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Hydrothermal synthesis and photoluminesent properties of Sb^{3+}-doped and (Sb^{3+},Mn^{2+})-co-doped calcium hydroxyapatite

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Sb^{3+}-doped and (Sb^{3+},Mn^{2+})-co-doped calcium hydroxyapatites were synthesized from a hydrothermal system, and the photoluminescent properties of these materials were investigated. The position of the emission peak of Sb^{3+} varies significantly with the amount of F^- and Cl^- anions and the F^-/Cl^- ratio in the reaction system. Energy transfers from Sb^{3+} to Mn^{2+} in the as-synthesized (Sb^{3+},Mn^{2+})-co-doped hydroxyapatite compounds have been observed. No reducing atmosphere is needed to prevent the oxidation of Mn^{2+} ions in the hydrothermal synthesis of the (Sb^{3+},Mn^{2+})-co-doped calcium hydroxyapatite.

Introduction

The apatites with a formula of $M_5(PO_4)_3X$, where M stands for Ca, Sr, Ba and X for F, Cl, Br or OH have been studied for their technological importance as phosphor materials and as laser hosts.[1,2]

Calcium halophosphate doped with antimony and manganese ions is an important commercial phosphor. It has been widely used until today because of its cheap price and excellent luminescent properties.[3] The activator Sb^{3+} ions in the compound absorb the 254 nm radiation of the Hg discharge and emit energy in a band peaking near 480 nm in lamps. In the mean time, a part of the energy absorbed by Sb^{3+} ions is transferred to the additional activator Mn^{2+} ions and cause them to emit orange–red light with the emission peaking at about 580 nm.[4] The combination of these two emissions renders the (Sb^{3+},Mn^{2+})-co-doped calcium halophosphate materials ideal phosphors for lighting.

The calcium halophosphate has a hexagonal structure and the Ca atoms occupy two different sites. The Ca atoms in the Ca(I) sites are surrounded by six oxygen atoms and those in the Ca(II) sites are directly bonded with one halogen atom as well as five oxygen atoms. The activator Sb^{3+} ions are located at the Ca(II) sites in the Sb^{3+}-doped halophosphate crystal structure and the nearest-neighbor halide ions are substituted by oxygen atoms to provide charge compensation.[5] When the Sb^{3+} ion-doped calcium fluoro- and chlorophosphates were prepared in the absence of oxygen by a high temperature solid-state method, Soules *et al.*[6] found that the normal emission band peaking at around 480 nm was replaced by a higher energy emission band at around 400 nm. They attributed this change to the location of the activator Sb^{3+} ions at the uncompensated Ca(II) sites. They also calculated the ground and excited states of the antimony luminescent center in fluorophosphate using the Wolfsberg–Helmholtz semi-empirical molecular orbital linear combination of atomic orbitals (MO-LCAO) method and used approximate adiabatic configuration coordinate diagrams to explain the shift of the emission band at around 480 nm to 400 nm in the absence of oxygen.

So far, without exception, commercial halophosphate phosphors have been prepared through a high temperature solid-state reaction that is thought to be energy-consuming and not easily controllable. A promising alternative synthetic method would be the hydrothermal technique, which has been successfully employed to prepare phase-pure, high-quality ceramic (oxides) and zeolitic materials.[7–9] This technique requires milder reaction conditions than the high temperature solid-state method.[10] Recently, the hydrothermal synthesis of phosphors has attracted considerable interest.[11–13] Manganese-doped Zn_2SiO_4 is mainly used as a green phosphor in lamps and cathode ray tubes. Li *et al.*[14] synthesized Zn_2SiO_4 by a hydrothermal method and investigated the relationship between the morphologies and the additional ions. We obtained photoluminescent $ZnWO_4$ crystals with various morphologies and particle sizes from a hydrothermal system.[15]

Calcium hydroxyapatite has a hexagonal structure essentially the same as that of calcium halophosphate except that the halide anions in the latter are substituted by hydroxy groups in the former. This material is the prototype of animal hard tissues and the synthesized materials find wide applications, such as bioceramics, chromatographic adsorbents, acidic and basic catalysts, cosmetic materials and so on.[16–18] Trabelsi-Ayedi and co-workers[19] synthesized Eu^{3+}-doped $Ca_5(PO_4)_3OH$ through a high temperature solid-state method and investigated the luminescent properties of Eu^{3+} in the compound. No Sb^{3+}- and Mn^{2+}- doped or (Sb^{3+},Mn^{2+})-co-doped calcium hydroxyapatite has been reported yet in the literature. In this paper, the synthesis of Sb^{3+}-doped and (Sb^{3+},Mn^{2+})-co-doped hydroxyapatites from a hydrothermal system is described. We found that the luminescent properties of the Sb^{3+}-doped hydroxyapatite changed with the addition of halide ions in the hydrothermal reaction system. And energy transfers from the Sb^{3+} ions to the Mn^{2+} ions were observed for the (Sb^{3+}, Mn^{2+})-co-doped hydroxyapatite compounds.

Experimental

In order to synthesize the Sb^{3+}-doped calcium hydroxyapatite hydrothermally, 85% H_3PO_4 was dissolved in distilled water, to which was added the Sb powder and $Ca(OH)_2$ successively under continuous stirring. Aqueous ammonia solution (25%) was dropped into the reaction system to adjust the pH value of the system to 8. In a typical synthesis procedure, the molar composition of the initial mixture was $Ca(OH)_2 : 0.67H_3PO_4 : NH_3{\cdot}H_2O : 0.018Sb : 25H_2O$. The reactants were stirred until homogeneous, sealed in a Teflon-lined stainless steel autoclave and heated at 513 K for 4 days under autogenous pressure. The solid product was washed thoroughly with distilled water and dried at room temperature. The as-synthesized Sb^{3+}-doped

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$Ca_5(PO_4)_3OH$ was calcined at 1073 K for 4 h in order to see the effect of hydroxy removal on the photoluminescent properties of the material.

For the preparation of (Sb^{3+},Mn^{2+})-co-doped calcium hydroxyapatite, manganese acetate was first dissolved in water followed by the addition of 85% H_3PO_4. The rest of the synthetic procedure was the same as that for the preparation of Sb^{3+}-doped calcium hydroxyapatite. F^- and Cl^- ions in the reaction system were introduced through the addition of ammonium fluoride and ammonium chloride, respectively. The molar ratio of the halide ions to the PO_4^{3-} ions was fixed to 0.02 in all the relevant mixtures.

Inductively coupled plasma (ICP) analysis was performed on a PerkinElmer Optima 3300 DV spectrometer whereas the powder X-ray diffraction (XRD) was conducted on a Siemens D5005 diffractometer with Cu K_α radiation (λ = 1.5418 Å). The XRD scanning rate was 1° min^{-1}. A Netzsch STA 449C thermal analyzer was employed to obtain the thermogravimetric analysis (TGA) curves. The infrared (IR) spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The luminescent properties of the samples were measured on a PerkinElmer LS55 spectrometer. In order to obtain good spectral resolution, a slit width of 5.0 nm was selected for both excitation and emission measurements.

Results and discussion

The powder XRD patterns for the Sb^{3+}-doped calcium hydroxyapatite obtained from the hydrothermal system and the product calcined at 1073 K are shown in Fig. 1. All the peaks in the patterns are indexed on the basis of the crystallographic data for the known structure of $Ca_5(PO_4)_3OH$ (ICSD Code 16742[20]), suggesting that the as-synthesized sample is phase-pure. The ICP analysis for the as-synthesized Sb^{3+}-doped $Ca_5(PO_4)_3OH$ shows that there exists 38.5% Ca, 17.9% P and 2.1% Sb in the compound, corresponding to a molar ratio of Sb : Ca : P = 0.03 : 1.67 : 1.0.

When the halide ions are added to the hydrothermal reaction system, they partly substitute for the hydroxy groups, and the reaction product should be designated Sb^{3+}-doped $Ca_5(PO_4)_3(OH,X)$, where X stands for F^- and/or Cl^-. The powder X-ray diffraction patterns for the Sb^{3+}-doped calcium hydroxyapatites synthesized in the presence of halide ions in the hydrothermal reaction system are displayed in Fig. 2. It is seen that the as-synthesized products all correspond to $Ca_5(PO_4)_3OH$ on the basis of these XRD patterns except that the peak intensities vary with the addition of halide ions and the variation of the F^-/Cl^- ratio (see also Fig. 1). The addition of Cl^- anions to the reaction system with a smaller F^-/Cl^- ratio or without F^- anions enhances the crystallinity of the material to a considerable extent. We also simulated the XRD pattern for $Ca_5(PO_4)_3(OH,Cl)$ with a molar ratio $Cl^-/(PO_4)^{3-}$ = 0.02 and found that the pattern is essentially the same as that for the $Ca_5(PO_4)_3OH$, indicating that the existence of such a small amount of Cl^- in the structure has no effect on the XRD pattern. The intensity difference among the XRD patterns in Fig. 2 seems to be because the presence of the halide anions in the reaction mixtures affects the crystallization habit (morphology, particle size and crystallinity) of the compounds. How the presence of F^- and Cl^- ions and the F/Cl^- ratio influence the crystallization habit of the sample remains a matter for further investigation.

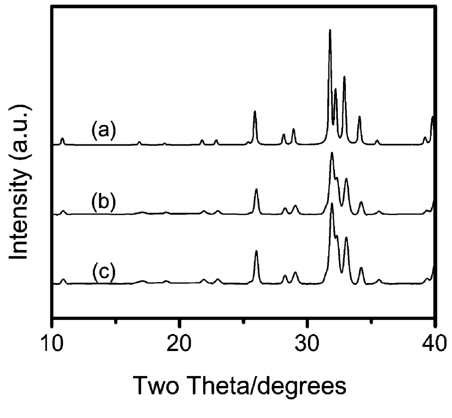

Fig. 1 Powder X-ray diffraction patterns of Sb^{3+}-doped $Ca_5(PO_4)_3OH$: (a) simulated pattern, (b) the pattern for the as-synthesized sample and (c) the pattern for the calcined sample of (b).

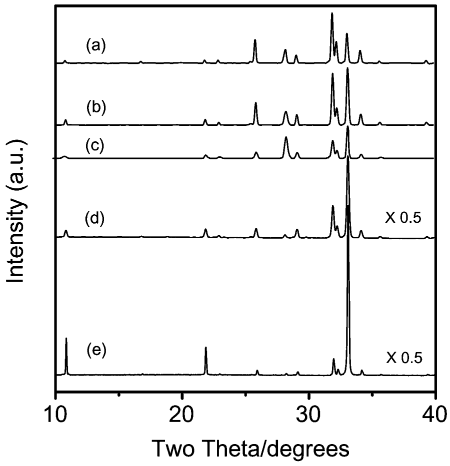

Fig. 2 Powder XRD patterns for Sb^{3+}-doped $Ca_5(PO_4)_3(OH,X)$ (X = F or Cl) synthesized in the presence of halide ions in the reaction system: (a) F^- ions only, (b) F^-/Cl^- = 2.0, (c) F^-/Cl^- = 1.0, (d) F^-/Cl^- = 0.5 and (e) Cl^- ions only. The molar ratio of the sum of the halide ions over the PO_4^{3-} ions is fixed at 0.02 in the reaction system. The peak intensities for patterns (d) and (e) are halved.

Fig. 3 shows the infrared spectra of the as-synthesized Sb^{3+}-doped $Ca_5(PO_4)_3OH$ and the calcined sample. After calcination at 1073 K, the absorptions at 1412 and 1458 cm^{-1} disappear and the absorptions at 1618 and 962 cm^{-1} become weaker, whereas the band at 3441 cm^{-1} characteristic of hydroxy groups is nearly extinct, suggesting that the vast majority of the OH groups in the structure of the sample have been removed upon calcination at this temperature. However, this hydroxy removal has no effect on the crystalline structure of the compound as confirmed by the XRD results (see Fig. 1), and a general formula of $Ca_{10}(PO_4)_6O$ is conceivable for the calcined sample. TGA indicates that the weight loss after calcination at 873 K is about 1.82%, well in accordance with the removal (1.79%) of OH groups as water molecules from the $Ca_5(PO_4)_3OH$ compound. The IR spectra for the Sb^{3+}-doped $Ca_5(PO_4)_3(OH,X)$ before and after calcination are identical to the respective ones for the as-synthesized Sb^{3+}-doped

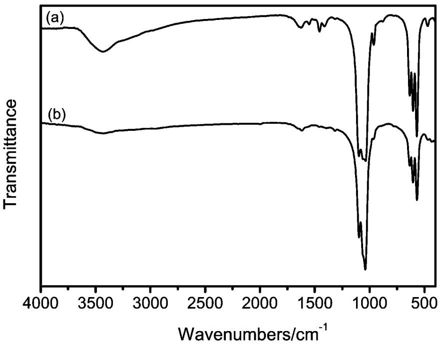

Fig. 3 IR spectra of Sb^{3+}-doped $Ca_5(PO_4)_3OH$: (a) before and (b) after calcination at 1073 K for 4 h.

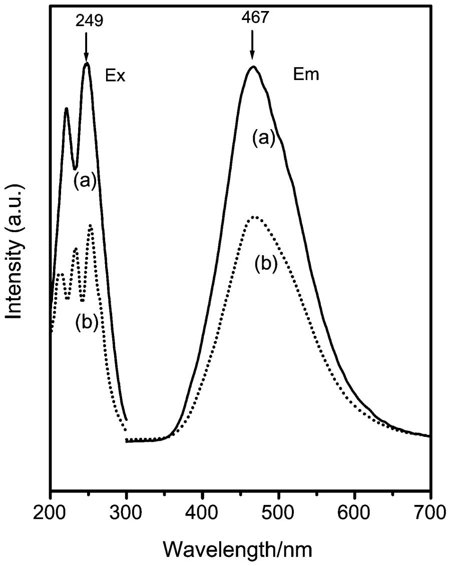

Fig. 4 Photoluminescent spectra of: (a) Sb^{3+}-doped $Ca_5(PO_4)_3OH$ and (b) the calcined sample of (a). For emission measurement, the excitation wavelength was 249 nm whereas for excitation measurement the emission wavelength was 467 nm.

$Ca_5(PO_4)_3OH$ and the calcined compound $Ca_{10}(PO_4)_6O$. Obviously, because the amount of halide anions in the Sb^{3+}-doped $Ca_5(PO_4)_3(OH,X)$ material is too small, the IR spectra can not differentiate this material from the Sb^{3+}-doped $Ca_5(PO_4)_3OH$, either before or after calcination.

The luminescent spectra of the as-synthesized Sb^{3+}-doped $Ca_5(PO_4)_3OH$ and the calcined sample are shown in Fig. 4. The emission bands for both spectra are at about 467 nm, and their half width is about 115 nm, narrower than that (140 nm) reported in the literature for a similar compound of Sb^{3+}-doped calcium halophosphate.[7] These emission bands are attributable to the $^3P_1 \rightarrow {}^1S_0$ transition.[21] The luminescent intensity of the as-synthesized Sb^{3+}-doped $Ca_5(PO_4)_3OH$ is higher than that of the sample calcined at 1073 K for 4 h. This luminescent intensity decrease after calcination is probably because the microenvironment of Sb^{3+} ions is changed when the sample is calcined at an elevated temperature. There are two peaks in the excitation spectrum of the Sb^{3+}-doped $Ca_5(PO_4)_3OH$, with one being at about 249 nm and the other at about 221 nm. While, there are three peaks at about 213, 232 and 252 nm in the excitation spectrum of the calcined sample, further confirming the microenvironment change of the Sb^{3+} ions in the structure of $Ca_5(PO_4)_3OH$ after calcination. All these excitations should be assigned to the $^1S_0 \rightarrow {}^3P_1$ transition. The triplet structure in the excitation spectrum of the calcined sample may result from the splitting of the excited states of $5s^2$ orbital interaction with the host lattice vibrations.[21]

The trivalent Sb^{3+} ions replace the Ca^{2+} ions at the Ca(II) positions of $Ca_5(PO_4)_3OH$, and the OH^- groups in the vicinity of the original Ca(II) cations should become O^{2-} ions around the Sb^{3+} cations in order to provide charge balance in the structure of the Sb^{3+}-doped compound. Therefore, the energy-consumption[22] of vibration of OH^- is very small in our product because there are no OH^- groups directly bonded with the Sb^{3+} cations in the structure. The photoluminescent behaviour of the Sb^{3+}-doped $Ca_5(PO_4)_3OH$ we synthesized is analogous to that of the calcium fluorophosphate synthesized by high temperature solid-state reaction in an oxygen atmosphere. The emission peak of Sb^{3+} ions at the compensated Ca(II) sites in the calcium fluorophosphate was at about 480 nm.[10] But there exist F^- ions in the structure of calcium fluorophosphate, whereas only OH^- ions are present in $Ca_5(PO_4)_3OH$. This difference may also explain why the emission peak (at 480 nm) for the fluorophosphate is 13 nm red-shifted in comparison with that for the hydroxyapatite compound obtained.

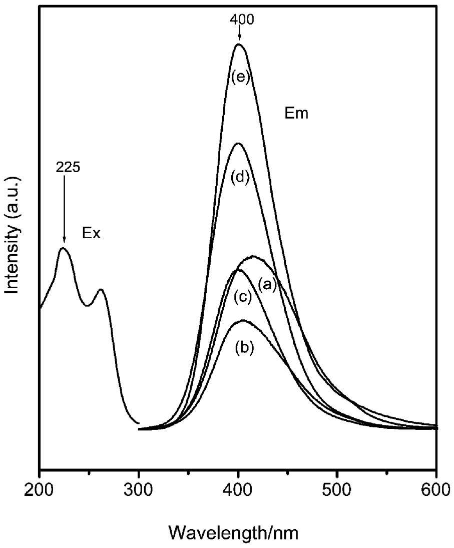

Fig. 5 Photoluminescent spectra of Sb^{3+}-doped $Ca_5(PO_4)_3(OH,X)$ ($X = F$ or Cl) synthesized from hydrothermal systems in the presence of halide ions: (a) F^- ions only, (b) $F^-/Cl^- = 2.0$, (c) $F^-/Cl^- = 1.0$, (d) $F^-/Cl^- = 0.5$ and (e) Cl^- ions only. The molar ratio of the sum of the halide ions over the $PO_4{}^{3-}$ ions was fixed at 0.02 in the reaction system. The excitation wavelength was 225 nm for the emission measurements and the emission wavelength was 400 nm for the excitation measurement.

It can be seen (Fig. 5) that the emission peaks of the Sb^{3+} ions in the Sb^{3+}-doped $Ca_5(PO_4)_3(OH,X)$ shift to about 400 nm from the original 467 nm of the Sb^{3+}-doped $Ca_5(PO_4)_3OH$ (see also Fig. 4). The extent of this shift depends on the relative amount of the halide anions in the reaction mixture (Fig. 5). The emission band is at about 416 nm if F^- ions only are present in the hydrothermal reaction system, whereas it shifts to higher energies when Cl^- ions are also added to the reaction mixture. When halide ions are present in the hydrothermal reaction system, some of them enter the crystal lattice of the calcium hydroxyapatite product. The halide ions surrounding the Sb^{3+} ions may form direct bonds with the latter and as a result, they affect the luminescent properties of the compound. In our reaction system, when F^- ions only are present or the amount of F^- ions is significantly larger than that of Cl^- ions, the F^- ions are the predominant halide species around the Sb^{3+} cations in the product, leading to an emission band at about 416 nm. When the amount of Cl^- ions is increased, the Cl^- ions also have chance to enter the coordination sphere around the Sb^{3+} ions, resulting in a blue-shift of the emission band. If Cl^- ions only exist in the reaction system, the halide anions around the Sb^{3+} cations are solely Cl^-, and the position of the emission band shifts to the minimum 400 nm. Obviously, the emission band position can be changed from 416 nm to 400 nm by simply varying the F^-/Cl^- ratio in the hydrothermal reaction system. Such a position shift has never been observed for the calcium halophosphate phosphors prepared through high temperature solid-state reaction methods. It can also be seen from Fig. 5 that the emission intensity varies with the F^-/Cl^- ratio in the reaction system. Close inspection reveals that the emission intensity is proportional to the crystallinity of the sample, which, in turn, is affected by the F^-/Cl^- ratio (see also Fig. 2).

For the previously reported (Sb^{3+},Mn^{2+})-co-doped calcium halophosphates, there existed an energy transfer from Sb^{3+} ions to Mn^{2+} ions in the process of photoluminescence. Therefore, a range of whitish color from near blue to orange can be obtained from a single material by changing the ratio of Sb^{3+} over Mn^{2+} ions.[2] Energy transfer from Sb^{3+} to Mn^{2+} is

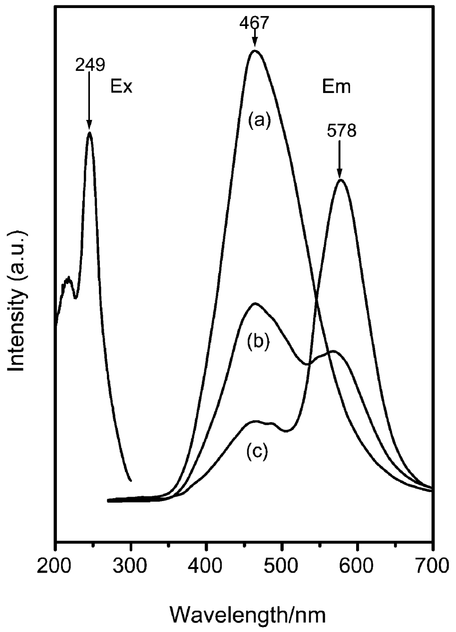

Fig. 6 Photoluminescent spectra of (Sb^{3+},Mn^{2+})-co-doped $Ca_5(PO_4)_3OH$ with various molar ratios of Sb^{3+}/Mn^{2+}: (a) Sb^{3+} ions only, (b) Sb^{3+}/Mn^{2+} = 1.5 and (c) Sb^{3+}/Mn^{2+} = 0.3. The excitation wavelength was 249 nm for the emission measurements and the emission wavelength was fixed at 467 nm for the excitation measurement.

also observed (Fig. 6) for the (Sb^{3+},Mn^{2+})-co-doped $Ca_5(PO_4)_3OH$ synthesized from the hydrothermal reaction systems without halide ions. When the amount of Mn^{2+} ions increases in the reaction system, the intensity of the Sb^{3+} emission band at about 467 nm is reduced, whereas the intensity of the Mn^{2+} emission band at about 575 nm is enhanced gradually. Meanwhile, the excitation spectra for the Sb^{3+}-doped and for the (Sb^{3+}, Mn^{2+})-co-doped compounds are essentially the same, confirming the energy transfer from Sb^{3+} ions to Mn^{2+} ions.

An energy transfer from Sb^{3+} to Mn^{2+} also occurs for the (Sb^{3+}, Mn^{2+})-co-doped compounds synthesized in the presence of halide ions in the reaction system (Fig. 7). When the amount of Mn^{2+} ions added to the reaction system is increased, the intensity of the Sb^{3+} emission band at around 400 nm decreases and that of the Mn^{2+} emission at about 575 nm is enhanced accordingly because of an energy transfer from the Sb^{3+} ions to Mn^{2+} ions present in the co-doped compounds.

The high temperature solid-state preparation of (Sb^{3+}, Mn^{2+})-co-doped calcium halophosphate phosphors needs a $N_2 + H_2$ atmosphere to prevent the Mn^{2+} ions from becoming oxidized at high temperatures, whereas in a hydrothermal reaction system, the water molecules render the system a non-oxidative medium, and in this medium no reductive protection atmosphere is needed to prevent the oxidation of metal ions. This is a further significant advantage of the hydrothermal technique over the solid-state method for preparation of phosphors.

Conclusion

Sb^{3+}-doped and (Sb^{3+},Mn^{2+})-co-doped calcium hydroxyapatites have been synthesized from hydrothermal systems. The photoluminescence band appears at around 467 nm for the Sb^{3+}-doped compound whereas it shifts to higher energies to a considerable extent in the presence of halide ions in the reaction system. Depending on the F^-/Cl^- ratio in the reaction mixture, the position of the Sb^{3+} emission band changes from 416 to 400 nm. Energy transfer from Sb^{3+} ions to Mn^{2+} ions has been observed for the (Sb^{3+},Mn^{2+})-co-doped calcium hydroxyapatites in the photoluminescence process. For the preparation of (Sb^{3+},Mn^{2+})-co-doped calcium hydroxyapatites through a hydrothermal technique, the reductive ($N_2 + H_2$) atmosphere used in high temperature solid-state methods is not needed, and the reaction conditions become milder. Wide color ranges of (Sb^{3+},Mn^{2+})-co-doped $Ca_5(PO_4)_3(OH,X)$ can be obtained, by varying the ratio of Sb^{3+}/Mn^{2+}, from a hydrothermal reaction system in the presence of halide ions. Hydrothermal synthesis would be a very useful method in the preparation of luminescent materials because of the milder reaction conditions and the ease of control.

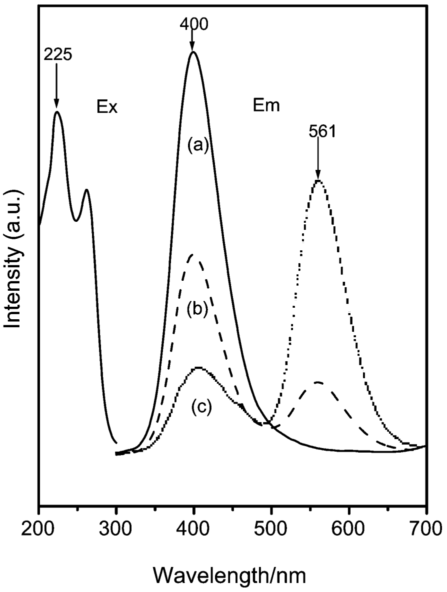

Fig. 7 Photoluminescent spectra of (Sb^{3+},Mn^{2+})-co-doped $Ca_5(PO_4)_3$-(OH,X) (X = F or Cl) obtained from a hydrothermal system in the presence of halides (F^-/Cl^- molar ratio is fixed at 0.5) with various molar ratios of Sb^{3+}/Mn^{2+}: (a) Sb^{3+} ions only, (b) Sb^{3+}/Mn^{2+} = 2 and (c) Sb^{3+}/Mn^{2+} = 0.3. The excitation wavelength was 225 nm for the emission measurements and the emission wavelength was 400 nm for the excitation measurement.

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