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Development of mechanoluminescent micro-particles $Ca_2MgSi_2O_7$:Eu,Dy and their application in sensors

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ABSTRACT

We have revealed that $Ca_2MgSi_2O_7$:Eu micro-particles emits green light under the application of a mechanical stress, called as mechanoluminescence (ML). The ML showed a similar spectrum as photoluminescence (PL), which indicated that ML is emitted from the same center of Eu^{2+} ions as PL. Such a green light of ML emission can be seen by the naked eye when pressing the sample. Furthermore, using lab-made AFM-ML system, the ML of single micro-particle under the application of micro force (10 μN) has been investigated.

1. Introduction

Mechanoluminescence (ML) is an interesting luminescence phenomenon, which is caused by mechanical stimuli such as grinding, cutting, collision, striking and friction [1]. It can convert mechanical energy into visible light efficiently. The ML sensor to detect environmental stress by emitting light is expected to be used widely in various applications such as the forecasting of an earthquake, the damage detection of an air plane or car [2,3]. In particular, the ML sensors have been found that they can be used as self-powered luminescence sensors [4]. It is well known that the human body can provide abundant mechanical energy, from body movement, muscle stretching, blood vessel contracting, and so on [5]. In this way, the mechanical energy provided by human body may be used as power to excite ML phosphors to emit luminescent signal [4]. This finding may be regarded as a guidance to design self-powered luminescence sensors.

In our previous results, we have found a series of silicate ML phosphors with various clolors, such as $Ca_2MgSi_2O_7$:Eu,Dy (green) [4], $SrCaMgSi_2O_7$:Eu (blue-greenish) [6], $Sr_2MgSi_2O_7$:Eu (blue) [7]. These phosphors possess not only strong ML intensity but also excellent stability. In particular, $Ca_2MgSi_2O_7$:Eu,Dy has good biocompatibility and bioactivity [8,9], which may be regarded as a potential candidate for self-powered biosensors. Usually the mechanical loads provided by human body are too small (usually uN) to be utilized efficently. How to covert weak mechanical stress to luminescence efficently is still a question. Currently, our group have developed an appartus that is constructed using an atomic force microscopy (AFM) and photomultiplier and observed ML light emission of $SrAl_2O_4$:Eu single particle induced by applying the micro force for the first time [10–13]. In this paper, $Ca_2MgSi_2O_7$:Eu,Dy micro-particles were prepared by a typical sol–gel method. Furthermore, using the new developed apparatus, ML properties of $Ca_2MgSi_2O_7$:Eu,Dy micro-particles were investigated. The results show that $Ca_2MgSi_2O_7$:Eu,Dy single micro-particle can covert the micro force to luminescent signal.

2. Experimental

$Ca_{1.98}MgSi_2O_7$:$Eu_{0.01}$, $Dy_{0..01}$ (CMSED) micro-particles were prepared by the typical sol–gel method [14]. The detailed experimental process was described below. Firstly, Tetraethyl orthosilicate (TEOS), water and nitric acid solution (1 mol L^{-1}) were mixed at a ratio of 1:8:0.16 (M/M/M). After strong stirring for 30 min, a certain amount of $Ca(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$ and $Dy(NO_3)_2 \cdot 2.7H_2O$ were added into the mixed solution. Then the mixtures were stirred for 5 h and transparent solutions can be obtained. The prepared solution was maintained at 60 °C for 6 h and dried at 120 °C for 1 day to obtain the dry gel. The dried gel was ground and preheated at 800 °C for 2 h in air. Finally, the powder was calcined at 1300 °C in reducing atmosphere (5%H_2/95%Ar) for 4 h to obtain the sample.

Phase purity and crystal structure of the obtained materials were determined by X-ray diffraction (XRD) (RINT-2000, RIGAKU). The ML spectrum measurement was carried out with a lab-made system, as reported previously [1], consisting of a universal testing machine (RTC-1310A, Orientec Corp.), a photon multichannel analyzer system (PMA100, Hamamatasu Photonics). The samples used to measure mechanoluminescence were made by mixing the powder (0.5 g) with an optical epoxy resin (4.5 g) to form a composite disk 25 mm in diameter and 15 mm thick. The AFM based on photo measurement system was consisting of AFM (Asylum MFP-3D), photomultiplier (PM), (R7400P, Hamamatsu) and oscilloscope (Tektronix, TDS 1012)/photocounter. The cantilever probe of AFM (OLYMPUS OMCL-AC160TS, Spring

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contact: 42 N/m, the radius of about 10 nm) provided micro force. The applied force was calculated automatically from the distortion of the AFM cantilever, measured from the laser deflection of the AFM [10]. Spectrofluorometer (FP6600, JASCO) equipped with a 150 W Xe lamp was used for PL measurement at room temperature.

3. Results and discussions

The XRD results (Fig. 1(a)) show that the prepared sample was chemically and structurally $Ca_2MgSi_2O_7$, which was consistent with the standard XRD pattern PDF 87-0046. This crystal structure has a tetragonal symmetry with a space group $P\bar{4}2_1m$. At the same time, the radius of Eu^{2+}(0.112 nm) and Dy^{3+}(0.099 nm) is very close to that of Ca^{2+}(about 0.099 nm) rather than Mg^{2+}(0.065 nm) and Si^{4+} (0.041 nm). Therefore, the Eu^{2+} and Dy^{3+} ions are expected to occupy the Ca^{2+} sites in the $Ca_2MgSi_2O_7$ host. The SEM image of the prepared sample was displayed in Fig. 1(b). From the SEM image, it can be observed that the prepared sample consists of particles with size distribution between 100 nm and 500 nm. In addition, there are some big aggregates existing due to high temperature heat-treatment.

The photoluminescence (PL) and ML spectra of $Ca_2MgSi_2O_7$:Eu,Dy are shown in Fig. 2(a). From this figure, it should be noted that PL and ML spectra are similar, only one emission band located at about 530 nm. This result suggests that the ML also originates from the same emitting center of Eu^{2+} ions and that the transition of Eu^{2+} ions between the $^8S_{7/2}$ ($4f^7$) ground state and the excited $4f^65d^1$ state is responsible for the green ML emission [4]. In addition, The CIE coordinates of CMSED is (0.3266, 0.6041). Based on the standard CIE coordinate–color graph (Fig. 2(b)), we can observe that this phosphor emit green light. The PL and ML images were shown in the inset. From these images, it can also be proved that PL and ML have the same green emission which further confirm that both emissions come from the same emitting center (Eu^{2+}). Why can CMSED micro-particles possess strong green ML? It is well known that the addition of Dy^{3+} in $Ca_2MgSi_2O_7$:Eu can induce the formation of trap centers, producing long afterglow [4]. Furthermore, $Ca_2MgSi_2O_7$ has a tetragonal structure with space group $P42_1m$. The

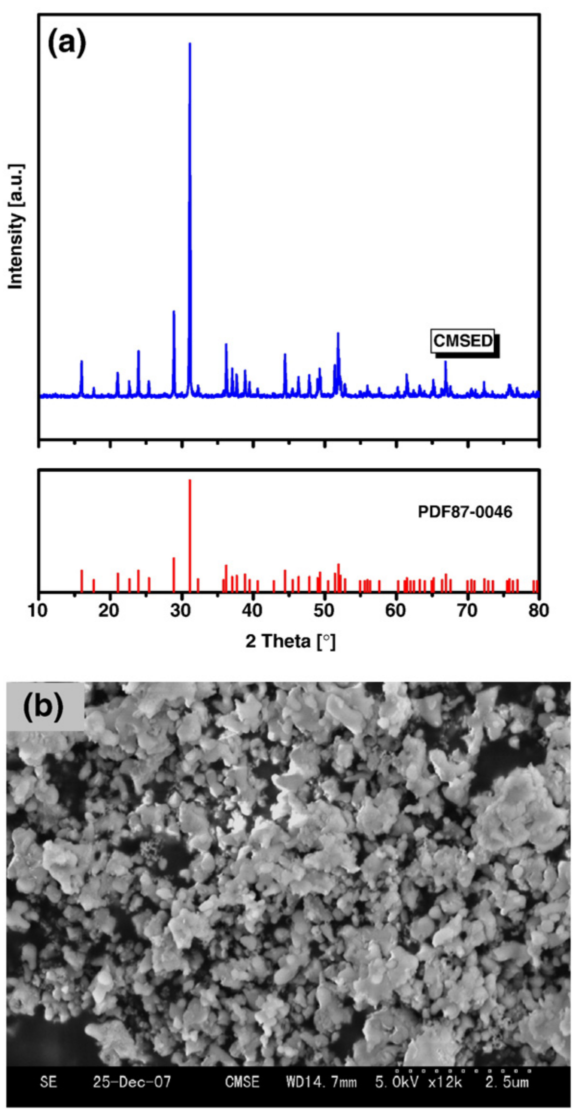

Fig. 1. (a) XRD pattern of the prepared sample. (b) SEM image of the prepared sample.

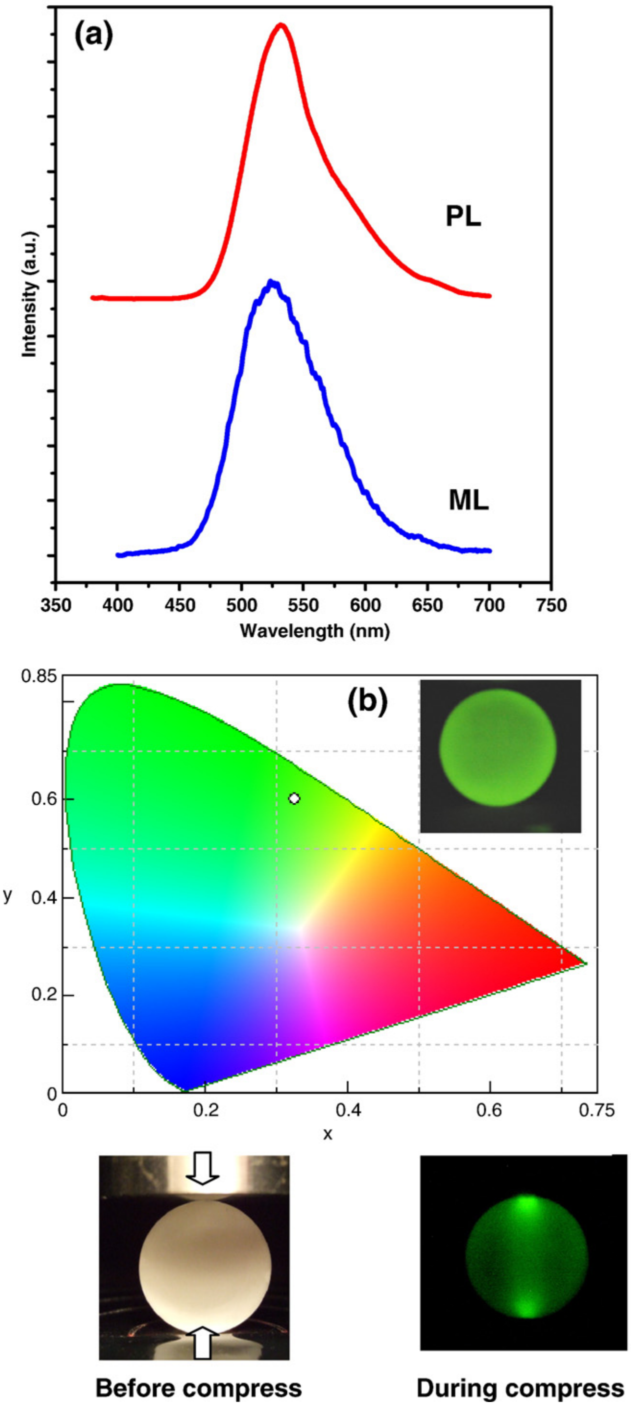

Fig. 2. ML and PL spectra of $Ca_2MgSi_2O_7$:Eu,Dy micro-particles. The inset is PL and ML images.