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Spectral properties and energy transfer in PbWO_4 co-doped with Cr^{3+} and F^-

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Abstract

A Cr^{3+} , F^- -co-doped PbWO_4 crystal was grown by the Czochralski method and its spectroscopic properties were investigated. In addition to the intrinsic luminescence of PbWO_4 , the sample showed ${}^2\text{E} \rightarrow {}^4\text{A}_2$ radiation of Cr^{3+} excited by x-radiation or UV-vis light. This indicated that the Cr^{3+} is submitted to a strong crystal field and a doping mechanism is hereby proposed that Cr^{3+} replaces W^{6+} with the cooperation of F^- . The reabsorption and resonant energy transfer mechanisms from host to Cr^{3+} were studied. As a result, the PbWO_4 intrinsic emission was intensively suppressed and the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ luminescence increased when excited by x-radiation compared to excitation by UV-vis light, and the decay constants of PbWO_4 host scintillation reduce. The significant ${}^2\text{E} \rightarrow {}^4\text{A}_2$ luminescence of this material may be of interest for further application.

1. Introduction

PbWO_4 (abbreviated to PWO) is a new generation of scintillation crystal and it has future applications in high-energy physics, particularly in the large hadron collider project, due to its fast decay time, high density and short radiation length [1, 2]. Another interesting property of PWO is that its scheelite structure is very hospitable in allowing the substitution of many other ions. Doping is normally used to improve the optical properties of PWO. La^{3+} and Y^{3+} , for instance, have been shown to increase the transmittance and enhance the radiation hardness of PWO crystals [3, 4]. On the other hand, PWO crystals doped with rare-earth ions, especially

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with Nd^{3+} , have been demonstrated to be a potential laser material, and a self-stimulating Raman laser with 56% optical frequency conversion efficiency has been achieved [5, 6]. All these features favour the incorporation of different optically active ions in this crystal matrix.

PWO is a defect system and these defect structures exert a significant influence on its optical and scintillating properties [7–10], but a detailed insight into the doping mechanism and the interplay between defects is still unclear. How to understand and then how to control these defect structures, therefore, have long been subjects of much scientific and technical interest. The Cr^{3+} ion is particularly suited to study the microstructures of PWO because it is arguable that the most studied optically impurity has spectra that are very sensitive to the possible lattice sites [11, 12]. It is also interesting that with the help of a co-dopant, the sites and the valence of chromium ions could be artificially manipulated, which should be beneficial to chromium ions to enhance their performances. In addition, Cr^{3+} is a very important laser active ion and its ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition has been applied in the laser field, with the ruby laser being an important landmark decades ago [13].

In this work, we study the spectroscopic properties of a PWO crystal co-doped with Cr^{3+} and F^- . Energy transfer from host to the Cr^{3+} ion is demonstrated and the effect of the co-doped fluorine is also tentatively discussed. Based on experimental results, a doping mechanism of Cr^{3+} and F^- in the PWO host is proposed.

2. Experiment

Pure and Cr,F-co-doped PWO crystals were grown from 5 N raw material using the Czochralski method. Chromium and fluorine were introduced in the form of Cr_2O_3 and PbF_2 , and their concentrations in the melt were 0.1 and 0.2 mol%, respectively. Samples of about 0.3 mm thickness were prepared with the *c* axis perpendicular to the broad face, and polished to optical transparency for optical absorption measurements, and other slices with dimensions of $8 \times 8 \times 2 \text{ mm}^3$ were cut for luminescence investigations. All crystals were found to be of good optical quality. Optical absorption spectra were recorded on a Perkin–Elmer Lambda 900 spectrophotometer. Two kinds of light source were used to examine the luminescent properties of samples at room temperature: (1) an F-30 x-ray tube (W anticathode target) on a Fluormain x-ray excited luminescence (XEL) spectrometer, which characterizes the body luminescence of materials; (2) a 450 W Xe lamp on a Fluorolog-TAU-3 spectrometer, which depicts the surface luminescence of materials. The fluorescence lifetimes were measured by excitation with pulsed x-rays and detected by a S-1 photomultiplier tube. The time resolution of the x-ray excited fluorescence is 97 ps.

3. Experimental results and discussion

Figure 1 shows the unpolarized absorption spectra of pure and doped PWO crystals at room temperature. A strong absorption band centred around 430 nm and a weak one in the range 530–800 nm are observed. They should be assigned to the spin-allowed ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transitions of Cr^{3+} . No evidence of any higher valence state chromium ion is found in the PWO:Cr,F matrix after analysis of the absorption spectra in the near-infrared wavelength region.

A comparison of x-ray excited luminescence between pure and Cr,F-co-doped PWO crystals is displayed in figure 2. In the case of Cr,F-co-doped PWO, a wide luminescence band in the range 450–720 nm predominates, and it is overlapped by a narrow spectral line peaking at 645 nm. The PWO host luminescence in the range 350–580 nm, which is ascribed to an auto-localized exciton luminescence [10], is intensively suppressed with the co-addition

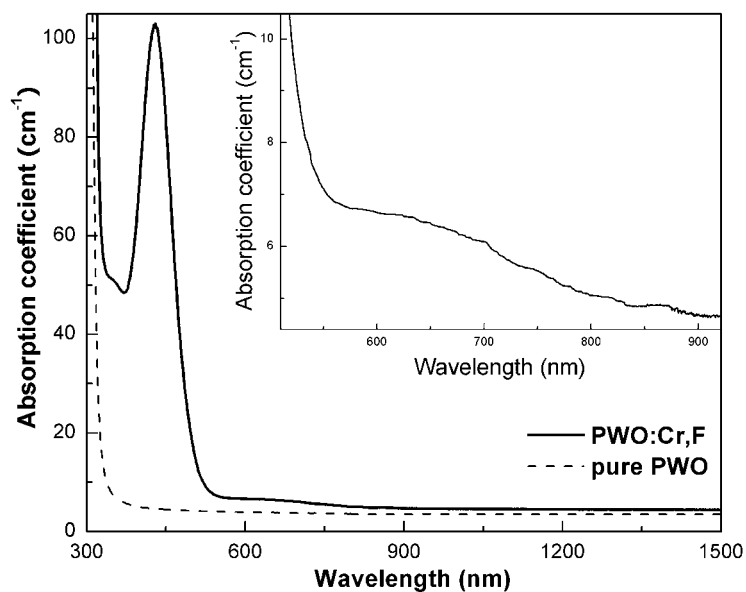


Figure 1. Optical absorption spectra of pure and Cr,F-co-doped PWO crystals. The inset shows the absorption spectra in the long wavelength region.

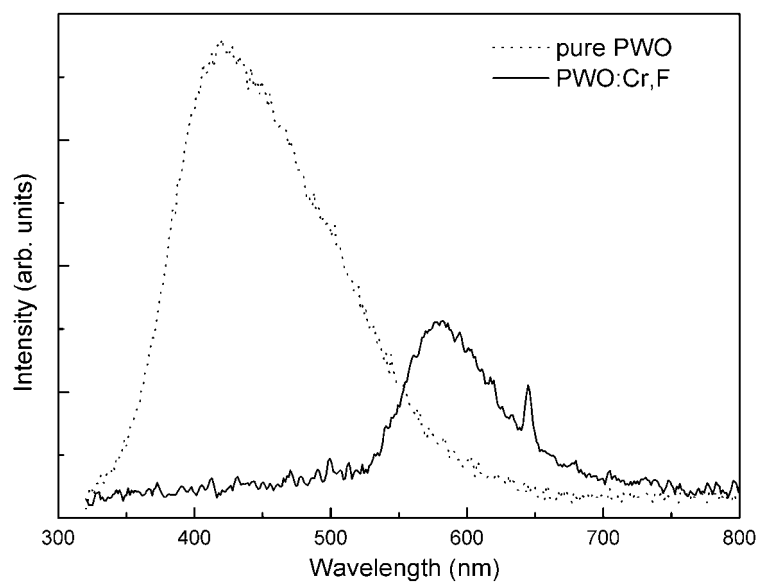


Figure 2. The x-ray excited luminescence spectra of pure and Cr,F-co-doped PWO.

of Cr^{3+} and F^- . The presence of 645 nm sharp luminescence, which is attributed to the spin-forbidden ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition (R line) of Cr^{3+} , indicates that Cr^{3+} ions are submitted to a strong crystal field [14] in F^- co-doped PWO.

Computer simulation suggests that the solution energy of trivalent cations in the PWO matrix is a strong function of the dopant's radius, and small ions have a tendency to substitute

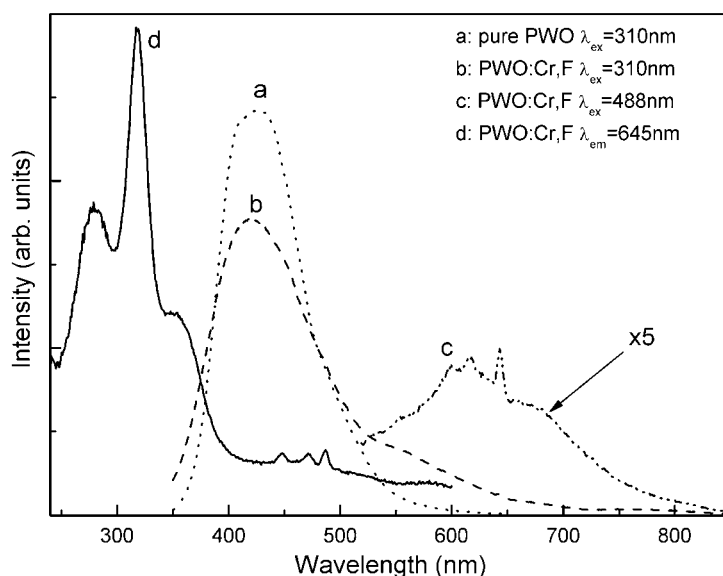
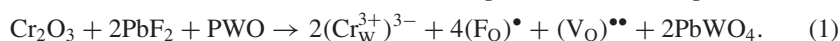


Figure 3. The emission and excitation spectra samples. (a) Emission spectrum ($\lambda_{\text{ex}} = 310$ nm) of pure PWO; (b) emission spectrum ($\lambda_{\text{ex}} = 310$ nm) of PWO:Cr,F; (c) emission spectrum ($\lambda_{\text{ex}} = 488$ nm) of PWO:Cr,F (for clarity, the curve was enlarged by factor of 5); and (d) excitation spectrum ($\lambda_{\text{em}} = 645$ nm) of PWO:Cr,F;

on the W site [15]. Taking into account the bond distances between Pb–O (2.58 and 2.64 Å) and W–O (1.79 Å) in the PWO crystal [16], it is expected that the substitution of Cr^{3+} for W^{6+} will put itself in a strong crystal field environment. On the other hand, the co-doped F^- replaces O^{2-} and induces an excess positive charge in the system. This process will prevent the substitution of Pb^{2+} by Cr^{3+} , which would also give rise to an excess positive charge. One should note that in contrast to the divalent oxygen, the monovalent fluorine attracts fewer electrons, which is helpful for the stability of Cr^{3+} in PWO. Of course, further work should be done to illustrate the effect of F^- . Therefore, the defect reaction in Cr,F-co-doped PWO can be expressed as:



‘PWO’ represents the PWO bulk crystal as a whole. From equation (1), it can be imagined that the introduction of Cr^{3+} and F^- will lead to the appearance of red luminescence, which is attributed to the $(\text{V}_O)^{\bullet\bullet}$ defects [17]. The hypothesis is in good agreement with the experimental results, as shown in figure 2.

Figure 3 presents the results of photoluminescence (PL) of pure and doped PWO. Similar to that of the pure PWO crystal, the emission spectrum ($\lambda_{\text{ex}} = 310$ nm) of a sample containing Cr^{3+} and F^- is dominated by blue and green bands (350–580 nm), although their intensities weaken compared to those of pure PWO crystal. It seems that the impurities, Cr^{3+} and F^- , exert a limited effect on those WO_4 tetrahedra nearby, and make a contribution to the blue and green luminescence [18, 19]. In contrast to the pure crystal, PWO:Cr,F emits a band in the 600–720 nm spectral regions which overlaps a weak R line of Cr^{3+} at 645 nm. This broad luminescence band is associated with the $(\text{V}_O)^{\bullet\bullet}$ defect, which is consistent with previous discussions.

It should be noted that the profiles of the excitation spectrum for the 645 nm band of Cr^{3+} ion in the wavelength region shorter than 350 nm are very similar to that for intrinsic luminescence (420 nm) of pure PWO crystal, as indicated in figure 3. This implies that the

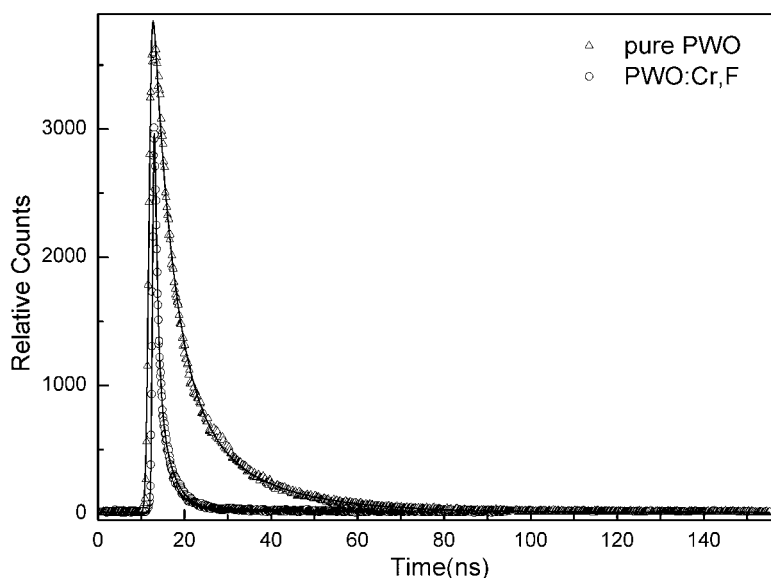


Figure 4. The fluorescence decay profiles of pure and Cr,F-co-doped PWO excited by x-radiation. The solid lines denote fitting results.

645 nm band in PWO:Cr,F excited by UV light could be produced through host-sensitization. That is to say, the PWO matrix might transfer energy to Cr³⁺ ions. The prominence of the 310 nm band in the excitation spectrum of PWO:Cr,F provides direct evidence for the existence of energy transfer from the matrix to impurities. However, 488 nm is more effective than 310 nm in exciting the R line of Cr³⁺. On the other hand, a spectral overlap region exists between the PWO host emission in the 370–530 nm spectral region (in figures 2 and 3) and the Cr³⁺ absorption involving the ⁴A₂ → ⁴T₁ transition (in figure 1). The system, therefore, satisfies one of the essential requirements for an energy transfer process. The energy transfer in PWO:Cr,F can be realized by reabsorption and/or resonant transfer of excitation energy from the PWO matrix to Cr³⁺ impurity centres. It is worth noting in the case of PWO:Cr,F that the PWO intrinsic luminescence (350–580 nm) is intensively suppressed and the R line of Cr³⁺ increases in the process of body luminescence (XEL) compared to those in the process of surface luminescence (PL), suggesting that a self-absorption process takes place in this system. The reabsorption could be one of the transfer energy mechanisms in PWO:Cr,F and hence could make a contribution to the R fluorescence of Cr³⁺.

Figure 4 exhibits the fluorescence decay profiles of pure PWO and PWO:Cr,F. The decay curve of pure PWO can be described by an equation with two exponential terms corresponding to the two decay times of 4.69 ± 0.09 ns and 17.18 ± 0.54 ns (the goodness of fit $R = 99.7\%$), respectively. These data coincide with the results of other authors [20]. The introduction of Cr³⁺ and F⁻ has an insignificant effect on the luminescent properties. It can be seen that with the incorporation of Cr³⁺ and F⁻ a distinct shortening of the decay time takes place. Its decay times decrease to 0.7 ± 0.01 ns and 3.32 ± 0.03 ns (the goodness of fit $R = 99.9\%$), respectively, which is evidence for the resonant energy transfer between the PWO intrinsic emission centres and Cr³⁺ ions. The energy transfer is achieved by a non-radiative process in which one ion returns to the ground state while another ion goes up to the upper level. In most cases, these cross-relaxation processes are based on electric dipole–dipole interaction [21].

In the PWO matrix, a binding energy calculation demonstrates a strong tendency toward pairs or cluster formation of the trivalent dopant [15], resulting in a small M^{3+} – M^{3+} distance in PWO lattice which is beneficial to the realization of resonant energy transfer. However, further investigations are needed.

4. Conclusion

In summary, we have reported the luminescence properties of PWO:Cr,F under excitation with UV–vis light and x-radiation, respectively. The ${}^2E \rightarrow {}^4A_2$ luminescence of Cr^{3+} in tungstate at room temperature is firstly found. The doping mechanism for Cr^{3+} occupying the W^{6+} position is presented and the energy transfer mechanisms from host to Cr^{3+} are demonstrated. Both reabsorption and resonant energy transfer processes contribute to R fluorescence. As a result, the R line radiation of Cr^{3+} excited by x-radiation increases and the decay time of the PWO host emission shortens. Considering the low cost, the well-developed growth technique of large size crystals and the stable physical–chemical properties, it is of interest to develop PWO:Cr,F as a new laser material. Further investigations are underway.

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