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Citric acid-assisted phase controlled synthesis of $NaYF_4:Yb^{3+},Tm^{3+}$ crystals and their intense ultraviolet upconversion emissions

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ABSTRACT

The selective synthesis of cubic and hexagonal $NaYF_4$ crystals was successfully performed by a facile citric acid assisted hydrothermal method. The crystal phase conversion was observed through tuning the added amount of fluoride. A possible growth mechanism was proposed for the formation of hexagonal $NaYF_4$ microcrystals (MCs). Under 980 nm excitation, intense ultraviolet (UV), blue, and weak violet upconversion (UC) emissions were obtained in the hexagonal $NaYF_4$:20%Yb^{3+}, 0.5%Tm^{3+} MCs. The 5-photon UC emissions from the $^1I_6$ level of Tm^{3+} ions were much stronger than the 4-photon UC emissions from the $^1D_2$ level and the 3-photon UC emissions from the $^1G_4$ level. The enhancement of UV UC emissions was attributed to higher crystallization degree and less luminescence quenching centers.

1. Introduction

In recent years, optically active trivalent lanthanide (Ln^{3+}) ions doped upconversion (UC) crystals have become very prominent owing to their unique optical properties arising from the 4f shell electrons [1,2] and their wide applications in color displays [3,4], short wavelength solid-state lasers [5], solar cells [6,7], biochemical diagnostics [8], and drug delivers [9,10]. Especially, ultraviolet (UV) UC fluorescence has become an appealing research topic [11–14]. As we have known, it can significantly influence the local environment around Ln^{3+} ions whatever variations of dimensionalities, crystalline phases, and surface defects. Precise control of these factors allows manipulation of the spectroscopic properties of UC crystals. Therefore, there has been growing interest to synthesis UC crystals with controlled size, shape, and composition. In these syntheses, related regulating reagents including oleic acid (OA) [15], ethylenediaminetetraacetic acid (EDTA) [16], trisodium citrate [17], ethylene glycol [18], and cetyl trimethyl ammonium bromide (CTAB) [19] have been used to control nucleation, growth, and crystallization of UC materials. However, these organic reagents induce strong quenching to UC fluorescence due to the organic residues on the crystal surfaces. This problem becomes more serious for UV UC fluorescence. Citric acid (CA) as a small chelating ligand has also been used as the morphology controller [20,21]. In virtue of the relatively weak morphology control ability, CA induces less organic impurities to the surfaces of the synthesized samples. As a consequence, efficient UV UC fluorescence is expected to be obtained easily.

With low optical phonon energy and high chemical stability, the fluoride crystals have been reported as the best UC candidate matrixes. Particularly, more efficient UV UC emissions can be obtained in Ln^{3+} ions doped $NaYF_4$ crystals. Among Ln^{3+} ions, Tm^{3+} ions have attracted increasing attention because their metastable levels are suitable for emitting blue and UV UC luminescence, and additionally their spectra change sensitively with surroundings. Despite the fact that UC luminescence have been widely investigated in Yb^{3+}/Tm^{3+} codoped $NaYF_4$ cryatals [22–24], the exploration of new approaches to obtain relative enhancement of high-order UV UC (for example the 5-photon UV UC) to violet UC luminescence as well as the relationship between the efficient UV UC luminescence and the material structure is still a challenge for the development of short-wavelength solid-state lasers. As the optical properties of the $NaYF_4$ phosphor depend not only on the electronic state but also on the crystal structure, many efforts have been made to synthesize Yb^{3+}/Tm^{3+} codoped $NaYF_4$ crystals with controlled crystal phase through various methods such as high temperature thermal decomposition [25,26], liquid–solid two-phase approaches [27], and hydrothermal routes [28,29]. Compared with the other methods, hydrothermal treatment occurs at relatively low reaction temperature ($<$250 °C) with very simple equipment and process. By controlling the reaction conditions,

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such as the reaction time, the reaction temperature, and the fluoride amount, cubic and hexagonal $NaYF_4$ crystals can be easily synthesized.

In this paper, Yb^{3+}/Tm^{3+} codoped hexagonal $NaYF_4$ microcrystals (MCs) were prepared by a facile hydrothermal route with CA as the surfactant. The phase conversion of $NaYF_4$ crystals was observed through tuning the added amount of fluoride. The mechanism of the crystal phase conversion was investigated by analyzing the reaction process. The hexagonal $NaYF_4$ MCs emitted bright UC light under 980 nm excitation. More significantly, intense UV UC emissions were obtained. The 5-photon UC emissions from the $^1I_6$ level of Tm^{3+} ions were much stronger than the 4-photon UC emissions from the $^1D_2$ level and the 3-photon UC emissions from the $^1G_4$ level. The mechanism of UV UC emission enhancement in the hexagonal $NaYF_4$ MCs was discussed in detail.

2. Results and discussion

2.1. Growth mechanism

The soft chemical process is known to have the advantage of good mixing of the starting material and excellent chemical homogeneity of the final product. In the experiment with CA, when rare-earth (RE^{3+}) ions are added into the precursor solution, CA reacts with them to form stable metal complexes. Under the hydrothermal condition, however, RE^{3+} ions are released into solution and react with Na^+ and F^- ions to form nuclei at early stage, and then these nuclei congregate together. In this process, the morphology, structure, and size of sample can be significantly affected by many facts including the type and concentration of the doping lanthanide ions, the amount of surfactant and fluoride, the reaction temperature and time, and so on. In previous publications, the size reduction and phase transformation have been observed by increasing the doping concentration of Gd^{3+} ions in $NaYF_4$ nanocrystals (NCs) and $NaYbF_4$ MCs [3,30]. The similar size reduction and morphology transformation from nanorods to nanoplates have been obtained by changing the doping concentration of Eu^{3+} ions in $NaYF_4$ NCs [31]. In other matrix such as $NaGdF_4$ and LnF_3 NCs, the dependence of phase and morphology on the doping concentration of lanthanide ions has also been investigated [32,33]. However, in our experiment, the doping concentrations of Yb^{3+} and Tm^{3+} ions in $NaYF_4$ crystals were fixed as 20 and 0.5% respectively due to that these concentrations were demonstrated good for UV UC emissions in our previous work [12]. It has been reported that no obvious morphology and phase transformation occurs in $NaY_{1-x}Yb_xF_4$ NCs substituted with Yb^{3+} ions although x is as large as 0.9, which is probably because of the similar radius and electron charge density between Y^{3+} and Yb^{3+} ions [32]. On the other hand, F^- ions serve as both reactants and mineralizers in the hydrothermal synthesis of the $NaReF_4$ crystals [34,35]. The change of F^- ion content affects not only the shapes and sizes but also the crystal phases of the samples. Therefore, we simply adjusted the NaF/RE^{3+} ratio to realize the transformation from cubic phase to hexagonal one because that the hexagonal $NaYF_4$ crystals are regarded as more suitable matrix for high efficient UC luminescence. As a consequence, we mainly focus on the effect of surfactant and fluoride on the synthesized products.

To investigate the possible effect of varied fluoride content on the final products, the ratio of NaF/RE^{3+} was selectively regulated from 4 to 24 with other synthetic conditions unchanged. As can be seen from Fig. 1(a), when the ratio of NaF/RE^{3+} is 4, the obtained nanocrystals (NCs) acquire irregular truncated octahedral morphology with an average length of approximately 200 nm. The corresponding XRD analysis of the sample reveals that all the diffraction peaks can be well assigned to orthorhombic phase YF_3 (JCPDS 34-0102) as shown in Fig. 1(f). When the ratio increases to 6, spherical nanoparticles with diameters of 100–200 nm appear as shown in Fig. 1(b). The XRD pattern shows that the obtained sample is pure cubic phase $NaYF_4$ (JCPDS 77–2042). When the ratio reaches 8, minor hexagonal diffraction peaks emerge in the XRD pattern. The nanospheres grow a litter bigger with diameters of 100–250 nm as shown in Fig. 1(c). However, only nanospheres can be observed in a large visual field, which also indicates that there is very small amount of hexagonal $NaYF_4$ crystals in the sample. When the ratio further increases to 12, regular hexagonal microplates appear instead of the nanospheres as shown in Fig. 1(d). The diameters and lengths of them are about 3.5–4 μm and 1–1.5 μm, respectively. The XRD pattern shows that the peaks corresponding to hexagonal phase are enhanced dramatically, whereas those corresponding to cubic phase are weakened. When the ratio finally increases to 24, diffraction peaks change to pure hexagonal phase $NaYF_4$ (JCPDS 16-0334) with no impurities, and all the obtained products are well-shaped hexagonal microprisms with diameters of 1.2–1.9 μm and lengths of 1.5–2 μm as shown in Fig. 1(e). Apparently, the $NaYF_4$ microprisms with perfect hexagonal end planes and smooth side surfaces are very straight, which indicates they are of high quality.

To illustrate the crystal structure variation of the final products, the possible reaction processes for the formation of both YF_3 and $NaYF_4$ crystals are summarized as follows:

$$Y^{3+} + Cit^{3-} \rightarrow Y^{3+} - Cit^{3-}(\text{complex}) \tag{1}$$

$$Y^{3+} - Cit^{3-} + 3F^- \rightarrow YF_3 + Cit^{3-} \tag{2}$$

$$Y^{3+} - Cit^{3-} + Na^+ + 4F^- \rightarrow NaYF_4 + Cit^{3-} \tag{3}$$

It can be clearly seen that the lack of F^- ions will make Eq. (2) perform easily than Eq. (3), YF_3 crystals appear. When more F^- ions are introduced into the reaction system, the ratio of F^-/Y^{3+} is large enough in Eq. (3). Thus, $NaYF_4$ crystals are obtained instead of YF_3 crystals.

The formation of the small orthorhombic YF_3 and cubic $NaYF_4$ NCs is probably due to the high CA/RE^{3+} ratio and the low NaF/RE^{3+} ratio. According to the literature, the chelating agent is a key element to the sizes of particles, high CA/RE^{3+} ratio is favorable for the formation of nanoparticles with small sizes [36]. In our experiment, the ratio of CA/RE^{3+} is 4, the restricting effect of CA on the crystal growth is speculated to be a little large. Simultaneously, there is probably not enough fluoride to supply the growth of NCs with low NaF/RE^{3+} ratios as 4 to 8. Consequently, small NCs can be synthesized. To demonstrate the restricting effect of CA, sample was also synthesized with the CA/RE^{3+} ratio as 1 and the NaF/RE^{3+} ratio as 6. It can be seen from Fig. S1, large hexagonal microprisms together with small nanoparticles are obtained. The XRD pattern shows that the obtained sample is hexagonal phase $NaYF_4$ (JCPDS 16-0334) mixed with cubic phase $NaYF_4$ (JCPDS 77-2042). The reason is that crystal growth can be accelerated by a small amount of CA absorbed on the crystal surfaces, so most of the cubic $NaYF_4$ nuclei transformed to large hexagonal $NaYF_4$ microprisms. However, the morphologies of the microprisms are irregular owing to the poor morphology control effect of less organic additive. Therefore, the ratio of CA/RE^{3+} was fixed as 4 in our experiment.

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2013.10.007.

As is recognized, the hexagonal phase is a thermodynamically stable phase and more ordered. The transition from the cubic phase