Design, fabrication and characterization of nanocaged 12CaO·7Al2O3:Tb3+ photostimulable phosphor for high-quality X-ray imaging

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HIGHLIGHTS

• Nanocaged C12A7:Tb3+ phosphors with sub-micrometer grain size were prepared.
• The residence time of the electrons trapped in the deeper traps exceeds 48 h.
• The conversion efficiency of the phosphor is ~1.28 pJ/mm2/mR.
• The high-quality X-ray image is related to the cubic structure of C12A7.

GRAPHICAL ABSTRACT

Abstract

It has been a challenge to realize high-quality X-ray imaging using oxide-based phosphors for avoiding halogenide-based materials and satisfying the requirements of environmental protection. In this study, lanthanide-doped nanocaged 12CaO·7Al2O3:Tb3+ (C12A7:Tb3+) X-ray imaging phosphors with strong photostimulated luminescence (PSL) have been prepared using a combustion method. X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared (FTIR) spectra, scanning electron microscopy (SEM) and transmission electron microscope (TEM) measurements suggest that single-phased C12A7:Tb3+ powders with an average grain size ranging from several hundred nanometers to several micrometers have been obtained at the ignition temperature from 700 to 900 °C. PSL, thermoluminescence (TL), electron spin resonance (ESR) and photoconductivity analyses indicate that the storage time of X-ray image exceeds 48 h due to the existence of deep traps in the C12A7:Tb3+ phosphor. High-quality X-ray imaging with a resolution of 15 line pairs per mm has been achieved using the phosphor. High conversion efficiency is achieved at 1.28 pJ/mm2/mR, suggesting the application potential of the phosphors in X-ray imaging and medical diagnostics.

Keywords:
Rare-earth ion
Photostimulated luminescence
Phosphor

1. Introduction

High-energy radiations, such as gamma rays and X-rays, which have the useful characteristics of short wavelength, high frequency, and deep penetration, have increasingly attracted the attention for applications in
material science and medical diagnostics [1–5]. Among the technologies employing X-rays, computed radiography (CR) has a low cost and good compatibility and portability compared with digital radiography and exhibits a salient feature in trauma orthopedics and neonatal imaging during operation [6,7].

At present, the imaging plates (storing latent images by X-ray irradiation) used in CR systems have prevented the development of CR because of the lack of new candidate coating phosphors for the imaging plate [6,8,9]. These phosphors are called X-ray storage or photostimulable phosphors. The X-ray energy stored in traps can be released as luminescence by stimulation with longer-wavelength light [10,11]. Generally, for halogenide-based photostimulable phosphors, F centers that act as deep traps, capturing electrons, play an important role in high-resolution X-ray imaging [12,13].

Thus far, the commercial photostimulable BaFBr:Eu2+ powders having strong blue photostimulable emission with a high sensitivity, fast response, and high conversion efficiency (CE) satisfy the requirements of the CR system, but there is a prevailing effort to prepare eco-friendly oxide-based photostimulable phosphors and to improve their stability and X-ray storage properties [14–16]. Lu2O3—a class of oxide-based compound—exhibits not only high chemical and thermal stability but also a large absorption coefficient for X-rays and γ-rays due to its high density (9.4 g/cm3) [17]. Recently, our group investigated X-ray imaging using lanthanide-doped oxide photostimulable phosphors with a grain size of several micrometers [18]. However, the effects of the grain size, the depth of the traps in the phosphor, and the X-ray irradiation conditions on the quality of X-ray imaging remain unclear.

On the other hand, for halogenide-based photostimulable phosphors, the scattering of the readout light originating from the microparticle grains reduces the quality of X-ray imaging [19], Schweizer et al. observed large scattering effects arising from the birefringence in halogenides with a hexagonal structure and found that these effects could be reduced using phosphors with a cubic structure [15,20]. Therefore, to overcome the aforementioned drawback and realize high-quality X-ray imaging, it is essential to design and fabricate oxide-based photostimulable phosphors with a cubic structure and sub-micrometer size.

12CaO·7Al2O3·7H2O (C12A7) has a cubic structure with a low synthesis temperature, may be a suitable candidate host. Because C12A7 possesses a unique nanocage structure, it can be defined as nanocaged C12A7. Its unit cell consists of 12 cages with two encaged O2− ions that maintain the charge neutrality [21,22]. These O2− anions are free from the framework and can be replaced by other anions such as OH− and H+, as shown in Fig. 1a [23,24]. Each cage has a mean effective charge of +1/3 (+4 charges for 12 cages), functioning as an F−-like center (trap) to capture electrons [25,26]. A large number of deep traps generated in halogenides lead to a stronger photostimulated luminescence (PSL) and allow higher-resolution X-ray imaging [17,27]. In particular, similar to the F center in halogenides, this research also can give the comprehension of how the nanocages in C12A7 work in improving the storage properties and the quality of X-ray imaging [28,29].

In this study, terbium-doped C12A7:Tb3+ photostimulable phosphors with sub-micrometer size were prepared using a combustion method. X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscope (TEM) revealed that C12A7:Tb3+ powders with an average grain size of several hundred nanometers were obtained at an ignition temperature of 700 °C. PSL, thermoluminescence (TL), electron spin resonance (ESR), and photoconductivity analyses indicated deep traps in the C12A7:Tb3+ phosphors and a storage time exceeding 48 h. The CE of the C12A7:Tb3+ X-ray storage phosphor was ~1.28 pJ/mm2/mR. Under the optimal conditions, high-quality X-ray imaging with a resolution of 15 line pairs per mm (lp/mm) has been achieved using the phosphor, which has a cubic structure and sub-micrometer grain size. This study is helpful for designing new X-ray imaging storage phosphors for the medical diagnostic applications.

2. Materials and methods

2.1. Materials

Tb3+-doped C12A7 powders were synthesized using a self-propagating combustion method. A mixture of Tb(NO3)3·6H2O (99.99%), Ca(NO3)2·4H2O (99.99%), Al(NO3)3·9H2O (99.99%), β-alanine and urea with the molar ratio of 12x:12(1−x):14:9.6:14 was employed as the initial materials. The mixed solution was ignited in a furnace at 700, 800 and 900 °C, respectively. During the combustion, a reducing atmosphere was produced, and oxygen vacancies were generated [30]. To confirm the absence of unreacted nitrates, β-alanine, and urea, a comparative study on microstructure and optical properties between the as-prepared and annealed samples was carried out. The annealed sample was acquired by heat-treated the as-prepared sample (ignited at 700 °C) at 1000 °C in air for 6 h. An optimal concentration of Tb3+ (0.5 mol%) has been chosen according to our earlier work [18]. To realize X-ray imaging, the as-prepared powders were pressed into compact

Fig. 1. (a) One cage of C12A7 with an encaged free O2− ion, which can be replaced by electrons or other anions, such as H+ or OH−. (b) XRD patterns of the as-prepared C12A7:0.5%Tb3+ powders ignited at different temperatures and the sample annealed at 1000 °C in air.
pellets with a diameter of ~20 mm at a pressure of ~200 MPa. To measure the photoconductivity, C12A7:0.5%Tb3+ ceramics were prepared at 1600 °C in a reducing atmosphere using the as-prepared powders as precursors.

2.2. Methods

The crystal structures of the C12A7:Tb3+ powders were examined using a Rigaku D/max-RA XRD spectrometer with Cu Kα radiation (λ = 0.15418 nm). The morphologies of all the C12A7:0.5%Tb3+ samples were inspected using a field-emission scanning electron microscope (Philips XL 30). EDS spectra of the samples were performed using a scanning electron microscope (XL30 ESEM-FEG). The FTIR transmittance spectra were obtained using an FTIR spectrometer (Nicolet 6700). All the samples were mixed with KBr at a weight ratio of 3:100 and then ground and pressed at a pressure of 10 MPa to obtain pellets. The transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out using a Field Emission Transmission Electron Microscope (TEM, JEOL-2100F). Photoluminescence (PL), PL excitation spectra, afterglow, PSL, and TL emission electron microscopy (HRTEM) were carried out using a Field Emission Transmission Electron Microscope (TEM, JEOL-2100F). Photoluminescence (PL), PL excitation spectra, afterglow, PSL, and TL were measured using an X-band ESR spectrometer (EMXplus, Bruker). ESR spectra were obtained using a semiconductor device analyzer (Agilent B1500A). ESR spectra were measured using an X-band ESR spectrometer (EMXplus, Bruker).

The power and frequency of the microwaves were 2 mW and 9.385 GHz, respectively. X-ray imaging was performed under irradiation using a semiconductor device analyzer (Agilent B1500A). ESR spectra were obtained using an X-band ESR spectrometer (EMXplus, Bruker). Transmittance spectra were obtained using an FTIR spectrometer (Nicolet 6700). All the samples were mixed with KBr at a weight ratio of 3:100 and then ground and pressed at a pressure of 10 MPa to obtain pellets.

3. Results and discussions

3.1. XRD, EDS and FTIR characterization

The XRD patterns of the as-prepared C12A7:0.5%Tb3+ ignited at different temperatures and the sample annealed at 1000 °C in air are presented in Fig. 1b. All the observed diffraction peaks are assigned to the standard C12A7 diffraction data (JCPDS: No. 09-0413). No impurity phase related to terbium is observed, indicating that single-phased C12A7:Tb3+ powders are obtained. Because the ionic radius of Tb3+ (0.092 nm) is close to that of Ca2+ (0.099 nm) and larger than that of Al3+ (0.039 nm) as reported in our earlier work, it can be inferred that Tb3+ ions preferentially occupy the sites of Ca2+ ions in C12A7 [18].

To confirm the absence of unreacted nitrates, β-alanine, and urea in the samples prepared at a low ignition temperature, the EDS and FTIR transmittance spectra of the as-prepared samples ignited at different temperatures and the sample annealed at 1000 °C in air have been acquired and are shown in Fig. 2a and b. Based on the spectra shown in Fig. 2a, the chemical compositions of all the samples are determined. The peaks corresponding to carbon element are attributed to the conducting resin used in the test process, and the oxygen, aluminum, and calcium peaks indicate the formation of the C12A7 host. No signal related to nitrogen element has been detected, indicating that there are no unreacted nitrates, β-alanine, or urea. As shown in Fig. 2b, the spectral shapes are similar for all the samples. The observed absorption peaks in the 450–850 cm⁻¹ region are assigned to the C12A7 characteristic absorption (400–465 cm⁻¹, the bending mode in tetrahedral AlO₄; 577 cm⁻¹, the Al—O bond stretching; 844 cm⁻¹, the Al—O stretching mode in tetrahedral AlO₄) [31]. Additionally, there are two sharp peaks around 2880 and 2920 cm⁻¹ and two broad peaks around 1400 and 3500 cm⁻¹. Because the two sharp peaks are also observed for C12A7 powders prepared at 1350 °C by a solid-state reaction method, they are attributed to the C—H bending modes due to ethanol adsorbed on the surfaces of C12A7 grains [32]. The absorption intensities of the two broad peaks decreased as the ignition temperature increases, indicating that these two peaks are related to absorbed water or encaged OH— anions in the C12A7 samples. As reported in our earlier work, on the basis that the broad peak around 3500 cm⁻¹ can be decomposed in two peaks, the peak around 3437 cm⁻¹ is attributed to the water-absorption band of the KBr transparent disk, and the distinguishable and repeatable peak around 3590 cm⁻¹ originates from the encaged OH— anions [18,31]. The broad peak around 1440 cm⁻¹ is ascribed to the O—H bending mode in the absorbed water [33]. Delimaris et al. reported that the remaining carbon residue was removed when MnO₃—CeO₂ powders prepared at an ignition temperature of 500 °C were calcined at 550 °C for 2 h [34]. Paraschiv et al. found that the carbonaceous residue, urea, and nitrate used in the oxide-preparation process were decomposed in the temperature range of 500–550 °C [35]. In the present study, for the sample annealed at 1000 °C, the intensities of the two broad peaks decrease dramatically compared to the other samples.
prepared at different ignition temperatures, but all the absorption peaks remain. No sharp absorption peaks related to unreacted nitrates, β-alanine, or urea are observed in the ignition-temperature range of 700–900 °C, indicating that the single-phased C12A7 has been prepared at ignition temperatures above 700 °C using a fuel mixture of β-alanine and urea via a combustion reaction method.

3.2. SEM and PL

FE-SEM images of the C12A7:0.5%Tb3+ powders ignited at different temperatures and the sample annealed at 1000 °C in air are shown in Fig. 3a–d. For the samples ignited at different temperatures, it can be found that the average grain size increases from several hundred nanometers to several micrometers as the ignition temperature increases from 700 to 900 °C. This result is in good agreement with that reported by Lanöf et al., who prepared single-phased CaAl2O4 nanopowders at an ignition temperature higher than 300 °C using a flue mixture of β-alanine and urea via a vigorous combustion reaction [36]. Thus, it is possible to obtain grain sizes varying from several hundred nanometers to several micrometers at higher ignition temperatures. However, for the sample annealed at 1000 °C in air, the grains are agglomerated, and the average grain size remains almost the same as that of the as-prepared sample. This phenomenon is explained by the result reported by Hayashi et al., who found that water desorption occurred without any crystal-structure change after C12A7 was heated at temperatures higher than 1000 °C in the ambient atmosphere [37].

TEM images of the C12A7:0.5%Tb3+ powders ignited at different temperatures and the sample annealed at 1000 °C in air are shown in Fig. 4a–d. It can be seen that the grain size increases from several hundred nanometers to several micrometers as the ignition temperature increases from 700 to 900 °C. For the sample annealed at 1000 °C in air, the grain size remains almost the same as that of the initial sample. The TEM observations are in good agreement with the FE-SEM analysis. A typical HRTEM image of the as-prepared C12A7:0.5%Tb3+ powders ignited at 700 °C is shown in Fig. 4e. The lattice-plane spacing of 0.3784 nm, corresponding to the (3 1 0) plane of the C12A7 host, can be acquired.

Emission and excitation spectra of the as-prepared C12A7:0.5%Tb3+ powders ignited at different temperatures and the sample annealed at 1000 °C in air are shown in Fig. 5a and b. For the samples prepared under different conditions, the emission and excitation spectra are similar. For 239 nm excitation, all the emission peaks of the phosphors are related to Tb3+ ions as reported in our earlier work [18]. In particular, strong blue and green emission peaks around 480 and 541 nm are attributed to the transitions of the Tb3+ ions from the 5D4 state to the 7F4 and 7F5 states, respectively [38,39]. Each of the excitation spectra monitored at 541 nm exhibits an intense broad band around 239 nm originating from the 4f-5d transition of Tb3+, as well as several weak peaks originating from the 4f-4f transitions of Tb3+.

For the sample annealed at 1000 °C in air, the blue and green emission intensities are weaker than those of the other three samples. This can be ascribed to the oxidation of Tb3+ to Tb4+ in the C12A7 host after the heat-treatment in air. Since Tb4+ has no contribution to the blue and green emissions, its presence in the host leads to the decrease in the number of Tb3+ luminescent centers and the quenching of the blue and green emissions [40,41].

The SEM and PL analyses of the samples suggest that, as the ignition temperature increases, the grain size increases, but the luminescence intensity shows almost no change. For improving the quality of X-ray imaging, the as-prepared sample ignited at 700 °C is selected for the following measurements.

3.3. Storage properties

Fig. 6a shows the afterglow decay curves of the as-prepared and annealed phosphors monitored at 541 nm after 5 min of 239 and 488 nm irradiation, respectively. For the as-prepared phosphor, the afterglow intensity after 239 nm excitation is stronger than that after 488 nm excitation because the wavelength of 239 nm corresponds to the allowed 4f-5d transition. The afterglow decay lasts up to ~30 min, indicating the presence of shallow traps in the C12A7. In addition, the annealed phosphor exhibits a weaker afterglow intensity and shorter afterglow time compared to the as-prepared phosphor under the same irradiation conditions, indicating the annihilation of more oxygen vacancies and the decrease in the number of shallow traps after the high-temperature annealing in air. It can be induced that, after the sample has been kept in the dark at room temperature for 30 min, the
Fig. 4. (a–c) TEM images of the as-prepared C12A7:0.5%Tb³⁺ powders ignited at different temperatures (700, 800, and 900 °C), (d) the sample annealed at 1000 °C in air for 6 h (the initial sample: C12A7:0.5%Tb³⁺ powders ignited at 700 °C) and (e) HRTEM image of the as-prepared C12A7:0.5%Tb³⁺ powders ignited at 700 °C.

Fig. 5. (a) Emission and (b) excitation spectra of the as-prepared C12A7:0.5%Tb³⁺ powders ignited at different temperatures and the sample annealed at 1000 °C in air.
electrons in the shallow traps are released, and only those in the deeper traps remain.

To investigate the nature of deeper traps, the PSL decay curves (monitored at 541 nm) of the as-prepared and annealed samples stimulated at 808 nm with a 30-min delay after 5 min of 239 nm UV irradiation are shown in Fig. 6b. In the initial stage, the sharp rising and falling edges of the PSL decay curves are observed as the infrared stimulation is turned on and off alternately. The spiky rising signal is attributed to the contribution of the electrons released from the shallow traps under the stimulation with 808 nm light. This phenomenon was also found in a Cr³⁺-doped LiGa₅O₈ system and it was believed to originate from the total contribution of the shallow and deeper traps [42]. On the basis that the latter rising edge is lower than the former falling edge as reported in our previous study, the corresponding order of kinetics is found to be close to 1, implying that the retrapping process related to deeper traps does not happen in our case [18].

For the annealed sample, the observed PSL intensity is lower than that of the as-prepared sample, indicating the annihilation of more oxygen vacancies and the decrease in the number of deeper traps. This result is consistent with the aforementioned afterglow analysis. For the as-prepared C₁₂A₇:Tb³⁺ phosphors ignited at 700 °C, the obvious PSL signal is found as the decay time exceeds 48 h (Fig. 6b, inset). This indicates that the information can be stably stored for more than 48 h, satisfying the requirement of X-ray storage phosphors [6]. Our results suggest that the as-prepared powders ignited at 700 °C can be used as photostimulable phosphors coated on the surface of imaging plate.

To determine the depth of the deeper traps in the host and to study the X-ray storage property, the TL curves of the C₁₂A₇:0.5%Tb³⁺ phosphors monitored at 541 nm with a 30-min delay after X-ray or 239 nm UV irradiation are shown in Fig. 6c. Each of these curves exhibits a similar shape, with two broad peaks around 355 and 450 K. The depths (E in eV) of the deeper traps are calculated using Urbach’s formula: E = Tₑ/500, where Tₑ (in K) is the glow-peak temperature [11]. The depths of the deeper traps in the C₁₂A₇ are estimated to be 0.71–0.74 and 0.90–0.91 eV, respectively. Generally, for optical or X-ray storage materials, F⁺-like centers play an essential role in capturing electrons [43]. For the C₁₂A₇ host, it has been found that the positively charged cages behaving like F⁺-like centers can capture electrons (forming localized electronic state), and its energy-level positions relative to the bottom of the narrow cage conduction band (CCB) are in the range of 0.6–1.1 eV [44,45]. Our TL results are in accordance with the theoretical

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Fig. 6. (a) Afterglow decay curves of the as-prepared and annealed phosphors monitored at 541 nm after 5 min of 239 and 488 nm irradiation, respectively. (b) PSL decay curves (monitored at 541 nm) of the as-prepared and annealed samples stimulated at 808 nm with a 30-min delay after 5 min of 239 nm UV irradiation. (c) TL curves of the C₁₂A₇:0.5%Tb³⁺ phosphors monitored at 541 nm with a 30-min delay after X-ray and 239 nm UV irradiations, respectively.

Fig. 7. (a) ESR spectra of the as-prepared C₁₂A₇:Tb³⁺ phosphors ignited at 700 °C as a function of the decay time with a 30-min delay after 12 min of the 254 nm irradiation. (b) Time responses of the photocurrent under 239 and 488 nm excitations, respectively.
data. The two deeper traps in the C12A7:0.5%Tb3+ may originate from the different cage surroundings due to lanthanide doping.

To confirm the origin of the F⁻⁻-like center and to determine the storage time of the phosphors, ESR spectra of the C12A7:0.5%Tb3+ phosphors as a function of the decay time with a 30-min delay after 12 min of the 254 nm irradiation were measured and are shown in Fig. 7a. For the unirradiated sample, only broad signals of superoxide (O₂⁻) appears, and no ESR signal related to electrons stored in the F⁻⁻-like centers is observed [46]. For the sample irradiated with UV light (254 nm), it can be found that the sharp ESR signals related to electrons stored in the F⁻⁻-like centers (unoccupied cages) are superimposed on the broad signals of superoxide (O₂⁻) and the sharp ESR signal intensity hardly changes as the decay time increases from 0 to 12 h. This result indicates that the electrons are captured in the cages for a very long time, which is in good agreement with the observed PSL at the decay time exceeding 48 h.

To investigate the storage properties of the sample ignited at 700 °C, the time responses of the photocurrent under the 239 or 488 nm excitation are shown in Fig. 7b. It can be found that the photocurrent is approximately zero when the excitation is absent. Under UV (239 nm) or visible (488 nm) light excitation, the time-dependent photocurrent exhibits a rapid increase in the preliminary stage and gradually reaches to a saturating value as the response time exceeds 2 h. The detected photocurrent is ascribed to the contribution of the moving electrons in the CCB. This result suggests that the storage mechanism in our case can be described by the conduction-band model [47]. It can be found that the photocurrent under 239 nm irradiation is 50 times stronger than that under 488 nm irradiation. This is due to the fact that the 239 nm excitation corresponds to the allowed 4f-5d transition and the electrons jump to the CCB more easily than the electrons in the 5D3 state in the case of the 488 nm excitation. This result is consistent with the excitation spectral analysis. After the external irradiation, each of the photocurrent decay curves displays a decreasing trend with two components (rapid and slow parts) and takes ~20 h to return to zero. The rapid and slow components may be due to the shallow and deep traps, respectively. These results are consistent with the afterglow and PSL analyses.

3.4. Performance of X-ray storage phosphors

To study the dynamic range of the X-ray storage phosphors, the normalized PSL intensity with respect to the X-ray irradiation time was measured and is shown in Fig. 8a. When the irradiation time is shorter than 40 min, the PSL intensity is almost proportional to the irradiation time. Because the applied X-ray dose depends linearly on the X-ray irradiation time, as shown in the inset of Fig. 8a, the C12A7:0.5%Tb3+ phosphor exhibits a large dynamic range (2.8 mGy–6 Gy). When the irradiation time is longer than 60 min, the PSL intensity becomes saturated. The changing trend of the normalized PSL intensity is in line with the photocurrent analysis, suggesting that the number of deep traps does not vary with the X-ray irradiation time.

Another important performance parameter of the X-ray storage phosphors is the CE, which is the total energy of stimulated light per unit area and per unit of X-ray dose absorbed by the phosphor.
(in pJ/mm²/mR), i.e., the total amount of energy released (E_{tot}) divided by the absorbed X-ray dose. The CE is defined as the released photon energy (E_{tot}) per absorbed X-ray dose and it is empirically obtained using the following equation:\[28\]

\[
CE = \frac{E_{tot}}{\text{absorbed X-ray dose}}
\]

where E_{tot} is the area below the PSL curve.

For simplicity, E_{tot} can be expressed as I_0 \cdot \tau. Here, I_0 is the intensity of the PSL at the beginning of the stimulation experiment and \( \tau \) is the time constant at which the PSL intensity drops to 1/e of its initial value. Therefore, the CE can be calculated by the following equation:\[27\]

\[
CE = \frac{I_0 \cdot \tau}{\text{absorbed X-ray dose}}
\]

To determine the CE of the X-ray storage phosphors, the PSL decay curve under continuous photostimulation is given in Fig. 8b. The stored total amount of photostimulable energy (in pJ) upon exposure to a precisely known X-ray dose (in mR) can be obtained. The unit area is the readout area (in mm²). The CE of the C12A7:Tb³⁺ phosphors is calculated to be ~1.28 pJ/mm²/mR, which is close to that of BaFBr:Eu³⁺ phosphor (2–4 pJ/mm²/mR)\[48,49\].

To apply the phosphors for X-ray imaging, a digital photo of a steel mask plate with a carved three-crossed-finger-fork pattern used as an object is shown in Fig. 8c. An X-ray image of the C12A7:0.5%Tb³⁺ phosphor under X-ray irradiation along with 808-nm stimulation is shown in Fig. 8d. In the X-ray image, the three-crossed-finger-fork pattern with green 541 nm emission is clearly observed. To obtain a high-resolution X-ray image, the X-ray irradiation time has been used in the range of 60–120 min, and the X-ray image was recorded using a digital camera (Canon) with an exposure time of 30 s. As shown in Fig. 8e, for each finger-fork pattern, the distance between the adjacent fingers is 30 μm. The leftmost damaged patterns marked in Fig. 8c and d can be distinguished from the other two normal patterns. Thus, the resolution of the C12A7:0.5%Tb³⁺ phosphor can be regarded as ~15 lp/mm, which is superior to that of commercial BaFBr:Eu³⁺ phosphors\[15,50\]. The high-quality X-ray imaging is attributed to the C12A7:0.5%Tb³⁺ phosphor can be regarded as ~15 lp/mm, which is superior to that of commercial BaFBr:Eu³⁺ phosphors.


