggesting a large amount of released energy from shallow traps. Persistent luminescence decay profiles of Li$_2$ZnGeO$_4$:Mn$^{2+}$ at extremely low temperature (−80 °C) were measured by integrating the emission from 500 nm to 600 nm, as recorded in Figure 6(c). Moreover, the activation energy of trap (trap depth) was calculated by simulating the TL glow curves, following the well-established Randall-Wilkins equation (see experimental part). The relevant trap depth and trap width of the fitting function were extracted from above-mentioned Randall-Wilkins method. The obtained trap parameters from the TL glow curves can be also utilized as input values for the simulation of the persistent luminescence decay profiles at different temperatures. For example, the TL glow curve of Li$_2$ZnGeO$_4$:Mn$^{2+}$ made by SSR contains two peaks, and the corresponding trap depth was calculated to be 0.812 eV and 0.865 eV, respectively. For Li$_2$ZnGeO$_4$:Mn$^{2+}$ made by MASS, the trap depth was calculated to be 0.665 eV. The simulated persistent luminescence decay curves of Li$_2$ZnGeO$_4$:Mn$^{2+}$ made by
MASS are shown in Figure S12. Clearly, the simulated afterglow performance at low temperature (such as -40 °C or -20 °C) is better than that at room temperature, which is in good agreement with the experimental low-temperature afterglow performance in the manuscript. Such low-temperature visible (green-emitting) persistent luminescence may find its application at extreme conditions, such as optical thermometer and smart textiles\cite{23, 51, 52}. The preparation method is strongly associated with trap properties in the case of Li$_2$ZnGeO$_4$:Mn$^{2+}$, thus determining the scope of applications of trap-controlled persistent phosphors. On the other hand, trap re-distribution upon light stimulation was also identified in Li$_2$ZnGeO$_4$:Mn$^{2+}$ prepared by MASS (in Figure 6(d)), following the TL procedure above-mentioned. Upon 420 nm light stimulation, charge carriers were observed to transfer towards lower energy levels. Figure S13 presents TL glow curves after variable illumination durations (0 s, 30 s, 60 s, 120 s) from 420 nm LED. An optical de-trapping process of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor from MASS at low temperature (−80 °C) was observed upon 420 nm illumination. All these results indicate the presence of optically active traps within the Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor.
Figure 5. Low-temperature glow-in-the-dark applications. The paper was printed with bamboo patterns using Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor by MASS. Images of bamboo patterns were under (a) daylight, or (b) glowing in-the-dark after cessation of UV irradiation. The patterns were fully charged and kept in freezer (c). The temperature was fixed at −18 °C in freezer. (d) Afterglow (AG) images of bamboo patterns at low temperature. (e) AG images of emergency sign at low temperature.
Figure 6. (a) Charging temperature dependent TL glow curves of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by MASS. The charging temperature was chosen at low temperature range (−80 °C, −60 °C, −40 °C, −20 °C and 0 °C); (b) TL glow curves without fading (red curve) and after 30-min fading (blue curve); (c) Persistent luminescence decay profile at −80 °C; (d) Trap distributions of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor before (red curve, TL$_{LED \ OFF}$) or after light stimulation (green curve, TL$_{LED \ ON}$). The charging and light stimulation sources were a 254 nm UV lamp and 420 nm LED, respectively.

3.4. Trap Re-shuffling towards Two Directions

To further study the charge transfer processes and physical mechanisms, high-energy X-ray irradiations were also employed. Figure 7(a) displays TL glow curves upon X-ray irradiation for different durations (from 1 min to 25 min). Variable durations of X-ray irradiation were performed at RT and the TL parameters were kept constant. Different from UV charging, TL
glow curves upon X-rays irradiation exhibited two peaks centered around 60 °C and 145 °C. The filling of deep traps at 145 °C needs a longer time (more than 10 min), indicating there are different charging processes for the two traps centered at 60 °C and 145 °C. In addition, simulation was also made for the TL glow curve upon X-ray irradiation (at RT). The trap depth for the two traps (in Figure 7 (a)) was calculated to be 0.859 eV and 1.088 eV, respectively. Moreover, a trap re-distribution experiment was performed, following the TL procedure shown in Figure 3(a). 15-min X-ray irradiation of Li₂ZnGeO₄:Mn²⁺ phosphor \(T_{\text{charge}} = 25 \, ^\circ\text{C}\), was followed by rapid cooling to light stimulation temperature, \(T_{\text{stimuli}}\), and the sample was held at \(T_{\text{stimuli}} = -80 \, ^\circ\text{C}\) (b), \(-60 \, ^\circ\text{C}\) (c) or \(-40 \, ^\circ\text{C}\) (d)) for 1 minute with 420 nm LED on and LED off, respectively. In Figure 7(b), (c), and (d), TL glow curves were recorded without light stimulation (TL1, red curve, LED off) or after 1-min light stimulation (TL2, green curve, LED on). Impressively, trap re-shuffling towards both lower energy level (shallow traps) and higher energy levels (deep traps) upon light stimulation was identified. To the best of our knowledge, it is the first observation of the two-directions trap re-shuffling behavior in persistent phosphors ever reported. All these results indicate there are optically active trapping defects with photo-stimulated re-trapping behavior and the charge carrier transfer among different traps is possible upon appropriate external stimulation, such as light stimulation. Thus, the effect of re-trapping, which is often ignored elsewhere, should be taken into consideration in the Li₂ZnGeO₄:Mn²⁺ persistent phosphor.

The possible mechanism behind trap re-distribution or the two-directions trap re-shuffling is proposed in Figure 8. As a schematic representation, it is assumed both trapping and de-trapping processes occur through the intervention of the conduction band. Upon X-ray irradiation at RT (charging step), a large number of electrons are excited from the valence band (VB) to the conduction band (CB), resulting in the formation of electron-hole pairs. These
excited electrons and holes can lead to the typical emission from Mn$^{2+}$ ions ($^4T_1 \rightarrow ^6A_1$ transition), as given in Figure 8(a). Meanwhile, the excited electrons (or holes) are captured by traps with energy levels higher than the ambient thermal energy. On the basis of the TL results, there is a broad trap distribution upon X-ray irradiation, with two main peaks centered around 60 $^\circ$C and 145 $^\circ$C. After the cessation of the X-ray excitation, trap release happens at RT, giving rise to persistent luminescence in Figure 8(b). When the ambient temperature drops down to the low temperature of $T_{stimuli} (-80$ $^\circ$C, $-60$ $^\circ$C or $-40$ $^\circ$C), these charge carriers are still captured and they cannot be released at ambient temperature due to the lack of thermal activation energy, as shown in Figure 8(c). Following the TL procedure shown in Figure 3(a), 15-min X-ray irradiation was performed on Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor at 25 $^\circ$C. By rapid cooling to light stimulation temperature (such as -80 $^\circ$C), 1-minute light stimulation at -80 $^\circ$C (with 420 nm LED on or off) was made before heating up. Without light simulation (420 nm LED off), only the two peaks (with trap depth 0.859 eV and 1.088 eV, respectively) were observed. The filling of deep traps (1.088 eV) and medium traps (0.859 eV) is due to the pre-irradiation (15-min X-ray irradiation) at 25 $^\circ$C. In fact, there are shallow traps in Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor made by MASS (as discussed above), but the shallow traps were not filled (or were instantly emptied) due to the ambient thermal energy at 25 $^\circ$C. Thus, for the presence of deep traps (1.088 eV) and medium traps (0.859 eV) without light simulation in Figure 7(b) is reasonable. If the 420 nm LED is on (with light simulation at -80 $^\circ$C), de-trapping and re-trapping may happen in the phosphor. Upon external light stimulation, charge carriers are released, leading to light emission, as illustrated in Figure 8(d). In the meantime, a proportion of charge carriers are re-trapped within trap energy levels. It should be mentioned that there is a broad distribution of trap energy levels (-80 $^\circ$C to 100 $^\circ$C) in Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by MASS. However, in the first charging step upon X-ray irradiation at RT, only higher energy levels (moderate and deep-lying traps) were filled (see illustration of traps information after X-ray irradiation in Figure 8(e)). Charge carriers in lower energy levels (shallow traps) could be rapidly emptied due to
the ambient thermal energy (at RT). Upon light stimulation, re-trapping happens within shallow, medium and deep traps in Figure 8(f) and (g), thus showing the two-directions trap re-shuffling behavior in Figure 8(h). It should also be noted that trap filling cannot be achieved with 420 nm light simulation. Therefore, charge carriers from the deep trap (1.088 eV) and medium trap (0.859 eV) are released and re-trapped within the trap energy levels. However, the ratio of re-trapping rate to de-trapping rate ($\Delta v = \frac{v_{\text{re-trapping}}}{v_{\text{de-trapping}}}$) is different among deep, medium, and shallow traps with extra external energy. For medium traps, $\Delta v < 1$; However, for shallow and deep traps, $\Delta v > 1$. In the case of shallow traps, charge carriers may come from both medium and deep traps. All these observations indicate re-trapping happens within defect energy levels. Upon photo-stimulation, charge carriers indeed transfer among different traps, or at least in the case of Li$_2$ZnGeO$_4$:Mn$^{2+}$ persistent phosphor.

Figure 7. (a) TL glow curves upon X-ray irradiation at RT for different durations (from 1 min to 25 min). TL profiles were recorded by heating up to 220 °C with a fixed heating rate of
60 °C/min; (b), (c), (d) Trap distributions of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor without light stimulation (TL1, red curve, LED off) or after 1-min light stimulation (TL2, green curve, LED on). 15-min X-ray irradiation was followed by a rapid cooling to light stimulation temperature ($T_{stimuli}$). The sample was held at $T_{stimuli}$ for 1 minute with 420 nm LED on and LED off, respectively. $T_{stimuli}$ was chosen at −80 °C (b), −60 °C (c) or −40 °C (d).

**Figure 8.** Proposed mechanism of trap re-distribution in Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor. (a) Charging at RT, (b) persistent luminescence at RT, (c) fading at low temperature, (d) trap releasing and re-shuffling upon light stimulation. Illustrations of traps information after (e) X-ray irradiation at RT, (f) the start of light stimulation, (g) trap re-shuffling at low temperature, and (h) trap re-distribution after light stimulation.
4. Conclusion

In summary, green-emitting persistent phosphors Li$_2$ZnGeO$_4$:Mn$^{2+}$ are prepared via conventional SSR and MASS synthesis. Sample by SSR shows the optimum working temperature, $T_{\text{optimum}}$ of 20 °C, indicating its potential advantages for room-temperature night-vision application. Trap distribution of Li$_2$ZnGeO$_4$:Mn$^{2+}$ is modulated upon a simple MASS approach. Low-temperature green emitting persistent luminescence is achieved via MASS synthesis due to the modulation of trap distribution into shallow trap range. Such an appealing shallow-trap-occupation feature offers great promise in low-temperature glow-in-the-dark applications. Moreover, a series of temperature dependent trapping, de-trapping and re-trapping measurements are designed to shed light on trap information. More impressively, trap re-shuffling is identified towards both lower energy level (shallow traps) and higher energy levels (deep traps) upon 420 nm light stimulation. These findings indicate there are optically active trapping defects with photo-stimulated re-trapping behavior in Li$_2$ZnGeO$_4$:Mn$^{2+}$ persistent phosphor. This work not only provides a fundamental advance in revealing re-trapping behavior, but also offers a guidance for the modulation of trap distribution in persistent phosphor using a facile approach.

Supporting Information
Supporting Information is available online or from the author.

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References


[40] J. T. Randall, M. H. F. Wilkins, Phosphorescence and electron traps-I. The study of trap


Modulating Trap Distribution of Persistent Phosphors upon Simple Microwave-assisted Solid-state Reactions

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Graphical abstract

Trap distribution of Li₂ZnGeO₄:Mn²⁺ is modulated into shallow trap range upon a simple microwave-assisted solid-state approach. Trap re-shuffling is identified towards both lower energy level (shallow traps) and higher energy levels (deep traps) upon light stimulation. This work provides a fundamental advance in revealing re-trapping behavior and offers a guidance for the modulation of trap distribution using a facile approach.
Supporting Information

Modulating Trap Distribution of Persistent Phosphors upon Simple Microwave-assisted Solid-state Reactions

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Figure S1. XRD patterns of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphors prepared using microwave-assisted solid-state (MASS) method. Different durations of MASS reaction were employed from 24 min to 36 min with a duration interval of 2 min.
**Figure S2.** Crystal structures of Li$_2$ZnGeO$_4$ (a) and Li$_2$GeO$_3$ (b). The elements of Li, Ge, Zn and O are depicted in green, blue, orange and red, respectively.
Figure S3. XRD patterns of samples with excess ZnO precursor prepared by MASS.

Figure S4. XRD patterns of Li₂ZnGeO₄:Mn²⁺ phosphor prepared upon conventional solid-state reaction (SSR) at 1200 °C. XRD patterns of standard Li₂ZnGeO₄ reference were also illustrated for comparison.
Figure S5. Photoluminescence and photoluminescence excitation spectra of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by conventional SSR method.

Figure S6. Excitation-wavelength dependent persistent luminescence decay profiles of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by MASS.
Figure S7. Emission spectra of Li₂ZnGeO₄:Mn²⁺ phosphor prepared by MASS reaction, monitoring at different excitation wavelengths (from 250 nm to 350 nm).

Figure S8. Normalized emission spectra of Li₂ZnGeO₄:Mn²⁺ phosphor prepared by MASS reaction, monitored at different excitation wavelengths (from 250 nm to 350 nm).
Figure S9. Thermal quenching behavior of Li$_2$ZnGeO$_4$:Mn$^{2+}$ phosphor prepared by MASS reaction. The intensity was normalized and plotted by integrating the temperature-dependent emission spectra from 500 nm to 600 nm.
**Figure S10.** TL glow curves of Li$_2$ZnGeO$_4$·Mn$^{2+}$ phosphor from SSR method (without fading or with 30-min fading) after charging at 25 °C and −45 °C. The differences between two TL glow curves at each temperature were filled in red and green. Insert plotted the total afterglow output at −45 °C and 25 °C.

**Figure S11.** Comparison of TL glow curves of Li$_2$ZnGeO$_4$·Mn$^{2+}$ phosphor from MASS and SSR methods. The same TL parameters were employed (UV charging at −40 °C, no fading time, and a constant heating rate of 60 °C/min).
Figure S12. Simulated persistent luminescence decay curves of Li$_2$ZnGeO$_4$:Mn$^{2+}$ made by MASS, at different ambient temperatures.
Figure S13. Optical de-trapping process of Li2ZnGeO4:Mn2+ phosphor prepared using MASS upon 420 nm illumination at −80 °C. TL glow curves were recorded after variable illumination durations (0 s, 30 s, 60 s, 120 s) using a 420 nm LED.