Surface structure of Er^{3+}-doped LaOCl nanophosphors modified using acetyl chloride

Tomoya KONISHI, Saori NII, Shin ITAMI and Nagatoshi NISHIWAKI*

Center for Collaborative Research, Anan National College of Technology, Anan, Tokushima 774–0017, Japan
*School of Environmental Science and Engineering, Kochi University of Technology, Kami, Kochi 782–8502, Japan

Paper

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Upconversion emissive ceramic nanophosphors like Er^{3+}-doped LaOCl are useful for advanced security printings and fluorescence bioimaging techniques. For such applications, functional polymers are necessary for surface modification in order to provide adsorptivity, steric stability as well as other processes. Surface modification, however, brings about a potential degradation of the emission intensity of doped rare earth ions contingent upon the vibration energy of the surrounding environment. It is necessary to understand the structure of surface modification in relation to emission intensity. In this study, we demonstrate the surface modification of Er^{3+}-doped LaOCl nanophosphor with simple acetate anions using the compounds acetyl chloride and aqueous sodium acetate, respectively. We report that the surface modification using acetyl chloride has little effect upon degrading emission intensity as it does not increase surface hydroxy groups.

1. Introduction

Some rare earth (RE)-activated ceramic phosphors exhibit a frequency upconversion (UC) phenomenon which converts near-infrared (NIR) excitation light with lower energy into visible light with higher energy. UC occurs by a multi-step excitation in discreet energy levels of trivalent RE ions. The discreet energy levels are formed by 4f electrons which are shielded by outer 5s and 5p electrons from electric perturbations of the host matrix. For the practical use of UC phosphors, it is essential to choose an appropriate matrix with low maximum phonon energy for efficient emissions[1] and high chemical durability. For example, trivalent erbium-doped lanthanum oxychloride (LaOCl:Er^{3+}) nanophosphor shows efficient UC emission[2] due to the low phonon energy of the LaOCl host ($\sim$400 cm^{-1}).[3]

Such upconversion nanophosphors (UCNPs)[4] find advantages in security printings[5],[6] and fluorescence bioimaging (FBI) techniques.[7],[8] Protection against forgery and counterfeiting is greatly enhanced by the excitation with near infrared light and the complicated peak pattern on the emission spectrum. The FBI, using UCNPs, also extends the duration of observation since ceramic phosphors do not show color-fading and NIR light does not cause damages to bio-systems. For such applications, the surface of UCNPs must be modified with functional polymers.[9],[10] For example, when UCNPs are used for pigments on security printings, surface modification prevents sedimentation and agglomeration as well as works as a binding agent to stick to papers. For use in FBI probes (or markers), the surface of UCNPs must be modified with poly(ethylene glycol) (PEG)-based bio-compatible polymers enabling specific adsorption to target tissues.[11]–[14]

Surface modification is thus indispensable for functionality in practical uses, as listed above, but on the other hand, surface modification more or less degrades the intensity of emissions.

This is because the multi phonon non-radiative relaxation rate is considerably enhanced by surface modifiers and the undesired incorporation of hydroxy groups whose vibration energies are much higher than the phonon energy of the host lattice. Hydroxy groups are likely incorporated through aqueous reactions which are one of the conventional methods of surface modification of UCNPs. For example, UCNPs are dispersed in an aqueous solution of modifying polymer molecules with many carboxy groups. It is reported that the modification mechanism is the electro-static adsorption of negatively charged carboxylate anions on a positively charged ceramic surface.[15] However, there have been few reports on the modification structure, especially the accidental incorporation of hydroxy groups, and the effects on the emission intensity.

It is necessary to develop a new process of surface modification where the degradation of the emission intensity is minimized. For this purpose, we demonstrate surface modifications of LaOCl:Er^{3+} UCNPs with acetate ions by using a conventional aqueous method and a new non-aqueous method to investigate the modification structures and effects on the emission intensities. An acetate ion itself does not have a special functionality but is suitable to investigate the modification structure using vibrational spectroscopy due to its simple molecular structure. The UC emission intensities of the two LaOCl:Er^{3+} samples are compared and discussed on the basis of their surface structures by surface-sensitive diffuse reflection infrared Fourier transform (DRIFT) spectroscopy and scanning electron microscopy (SEM).

2. Experimental procedure

2.1 Preparation of LaOCl:Er^{3+} nanophosphor

First, 0.5 M LaCl$_3$ aqueous solution and 0.02 M ErCl$_3$ aqueous solution were prepared by dissolving LaCl$_3$·7H$_2$O and ErCl$_3$·6H$_2$O in distilled water, respectively. Reagent-grade chemicals were used for the preparation of the aqueous solutions. The aqueous solutions (40 mL of the aqueous LaCl$_3$ and 2 mL of the aqueous ErCl$_3$) were mixed in a beaker so that the molar ratio of

† Corresponding author: T. Konishi; E-mail: konishi@anan-nct.ac.jp

Er to La was 0.2:100. The starting solution thus prepared was dried in a flask at 95°C to obtain mixed hydrated chlorides of lanthanum and erbium. The remnant was put in an alumina boat and loaded in a pre-heated muffle furnace to promote dehydration, self-hydrolysis[16),17)] and oxidation to form LaOCl:Er^{3+}. After calcining at 800°C for 1 h in the air, the sample was extracted from the furnace and cooled to room temperature.

The sample thus prepared was ground into a powder with an agate mortar and pestle for analysis. The powder X-ray diffraction (XRD) pattern was measured by using a PANalytical X'Pert PRO diffractometer and Cu $K_{\alpha 1}$ radiation. The microstructure was investigated by using SEM (Hitachi SU8010).

2.2 Surface modification of LaOCl:Er^{3+} nanophosphor

Surface modification of the LaOCl:Er^{3+} samples with acetate ions was performed using 1 M sodium acetate aqueous solution or neat acetyl chloride. 300 mg of the LaOCl:Er^{3+} sample prepared above and 3 mL of the aqueous sodium acetate were added together in a test tube and tightly capped, followed by heat treatment in an oil bath of 80°C for 2 h. The LaOCl:Er^{3+} sample in the test tube was retrieved by vacuum filtration and rinsed with acetonitrile (5 mL × 3) to remove excess sodium acetate. Another portion (300 mg) of the LaOCl:Er^{3+} sample was heated in 3 mL of acetyl chloride and retrieved in the same manner.

DRIFT spectra of the LaOCl:Er^{3+} samples before and after surface modification were recorded on a JASCO FT/IR-4200 spectrometer. The samples were diluted to 1% by weight in KBr before measurement. The UC emission spectra of the LaOCl:Er^{3+} samples before and after surface modification were measured under excitation by a 980-nm cw laser diode (LD) (L9418-04, Hamamatsu Photonics) equipped with a temperature controller (TED200, Thorlabs), and recorded on a Hitachi High-Tech F-7000 spectrofluorophotometer with 1.0 nm of bandwidth. Each sample was pressed into a pellet and laminated in a transparent film in order to prevent the undesired effects of particle size and surface roughness. All of the measurements were carried out at room temperature.

3. Results and discussion

Figure 1 shows the XRD pattern of the sample just after calcination. Since all of the peaks were attributed to the diffraction pattern of LaOCl (ICDD powder diffraction file number 01-088-0064), it is suggested that the sample obtained was almost pure oxychloride without any by-products; for example oxides or chlorides. The average particle size was ~600 nm according to dynamic light scattering measurement and SEM observation [**Fig. 2**(a)]. Figure 2(b) shows the microstructure of the
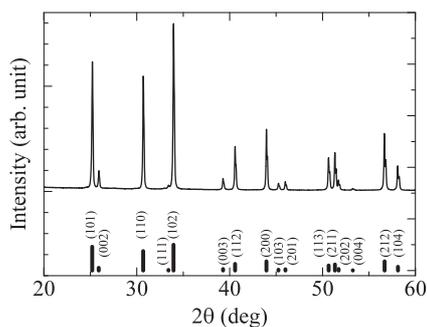
LaOCl:Er^{3+} sample after heating in aqueous sodium acetate. There were small crystals found on the surface. When the sample was heated in acetyl chloride, no remarkable change was observed in the microstructure [Fig. 2(c)].

UC spectra of the LaOCl:Er^{3+} samples before and after surface modification using aqueous sodium acetate were measured. As shown in **Fig. 3**, the irradiation by 980-nm LD on the sample before surface modification resulted in visible emissions around the 525–550 nm and 650–670 nm bands, which were assigned to the transitions of $^2H_{11/2}$, $^4S_{3/2}$ to $^4I_{15/2}$ and $^4F_{9/2}$ to $^4I_{15/2}$,
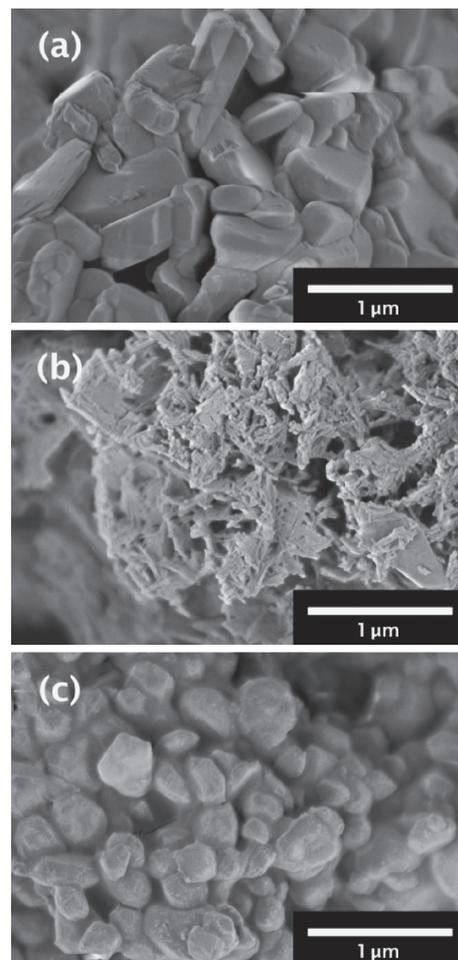

Fig. 2. SEM images of LaOCl:Er^{3+} samples (a) as-prepared, (b) after surface modification using sodium acetate, and (c) after surface modification using acetyl chloride.
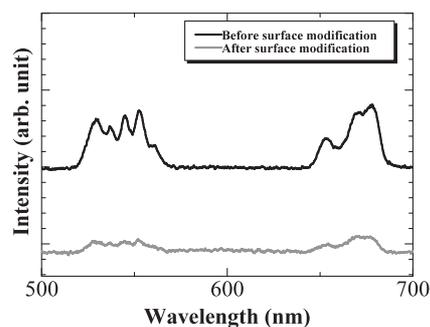

Fig. 1. Powder X-ray diffraction pattern of the LaOCl:Er^{3+} sample just after calcination.

Fig. 3. Upconversion emission spectra of LaOCl:Er^{3+} sample before and after surface modification using sodium acetate. The sample is excited at 980 nm.
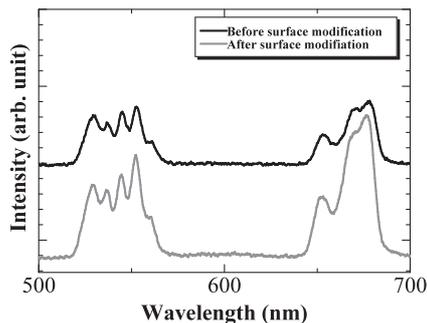
Fig. 4. Upconversion emission spectra of LaOCl:Er^{3+} sample before and after surface modification using acetyl chloride. The sample is excited at 980 nm.
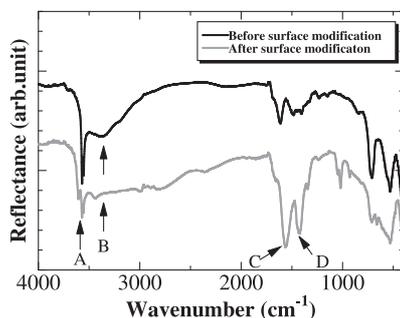

Fig. 7. Schematic models of plausible surface structure of LaOCl:Er^{3+} sample after surface modification using (a) aqueous sodium acetate and (b) acetyl chloride.

Fig. 5. DRIFT spectra of LaOCl:Er^{3+} sample before and after surface modification using sodium acetate.
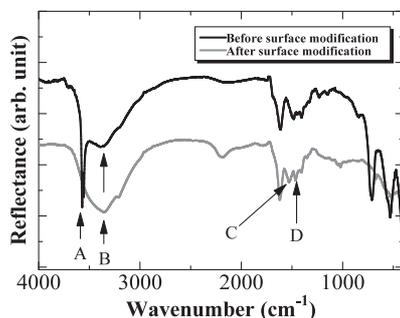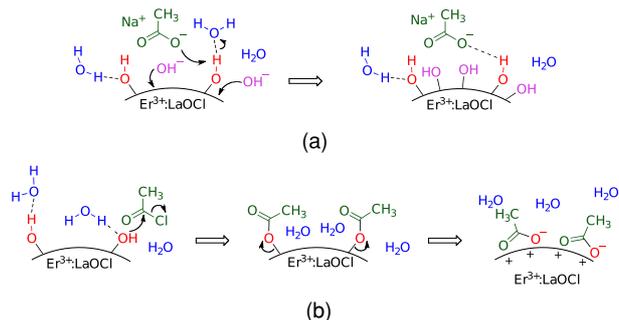

Fig. 6. DRIFT spectra of LaOCl:Er^{3+} sample before and after surface modification using acetyl chloride.

respectively.[2] However, the emission intensity considerably decreased due to the surface modification. Since the emission efficiency of Er^{3+} is affected by ligands, which have large vibration energy, the degradation of UC emission intensity implies a change in the surface structure [Fig. 2(b)]. On the contrary, surface modification using acetyl chloride did not decrease the visible emission intensity (**Fig. 4**).

Figures 5 and **6** show DRIFT spectra of the LaOCl:Er^{3+} samples before and after surface modification with aqueous sodium acetate and acetyl chloride, respectively. The spectra are plotted without Kubelka–Munk conversion,[18] which means that the signal is exaggerated in a higher wavenumber range.

The LaOCl:Er^{3+} sample as prepared had a sharp absorption band (denoted by 'A' in Figs. 5 and 6) near 3560 cm^{-1} and a broad absorption band (denoted by by 'B') centering at 3340 cm^{-1}. Both absorption bands are attributed to a stretching vibration of O–H bonds in hydroxy groups formed by ambient

moisture, but the broad band (B) was weakened after heating at 250°C for 1 h while the sharp band (A) remained unchanged. This implies that the sharp band (A) indicates chemisorbed hydroxy groups whereas the broad band (B) indicates water molecules physisorbed on the hydroxylated surface by hydrogen bonding. The broadening of the absorption band (B) was due to the hydrogen bonds perturbing the O–H stretching modes.

The DRIFT spectrum of the LaOCl:Er^{3+} sample after surface modification using conventional aqueous method is plotted in Fig. 5. The sharp absorption band (denoted by 'A') of surface hydroxy groups remained and several new peaks appeared in the vicinity. This implies that the surface was hydroxylated additionally in different forms by heating in a weak base of aqueous sodium acetate. The absorption bands at 1530 cm^{-1} (denoted by 'C') and 1460 cm^{-1} (denoted by 'D') indicate asymmetric and symmetric stretching vibration modes of carbonyl groups in the acetate anions, respectively. The acetate anions are adsorbed on the hydroxylated surface by hydrogen bonding as drawn in **Fig. 7**(a). The small crystals found on the particle surface [Fig. 2(b)] also imply the deposition of such acetates.

Figure 6 shows the DRIFT spectra of the LaOCl:Er^{3+} sample before and after heating in nonaqueous acetyl chloride. The sharp absorption band (denoted by 'A') by chemisorbed hydroxy groups disappeared while the broad absorption band (B) remained after heating. Also, weak absorption bands (denoted by 'C' and 'D') of acetate anions appeared. This change means that the chemisorbed hydroxy groups were replaced by acetate anions as illustrated in Fig. 7(b). The substitution of surface hydroxy anions with other anions is reported for several rare earth oxide hydrate.[19] In this case, however, the chemisorbed hydroxy groups were dehydrated and acetylated by acetyl chloride followed by the liberation of acetate anions. At this time, acetyl chloride generates HCl which may erode the surface of the LaOCl:Er^{3+} particles. Because the hydrolysis of acetyl chloride was caused by a small amount of surface water and hydroxy groups, the amount of generated HCl was also small. As Fig. 2(c) shows, the damage of the LaOCl:Er^{3+} surface by HCl was limited. It is likely that the acetate anions directly adsorbed on the surface forming ionic pairs with surface lanthanum ions together with hydrated water since the DRIFT spectrum with the enhanced broad absorption is similar to that of lanthanum acetate hydrate.[20] Similar chemisorptions of acetate anions on MgO surface[21] and TiO$_2$ surface[22] are also reported.

The DRIFT spectra showed the enhanced absorption bands by hydroxy groups after heating in aqueous sodium acetate (Fig. 5). The vibration energy of hydroxy groups is ~3500 cm^{-1} that is large enough to increase the non-radiative transition rates

of Er^{3+} by the multi-phonon relaxation process. The enhanced non-radiative transition rates decrease the lifetime of the first excited state $^4I_{11/2}$ of Er^{3+}, which in result suppress the further excited state absorption for upconversion emission. The emission intensity of LaOCl:Er^{3+} is hence decreased by heating in aqueous sodium acetate as a model case of the conventional surface modification process (Fig. 3). On the contrary, surface hydroxy groups were removed by heating in nonaqueous acetyl chloride and the emission intensity was maintained. Moreover, the emission intensity was not affected by physisorbed water as indicated by a broad absorption band (denoted by 'B' in Fig. 6). Further discussion including precise analysis of energy transfer rates will be given by decay curve measurements, which is beyond the scope of this paper. The total amount of surface acetate anions were less than those using aqueous sodium acetate because of the absence of physisorbed acetate anions. But the surface was firmly modified with chemisorbed acetate anions without being rinsed off by acetonitrile. It is thus suggested that heating in acyl chloride is useful to modify the LaOCl:Er^{3+} surface without degrading the emission intensity.

4. Conclusions

Upconversion emissive LaOCl:Er^{3+} nanophosphor was prepared through drying Er^{3+}-doped aqueous $LaCl_3$ followed by calcining in the air. Surface modification of the LaOCl:Er^{3+} nanophosphors was performed by heating in aqueous sodium acetate or acetyl chloride. Aqueous sodium acetate considerably degraded the emission intensity whereas acetyl chloride did not. Vibrational spectroscopic analysis of the modified surface found that heating in aqueous sodium acetate increased the chemisorbed hydroxy groups which resultantly suppresses the emission efficiency of Er^{3+}. On the contrary, heating in acetyl chloride replaced the undesired chemisorbed hydroxy groups with acetate anion modifiers. This method is naturally extended to any surface modification with functional molecules containing acyl chloride groups.

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