Construction of a novel mechanoluminescent phosphor \( \text{Li}_2\text{MgGeO}_4\cdot\text{Mn}^{2+} \) by defect control†

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Lattice defect plays a significant role in the optical properties of elastic mechanoluminescent materials, which could be modulated by cationic non-equivalent replacement. Here, a series of novel mechanoluminescent phosphors \( \text{Li}_2-x\text{MgGeO}_4\cdot\text{Mn}^{2+} \) (0 ≤ x ≤ 0.025) were synthesized via a high-temperature solid-state reaction method in an ambient atmosphere. The defect type and its relationship with optical performance were clarified via X-ray photoelectron spectroscopy, electron spin resonance, and thermoluminescence spectroscopy. Along with the introduction of Mn ions, the trap levels of oxygen vacancies become shallow, which are beneficial to produce long afterglow and mechanoluminescence. This study offers a feasible approach for developing new functional materials via defect control in self-reduction systems.

1. Introduction

As an indispensable member of mechanoluminescence (ML) materials, elastico-ML materials, quantitatively displaying the magnitude of external force through luminescence intensity without structural failure, have gradually attracted widespread interest due to the merits of repeatable, real-time, and reliable stress sensing.1−3 By virtue of achieving mechano-optical conversion in the entire gamut, their potential application involves multiple fields, such as stress sensors, biological imaging, and anti-counterfeiting.4−6 Recently, some novel ML phosphors doped transition metals or rare-earth ions are reported to have a non-centrosymmetric framework and low force-sensing threshold, which can generate local piezoelectric field under external stimuli and induce carrier delamination to promote the material emitting light.7−9 For example, yellow-emitting \( \text{ZnS:Mn}^{2+} \)2, blue-emitting \( \text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+} \)10 red-emitting \( \text{LiNbO}_3:\text{Pr}^{3+} \)11 \( \text{Sr}_2\text{Nb}_2\text{O}_7:\text{Pr}^{3+} \)12 and \( \text{CaZnOS:Mn}^{2+} \).13 It is worth noting that mechanoluminescence always emerges along with long afterglow, which has a close relationship with lattice defects.14−16 Hence, defect regulation could be a viable way to construct novel ML materials.

Our previous studies have found that the non-equivalent substitution of Mn ions for cations in some phosphates can produce extrinsic defects and change the distribution of intrinsic trap levels, which are helpful to obtain the desirable ML materials.17,18 Interestingly, the commonality of these hosts is that the crystal lattice contains \([\text{PO}_4]\) units and can stabilize \( \text{Mn}^{2+} \) ions in ambient atmosphere. Hence, the ‘self-reduction’ system could be a suitable candidate to develop ML materials. It has been reported that several germanates can also realize the self-reduction from \( \text{Mn}^{4+} \) to \( \text{Mn}^{2+} \) in ambient atmosphere owing to the presence of the \([\text{GeO}_4]\) groups.19 Among them, \( \text{Li}_2\text{MgGeO}_4 \) (named as LMG) was selected as a promising matrix to produce ML by doping \( \text{Mn}^{2+} \) ions, which crystallizes in an orthorhombic system with the space group of \( \text{Pmn}_2_1 \) (no. 31) and has a non-centrosymmetric character.

Here, we design a series of green-emitting ML phosphors \( \text{Li}_2-x\text{MgGeO}_4\cdot\text{Mn}^{2+} \) (abbreviated as LMGM, 0 ≤ x ≤ 0.025) by the traditional high-temperature solid-state reaction method in an ambient atmosphere. The relationship between defects and optical performances was studied in detail via XPS, EPR, and ThL measurements. Intrinsic oxygen vacancies modulated via the introduction of Mn ions were demonstrated to form shallow trap levels in LMGM, which contribute to the self-reduction, long afterglow, and ML. Moreover, the schematic energy level diagram was also proposed to expound the corresponding mechanism between defects and different phenomena. This study broadens our choice of constructing novel optical functional materials via defect control in self-reduction systems.
2. Experimental

2.1. Sample synthesis

A series of Li$_{2-x}$MgGeO$_4$:Mn$^{2+}$ (0 ≤ x ≤ 0.025) phosphors were synthesized by a solid state reaction at high temperature in ambient atmosphere. Raw materials of Li$_2$CO$_3$ (99.99%), MgO (99.99%), GeO$_2$ (99.999%), and MnO$_2$ (99.99%) were thoroughly mixed and homogeneously ground in an agate mortar. Then, these stoichiometric mixtures were preheated in a crucible at 600 °C for 24 h to decompose the carbonates and eliminate water. After cooling to room temperature, the pre-sintered samples were reground, sintered at 1200 °C for 24 h, and then cooled down to room temperature naturally. The as-prepared samples were ground again for further measurements to evaluate the ML properties of the samples. An appropriate amount (1.5 g) of the calcined powders was weighed and tableted with a tablet press, and the sample was placed in a silica boat for high-temperature annealing (1200 °C, 12 h). Finally, the obtained disc-shaped samples were used directly in the ML measurements.

2.2. Characterization

Powder XRD patterns were recorded on a D8 ADVANCE diffractometer (X’Pert Pro, PANalytical B. V., Netherlands) operating at 40 kV and 40 mA with Cu Kα radiation (λ = 1.5406 Å). The refinement data for the Rietveld analysis were collected in the step-scanning mode over the 20 range of 10°–140° at the interval of 0.017°. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra at room temperature were obtained using a fluorescence spectrometer (Edinburgh Instruments, FLS920, England) equipped with a 150 W Xenon lamp. The diffuse reflectance spectra were recorded using a UV/Vis/NIR spectrophotometer (Cary5000, America). X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific ESCALAB 250Xi (America) and calibrated to a C 1s electron peak at 284.8 eV. The X-band (9.844 GHz) EPR spectrum was recorded on a Bruker EMX-6/1 EPR spectrometer. The temperature-dependent luminescence properties were also studied using the same spectrophotofluorometer with a heating apparatus (Tianjin Orient Koji Co., Ltd, TAP-02). A grating spectrometer (ANDOR SOLIS, Kymera 328i, England) was used to obtain the ML spectra. The disc-shaped samples were placed at the bottom of a specially-made transparent tube, which faced the light inlet of the spectrometer. Then, a small ball that weighs 100 g was dropped vertically from different heights, which hits the surface of the samples. After irradiating with the UV light of 254 nm for 10 min, the long afterglow decay and thermoluminescence (ThL) curves were recorded using a fluorescence spectrometer and thermoluminescence meter (FJ427A1, CNCS, China), respectively.

3. Results and discussion

3.1. Crystal characterization

The XRD patterns of Li$_{2-x}$MgGeO$_4$:Mn$^{2+}$ (0 ≤ x ≤ 0.025) are displayed in Fig. 1a. All Bragg reflections match well with the standard Inorganic Crystal Database (PDF#04-008-1870), indicating that the incorporated Mn ions have negligible effects on the host lattice. Fig. 1b depicts the crystal structure of LMG, in which Li, Mg, and Ge are four-coordinated with O atoms, and the connected tetrahedra establish a rigid three-dimensional network structure by sharing the O vertices. Theoretically, all of the cationic sites could be suitable for the occupancy of Mn ions due to the same coordinated environment. According to the Shannon ion radius table (when CN = 4, r(Li$^+$) = 0.59 Å, r(Mg$^{2+}$) = 0.75 Å, r(Ge$^{4+}$) = 0.75 Å, r(Mn$^{2+}$) = 0.62 Å, r(Mn$^{4+}$) = 0.39 Å), Mn$^{2+}$ ions in the high-spin state (Mn$^{2+}$ HS) are most likely to substitute the Li$^+$ or Mg$^{2+}$ sites in the host. To further testify the site preference of dopants, the Rietveld refinement was implemented using the structure of LMG as the initial model using the TOPAS program.21,22 The possibility of Mn ions occupying all three cationic sites has been tested (Tables S1–4). Taking into account the negative or small occupancy ratio at Ge$^{4+}$/Mg$^{2+}$ sites, and the final unreasonable agreement factors, it is unexpected that Mn$^{2+}$ ions prefer to occupy the Li$^+$ sites. Then, the final refinement only considered the Mn$_{Li}$ occupancy and gave a reasonable result. The final plotting and the converged factors are presented in Fig. 1c and Tables S5 and 6. Clearly, the as-prepared Mn-doped samples crystallize iso-structurally to LMG in the regarded concentration range. In addition, the volume of the unit cell (175.17 Å$^3$) becomes larger than the initial one (174.74 Å$^3$) because Mn$^{2+}$ ions replace Li$^+$ sites, as illustrated in Fig. 1b.

3.2. Photoluminescence of Li$_{2-x}$MgGeO$_4$:xMn$^{2+}$

As shown in Fig. 2a, photoluminescence (PL) and photoluminescence excitation (PLE) spectra of Li$_2-x$MgGeO$_4$:xMn$^{2+}$ (x = 0.1%) are measured at room temperature. Monitored at the emission wavelength of 530 nm, the strong excitation band (235 nm–275 nm) originates from ligand–metal charge transfer (LMCT) from 3d$^6$ orbit of Mn$^{2+}$ to 2p$^6$ of O$^{2-}$.23,24 Besides, the peak at 430 nm belongs to the weak spin- and parity-forbidden transitions of Mn$^{2+}$ ions in the four-coordinated crystal field, which generally lead to green-emitting light.25,26 When excited by the light of 256 nm and 430 nm, the PL spectra exhibit similar emission bands centred at 530 nm with different intensities. Given the aforementioned results, The EPR spectroscopy was introduced as a useful technique to verify the valence state of the doped ions (Fig. 2b). Obviously, the sextet hyperfine resonance lines with a g factor of 2.016 (hv = ghH) around 3500 H correspond to the extended coupled exchange character of Mn$^{2+}$ ions due to the electron-nuclear interactions in a low-symmetric lattice environment.27–29 The high-resolution XPS spectrum of Mn 2p is also presented in Fig. S1.† The double fitting peaks at 641.63 eV and 652.71 eV coincide with the reported values of Mn$^{2+}$ ions, which prove the self-reduction process from Mn$^{4+}$ to Mn$^{2+}$ in the air for LMG.30,31 Enlightened by previous studies, the reason why the process happens in an ambient atmosphere is related to the lattice defects.17–19 In general, oxygen atoms are prone to escape from the lattice to form vacancies (V$_{O}$) at a high synthetic temperature, of which the trap levels can be regarded as the donors to
provide free electrons. The EPR spectrum was obtained to confirm the defect type (Fig. 2c), which displays the characteristic resonance signal with $g = 2.0041$ of VO for Li$_2$MgGeO$_4$:Mn$^{2+}$ ($x = 0.1\%$). Same conclusion can also be obtained from the high-resolution XPS spectrum of O 1s (Fig. S2†) that includes a deconvoluted peak at 531.17 eV. Accordingly, a defect-assisted model is put forward to explain the mechanism of self-reduction: when Mn$^{4+}$ ions enter the lattice, they will occupy the Li$^+$ sites to form positively charged defects $\text{Mn}^{\ddagger}\text{Li}$, and then the adjacent VO can provide enough free electrons to turn them into neutral defects (Fig. 2d).

Fig. 2e exhibits the PL spectra of Li$_{2-x}$MgGeO$_4$:xMn$^{2+}$ ($0.001 \leq x \leq 0.025$) at room temperature. It can be seen that the emission intensity increases with doped contents until reaching the maximum at $x = 0.015$ mol and then decreases as a result of concentration quenching. The effect is correlated with the Mn–Mn distance, which tends to be shortened with the increase of doping ions and facilitates non-radiative energy transfer between adjacent activators through exchange or multipolar interactions. For the sake of further certification, the following equation is utilized to calculate the critical distance ($R_c$):

$$R_c = 2\left[\frac{3V}{4\pi Nx}\right]^{1/3}$$

where $V$ is the unit cell volume of LMG, $x_c$ is the optimal concentration of Mn$^{2+}$ ions, and $N$ is the number of cationic sites per unit cell. The value is determined to be 22.32 Å, which is much longer than 5 Å. Thus, the multipolar interaction is deduced to be an essential factor for the process of concentration quenching. In addition, the peak positions of those emission bands are independent of dopant concentrations, which demonstrate that the mutual restriction or subtle modification between MnO$_4$ polyhedra hinders the further expansion of the lattice, as shown in Fig. 1b. The diffuse reflection (DR) spectra of the host and Li$_{2-x}$MgGeO$_4$:Mn$^{2+}$ ($x = 0.7\%$) were recorded and shown in Fig. S3.† A weak absorption from 250 nm to 300 nm is attributed to the intrinsic defects located in the forbidden gap. After doping Mn$^{2+}$ ions, one peak in the deep-UV region corresponds to the LMCT band in PLE,
Fig. 2  (a) The PLE and PL spectra of Li$_{2-x}$MgGeO$_4$:xMn$^{2+}$ ($x = 0.1\%$); the inset shows the photograph under UV light of 256 nm. (b) X-band powered EPR spectrum of Mn$^{2+}$ ions for Li$_{2-x}$MgGeO$_4$:xMn$^{2+}$ ($x = 0.1\%$). (c) X-band powered EPR spectra of V$^{4+}$ for Li$_{2-x}$MgGeO$_4$:xMn$^{2+}$ ($x = 0.1\%$). (d) Structural schematic of the V$^{4+}$-assisted self-reduction process. (e) The PL spectra of Li$_{2-x}$MgGeO$_4$:xMn$^{2+}$ ($0.001 \leq x \leq 0.025$) under the excitation of 256 nm; the inset shows the emission intensity versus Mn$^{2+}$ concentration. (f) The long afterglow spectra after delaying for different times of Li$_{2-x}$MgGeO$_4$:xMn$^{2+}$ ($x = 0.1\%$); the inset shows the long afterglow photograph after delaying 20 min in the darkroom.
and another located in the range from 400 nm to 500 nm should originate from the weak d–d transition of Mn\(^{2+}\) ions. Then, the Kubelka–Munk function is applied to further analyse the bandgap \(E_g\):\(^{41}\)

\[
\frac{1}{[F(R)\nu]^n} = A(\nu - E_g)
\]

where \(\nu\) is the photon energy, \(A\) is the proportional constant, and \(n = 1/2\) denotes the indirect band-gap transition. The absorption coefficient \(F(R)\) is calculated according to the following equation:\(^{42}\)

\[
F(R) = \frac{(1 - R)^2}{2R}
\]

The curve of \([F(R)\nu]^2\) to \(\nu\) is plotted, and the \(E_g\) can be obtained by extrapolating the linear portion to \([F(R)\nu]^2 = 0\). As shown in the inset in Fig. S3, the \(E_g\) of 4.48 eV in Li\(_{2-x}\)MgGeO\(_4\):Mn\(^{2+}\) (\(x = 0.7\%\)) is smaller than that in LMG, which manifests that the introduction of Mn\(^{2+}\) ions narrows the bandgap.

After illuminating about 10 min under ultraviolet light of 254 nm and delaying for different time periods, the long afterglow spectra of Li\(_{2-x}\)MgGeO\(_4\):Mn\(^{2+}\) (\(x = 0.1\%) were recorded and shown in Fig. 2f. The peak position remains unchanged with the increase in time, which is similar to that of PL. However, the intensity shows a decreasing trend, which reaches 55.54\% of the initial intensity at 60 min. In addition, the bright photograph taken after delaying 20 min in the inset of Fig. 2f demonstrates the potential application on emergency displays. Fig. S6 shows the ThL curve of the matrix. By virtue of Gaussian fitting, three signal peaks can be observed with the change of the dropping heights of the steel ball, which indicates that the samples are very sensitive to mechanical stimulation and have good application potential in the field of stress sensors as well as stress distribution visualization.\(^{46}\) As shown in Fig. 3e–g, the display effects of ML are dependent on the magnitude of stress.

3.3. Mechanoluminescence of Li\(_{2-x}\)MgGeO\(_4\):Mn\(^{2+}\)

By means of a free-falling steel ball (mass, 100 g) hitting the compressed powder samples from the height of 50 cm, the ML spectra were recorded and shown in Fig. 3a. All the curves have similar profiles and peak positions centred at 532 nm, indicating the same emitting centre for LMG. The inset shows the dependence of the ML intensity on the doping concentration, which reaches the maximum at \(x = 0.015\) mol and then decreases because of the strengthened non-radiative energy transfer between activators. As the surface of the sample was slightly scratched with a tweezer in a darkroom, bright green light was observed by naked eyes. Fig. 3b depicts the normalized ML and PL spectra of Li\(_{2-x}\)MgGeO\(_4\):Mn\(^{2+}\) (\(x = 0.7\%)\). Similar profile and peak wavelength between them demonstrate that the PL and the ML are both dated from the \(^4T_1(4S)\) \(\rightarrow\) \(^6A_1(6S)\) transition of Mn\(^{2+}\) ions. Noteworthily, the peak of ML shifts 6 nm towards a higher wavelength compared with that of PL, which can be ascribed to the enhancement of the local crystal field caused by lattice contraction under the specific mechanical stress. As the strength of the crystal field increases, the splitting degree of the energy level of the first excited state of Mn\(^{2+}\) ions becomes bigger, which reduces the energy required from the ground state \(^6A_1(6S)\) to the excited state \(^4T_1(4G)\).\(^{45}\) The CIE coordinate diagram (Fig. 3c) provides two photos (A and B) for Li\(_{2-x}\)MgGeO\(_4\):Mn\(^{2+}\) (\(x = 1.5\%)\) under the excitation of 283 nm and the friction stimulation, respectively. It can be seen that the colour purity of PL is better than that of ML. Under external forces, the local crystal field environment of activators presents various degrees of changes, which lead to multiple radiative transitions and lower the colour purity of ML. To further probe the relationship between external forces and elastic-ML performances, the falling height of the steel ball is adjusted within the range of 10 cm to 60 cm, which directly leads to the impulse change on the surface of the tableted sample. As shown in Fig. 3d, the peak positions are almost unchanged at various free-falling heights within a small interval of 10 cm. This could be because the tiny difference between the corresponding impacts is not enough to have an evident influence on the crystal field around the activators. Besides, the strengths of impact forces are clearly weaker than that of friction, which hardly induce an observable red-shift phenomenon similar to that shown in Fig. 3b. However, the ML intensity is linearly increased along with the change of the dropping heights of the steel ball, which indicates that the samples are very sensitive to mechanical stimulation and have good application potential in the field of stress sensors as well as stress distribution visualization.\(^{46}\) As shown in Fig. 3e–g, the display effects of ML are dependent on the magnitude of stress.

From the preceding discussion, lattice defects have an important effect on the phenomena of mechanoluminescence and long afterglow. Here, thermoluminescence (ThL) measurements can serve as a powerful method to discuss the trap distribution. Fig. S6f shows the ThL curve of the matrix. By virtue of Gaussian fitting, three signal peaks can be observed with the reasonable factor \(R^2 (0.99977)\), which are located at \(T_1 = 76.26 \degree C\), \(T_2 = 104.73 \degree C\), and \(T_3 = 134.93 \degree C\), respectively. Correspondingly, the depth of trap levels is obtained through the formula proposed by Urbach: \(E = T_m/500\), where \(T_m\) is the temperature of the ThL peak.\(^{37}\) It is demonstrated from different values (\(E_1 = 0.699\) eV, \(E_2 = 0.756\) eV, and \(E_3 = 0.816\) eV) that the energy levels of intrinsic defects appear in the forbidden band with a form of thermally averaged distribution. Furthermore, given the studies of Sakai and Matsuzawa, the aforementioned inappropriate distribution of trap levels is not conducive for ML and long afterglow theoretically in the host, which agrees with our findings via corresponding experimental tests. Nevertheless, for Li\(_{2-x}\)MgGeO\(_4\):Mn\(^{2+}\) (\(x = 1.5\%)\), the extra peak located at 174.48 \degree C with a depth of 0.895 eV should be attributed to the extrinsic Mn\(_{Mg}\) defects compared
with the result of LMG (Fig. 4a). Although the position is also not suitable for producing ML, it is very likely to release trapped electrons to adjacent shallower trap levels under external force and promote optical behavior. More importantly, the other three peaks with similar depths ($E_1 = 0.687$ eV, $E_2 = 0.745$ eV, and $E_3 = 0.813$ eV) to those of the host clearly become shal-
lower, which are related to the decline in the band-gap. In terms of the consequences mentioned above, it is concluded that long afterglow and ML in LMGM could originate from a part of intrinsic trap levels with suitable positions (0.60 eV–0.70 eV) modulated effectively by the introduction of Mn$^{2+}$ ions.

To sum up, the mechanism between lattice defects and optical performances can be explained, as shown in Fig. 4b: When irradiated by UV light, the electrons at VBM are pumped to CBM (the process ①). Then, a part of them relaxes non-radiatively to the lowest excited state $^4E(4D)$ of Mn$^{2+}$ ions through CB. Lastly, the green-emitting light can be produced via the electronic transitions from the excited state $^4E(4D)$ to the ground state $^6A_1(6S)$ (the process ②). In addition, under the stimulus of temperature or external mechanical force, some carriers easily captured by the shallow trap energy levels would detrap back to CB again and emit light via the same route (the process ●), which corresponds to the long afterglow and ML.

Conclusions

In this study, a series of green-emitting phosphors Li$_2$MgGeO$_4$:xMn$^{2+}$ were synthesized through a traditional high-temperature solid-state reaction method in ambient atmosphere. The typical Mn$^{2+}$-activated emission centred at 530 nm from $^4T_{1}(^4G) \rightarrow ^6A_{1}(^6S)$ transition is observed in PLE, PL, and DR spectra. The bivalent state of Mn ions is supported by XPS and EPR. The specific intrinsic defect is proved to be oxygen vacancies, which are the key factor to induce the self-reduction from Mn$^{4+}$ to Mn$^{2+}$ in the air. Besides, the Mn$^{2+}$-activated samples exhibit prominent behaviour of long afterglow and ML. Correspondingly, the relationship between lattice defects and optical properties is explained via ThL. Along with the introduction of Mn$^{2+}$ ions, the intrinsic trap levels can be effectively adjusted to suitable depths, which are responsible for the specific phenomena. This study offers a constructive prospect for developing novel functional optical materials via defect control in self-reduction systems.

Author contributions

Y. X. B. wrote the manuscript. L. W. and Y. Z. guided the research. Z. Z. Z., Y. F. K. and J. J. X. commented on this work.

Conflicts of interest

There are no conflicts to declare.

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Notes and references
