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Co/Cr co-doped $MgGa_2O_4$ nanoparticles: Microstructure and optical properties

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ABSTRACT

$MgGa_2O_4$ nanoparticles co-doped with Co^{2+}/Cr^{3+} ions were prepared by a citrate sol–gel method. Their microstructure and optical properties were studied using X-ray powder diffraction (XRD), infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), absorption and fluorescence spectroscopy. $MgGa_2O_4$ nanoparticles with the size of 10–30 nm were obtained when the precursor was annealed at 800 °C. Results indicated that Ga^{3+} and Mg^{2+} cations occupied the octahedral sites as well as the tetrahedral sites in samples. The inversion degree of Ga or Mg increased with increasing content of doping ions. Absorption spectra indicated that Co^{2+} and Cr^{3+} ions entered both the tetrahedral and octahedral sites of spinel structure by substituting Mg^{2+} and Ga^{3+} ions, respectively. Emission spectra of the co-doped $MgGa_2O_4$ showed a broad emission band peaking at 700 and 680 nm, relevant to the emission characteristic of octahedral Cr^{3+} and tetrahedral Co^{2+} ions.

1. Introduction

Spinel oxides are a group of compounds with the general formula of AB_2O_4, where A and B are two different cations. Many of the spinels possess interesting electronic and magnetic properties and show a wide range of applications, such as catalyst, ceramic, magnetic and host materials [1–4]. In the structure of spinel, oxygen ions form cubic closed-packed structure and A or B cations occupy two different crystallographic sites: octahedral and tetrahedral. The distribution of A and B cations in these two sites, which is affected by the combination and nature of the two cations, depends strongly on the temperature, impurity content, and particle size [5–8]. One of the interesting features for spinel is the wide range of cation distribution in this system. Some of the spinels have "normal" distribution where A and B cations occupy tetrahedral and octahedral sites, respectively. Some of the spinels are known to have the "inverse" distribution where A ions are located at the octahedral sites and one-half of the B ions are pushed to the tetrahedral sites. Other spinels are the "mixed" spinels with the formula $(A_{1-y}B_y)[A_yB_{2-y}]O_4$, where the brackets () and [] represent the tetrahedral and octahedral sites, respectively, and y denotes the inversion parameter. Studies of cation distribution in spinels have attracted much attention because they may allow better understanding of the correlations between structure and properties such as color, magnetic behavior, catalytic activity and optical properties etc., which are strongly dependent on the occupation of these two sites by metals [9–12].

Cation distribution in $MgGa_2O_4$ spinel is well known to be partially disordered under various conditions, which has been confirmed using X-ray diffraction analyses [13–15]. Recently, $MgGa_2O_4$ doped with transition metal ions have attracted much attention because they can exhibit strong emission and absorption bands in visible region [16–19]. The introduction of transition metal ions will affect the microstructure and optical properties of spinel. The previous studies showed that the inversion parameter increased with increasing Co content in the Co-doped spinel [20]. However, there is no report about Co/Cr co-doped nanocrystalline $MgGa_2O_4$ particles as far as we know. In this work, the dual doped $MgGa_2O_4$ nanoparticles with Co and Cr have been synthesized by sol-gel method and the local structural variations were investigated by means of X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR). The UV–vis absorption and luminescence properties of the materials were studied and the relationship between the structure and the optical properties was discussed.

2. Experimental

The Co^{2+}/Cr^{3+} co-doped $MgGa_2O_4$ nanoparticles were prepared by using citrate sol-gel method. Firstly, $Mg(NO_3)_2{\cdot}6H_2O$ and $Ga(NO_3)_3{\cdot}xH_2O$ were dissolved in deionized water, and proper amount of cobalt acetate and chromium nitrate was added. Then citric acid was added to the above solution with stirring. The mixed

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solution was stirred for 1 h and then heated in an 80 °C water bath until a highly viscous gel was formed. The gels were dried in an oven at 110 °C and then fired to 800 °C to obtain the $MgGa_2O_4$ nanoparticles.

The X-ray diffraction patterns of the doped $MgGa_2O_4$ nanoparticles were carried out on a Japan Rigaku D/Max-rA diffractometer using a Cu-target tube ($\lambda = 0.15418$ nm) and a graphite monochromator. The infrared spectra were recorded at room temperature using a Nicolet 8700 infrared spectrophotometer. X-ray photoelectron spectra (XPS) were measured using a Thermofisher ESCALAB 250 X-ray photoelectron spectrometer with monochromatized Al K_α X-ray radiation in ultrahigh vacuum ($<10^{-7}$ Pa). The binding energies were calibrated by using C1s peak (284.6 eV) of carbon impurities as a reference. The peaks were deconvoluted after background subtraction, using a mixed Gaussian–Lorentzian function. Diffuse absorbance spectra were recorded with a step of 1 nm on a Shimadzu UV-2550 spectrophotometer using an integration sphere at room temperature. $BaSO_4$ was used as reference. The photoluminescence spectra in the visible region were recorded by using a FLS900 fluorescence spectrophotometer.

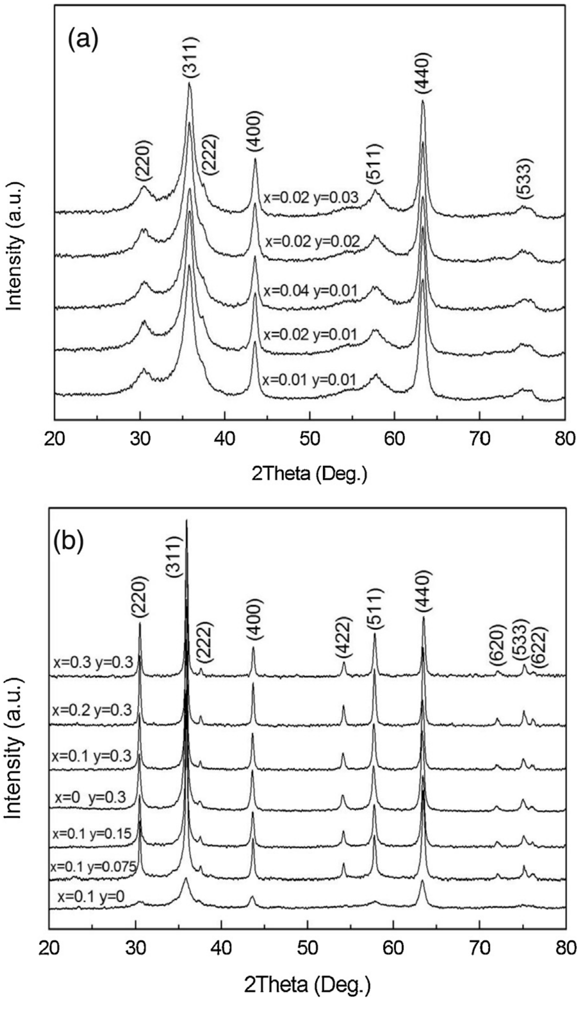

Fig. 1. XRD patterns of $Co_xMg_{1-x}Cr_{2y}Ga_{2(1-y)}O_4$ nanoparticles annealed at 800 °C.

3. Results and discussion

3.1. Synthesis of Co^{2+}/Cr^{3+} co-doped $MgGa_2O_4$ nanoparticles

Fig. 1 shows the XRD patterns of $MgGa_2O_4$ nanoparticles dual doped with different concentrations of Cr and Co. All the samples have been crystallized and the peaks indexed as (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (6 2 0), (5 3 3) and (6 2 2) crystal planes in the XRD patterns are assigned to the cubic $MgGa_2O_4$ spinel phase (JCPDS No. 10-113). It can be seen from Fig. 1a that the diffraction peaks are relatively broad for the samples with a small quantity of Co and Cr, indicating the small crystallite size of these samples.

The crystallite size was calculated by means of the Scherrer formula: $D = 0.9\lambda/(\beta\cos\theta)$, where λ is the X-ray wavelength (0.15418 nm), $\beta$is the full width at half-maximum (FWHM) intensity of the diffraction line, and θ is the diffraction angle. The size of crystal grain was about 10 nm for the samples with Co and Cr concentration lower than 5%, and the size was found to increase to about 30 nm when the concentration of the two ions are higher than 10%.

3.2. XPS studies

In order to study the chemical environments of the cations in the as-synthesized samples, high-resolution XPS spectra of Ga $2p_{3/2}$, Mg 1s and Cr $2p_{3/2}$ core levels as a function of doping concentration were measured and exhibited in Fig. 2a–c, respectively. Ga $2p_{3/2}$ spectra are asymmetric and can be deconvoluted into two peaks. The peaks at ~1117.0 eV and ~1119.0 eV are assigned to Ga at tetrahedral and octahedral sites in the structure of spinel, respectively. The assignment is consistent with the Ga $2p_{3/2}$ spectra analysis in other materials [20]. The fitted data is listed in Table 1. Those as-synthesized samples have partially inverse spinel structure with most of Ga^{3+} ions located at octahedral sites. The fraction of tetrahedral Ga^{3+} ions was calculated according to the area of those two peaks corresponding to tetrahedral and octahedral sites, respectively. It can be seen from Table 1 that the proportion of Ga^{3+} at tetrahedral sites increases with the increase of Co and Cr content in samples.

The dependence of Mg 1s XPS spectra on the composition is shown in Fig. 2b. All Mg 1s spectra can also be deconvoluted into two peaks through Gaussian–Lorentzian curve fitting. The peaks at ~1306 eV and ~1305 eV are assigned to Mg^{2+} ions in octahedral and tetrahedral sites, respectively [21,22]. The fraction of octahedrally coordinated Mg^{2+} ions increases from 0.48 to 0.68 with the increasing of Co and Cr content from $x = 0.02$, $y = 0.01$ to $x = 0.3$, $y = 0.3$ (Table 2).

Cr $2p_{3/2}$ spectra of Cr/Co: $MgGa_2O_4$ show one peak at about 576.5 eV and have slightly broaden at the left side (Fig. 2c), which indicates that Cr^{3+} ions occupy more than one coordination environment in the samples. The Cr spectra have little change with the composition.

3.3. Infrared spectroscopy

Fig. 3 shows the FT-IR spectra of Cr/Co: $MgGa_2O_4$ samples calcined at 800 °C in the frequency range of 400–850 cm^{-1}. The spectra show two main absorption bands at around 640 (ν_1) and 490 (ν_2) cm^{-1}, attributed to the stretching vibrations due to the interactions between the oxygen atom and the cations in the tetrahedral and octahedral positions, respectively [23].

With the increasing concentration of Co^{2+} and Cr^{3+} ions, the ν_1 and ν_2 bands shift toward the higher wave number. The variation in the band position, by increasing Co and Cr content, may be caused by the variation in the cation–oxygen bond length of the