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铀在某些磷酸盐中的发光光谱

LUMINESCENCE OF URANIUM IN SOME PHOSPHATES



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摘 要

研究了铀在某些磷酸盐体系中的固体荧光光谱特性并探讨了它们的发光机理。对各种焙烧条件下 $\text{NaH}_2\text{PO}_4 : \text{U}$ 的晶体结构和发光现象进行研究,发现当焙烧温度在 $200 \sim 600^\circ\text{C}$ 时该体系形成 $\text{NaPO}_3 : \text{U}$ 结晶,并发出很强的绿色荧光;当焙烧温度高于 650°C 时,晶体变成无定形,荧光强度衰弱。铀浓度的变化也会影响晶体结构,当 $\text{U}/\text{NaH}_2\text{PO}_4$ 的质量比大于 10^{-2} 时, NaPO_3 的晶体结构畸变,这时会出现荧光强度饱和现象。

LUMINESCENCE OF URANIUM IN SOME PHOSPHATES

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ABSTRACT

The solid fluorescence spectral properties of uranium in phosphates systems have been observed. The $\text{NaH}_2\text{PO}_4 : \text{U}$ system has been found to be an efficient green phosphor. The luminescence mechanism of the phosphor has been discussed. The crystal structure of $\text{NaH}_2\text{PO}_4 : \text{U}$ system under different conditions was also studied. Over a wide range of ignition temperatures ($200 \sim 600^\circ\text{C}$), the system with mass ratio of $\text{U}/\text{NaH}_2\text{PO}_4$ below 10^{-3} transforms in to $\text{NaPO}_3 : \text{U}$ crystal, which emits strong fluorescence. The system is non-crystalline with decreasing fluorescence intensity when the ignition temperature is higher than 650°C . The NaPO_3 crystal lattice has distorted as the mass ratio of $\text{U}/\text{NaH}_2\text{PO}_4$ of the system greater than 10^{-2} .

INTRODUCTION

The green luminescence of uranium in many minerals and other substances has been known for a long time. A lot of work are dedicated to spectroscopic studies of crystals activated by hexavalent uranium. In most of cases, the green luminescence of uranium in the oxide crystals is caused by UO_6^{6-} ^[1-6], but in some cases the luminescence is attributed to uranyl ions UO_2^{2+} ^[2]. Luminescence properties of uranium in alkali halide crystals^[7-12] and in alkaline earth fluorides^[13-17] have been also studied in more detail. Johstone and Wright^[16] used selective excitation of individual uranium (VI) sites in a calcium fluoride matrix for the determination of uranium with a nitrogen laser pumped tunable dye laser at 13 k. They also studied^[17] the dependence of fluorescence intensity in $\text{CaF}_2 : \text{U}^{6+}$ system on ignition temperatures.

The luminescence properties of uranium in phosphates, especially in NaH_2PO_4 is described in this paper. The $\text{NaH}_2\text{PO}_4 : \text{U}$ system was found to be a good phosphor which has high efficiency of luminescence. The dependence of fluorescence intensity on crystal structure under different conditions has been studied too.

1 EXPERIMENTAL SECTION

1 g of phosphate (Analytically Pure) was added to a 25 mL porcelain crucible with 1 mL of U_3O_8 in appropriate nitric acid solution. After being dried on a electric heater, the samples of phosphates : U systems were ignited in a muffle furnace at 300°C, but $\text{NaH}_2\text{PO}_4 : \text{U}$ at different temperature (from 200°C to 750°C) for 1 hour and then cooled to room temperature in air. The samples were ground in a mortar into homogeneous powder and then pressed into several pellets (12 × 6 mm, 1.5 mm thick, 130 mg sample each pellet).

All measurements were performed on a Spex Spectrofluorometer (FLUOROLOG-2 Model 112) at room temperature. A 450 W xenon arc lamp was used as a excitation source. The excitation and fluorescence spectra of samples were obtained by the respective scanning excitation monochromator and emission monochromator.

$\text{NaH}_2\text{PO}_4 : \text{U}$ system with different ignition temperatures (< 200~750°C) and different uranium concentration ($0 \sim 10^{-1}$ mass ratios of $\text{U}/\text{NaH}_2\text{PO}_4$) was examined by X-ray diffraction analysis on a diffractometer (Rotatory anode, Cobalt

target, type RU-200, Rigaku, Japan).

2 RESULTS AND DISCUSSION

2.1 Excitation and Fluorescence Spectra

The excitation spectra of $\text{NaH}_2\text{PO}_4 : \text{U}$ and $\text{Na}_4\text{P}_2\text{O}_7 : \text{U}$ are shown in Fig. 1. Two principal excitation peaks of $\text{NaH}_2\text{PO}_4 : \text{U}$ and $\text{Na}_4\text{P}_2\text{O}_7 : \text{U}$ are located in the ultraviolet region i. e. 330, 422 nm and 322, 420 nm respectively. The optimal excitation wavelength for $\text{NaH}_2\text{PO}_4 : \text{U}$ and $\text{Na}_4\text{P}_2\text{O}_7 : \text{U}$ are 330 and 322 nm respectively. In same way, we have selected the optimal excitation wavelength for other phosphates : U systems (Table 1).

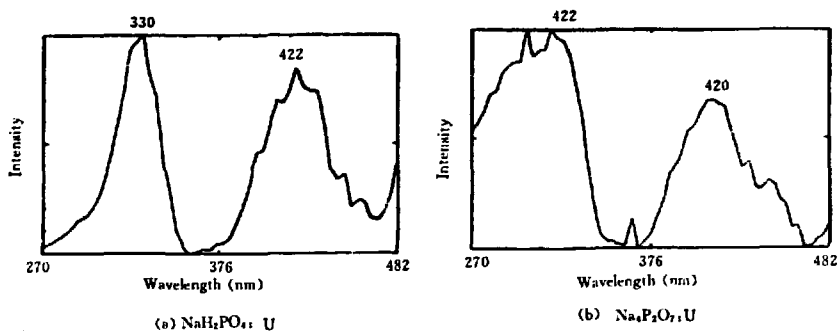


Fig. 1 Excitation spectra of $\text{NaH}_2\text{PO}_4 : \text{U}$ and $\text{Na}_4\text{P}_2\text{O}_7 : \text{U}$

The fluorescence emission spectra of these systems are shown in Fig. 2 (the mass ratio of U/phosphate is 10^{-3}). The data of their emission lines are listed in Table 1.

At room temperature, the fluorescence spectra of these phosphors consist of three to five lines. the spectra are distinguished from those of U (VI) in a UO_4^{6-} or UO_4^{2-} group^[2,15] (as in $\text{CaF}_2 : \text{U}$ (VI) or $\text{NaF} : \text{U}$ (VI) etc.), but are the same as those of it in the phosphate or sulphate solutions that have been reported^[18], except the line 482 nm was quenched. According to some authors results^[18,19], these emission lines correspond with the vibration frequency of $\text{O}=\text{U}=\text{O}$. The facts indicate that U (VI) in these solid phosphates is present in the form of uranyl. The luminescence center is the uranyl group $[\text{O}=\text{U}=\text{O}]^{2+}$, a linear molecular group UO_2^{2+} ions as activators incorporate into solid phosphates to form the phosphors. The distinguishable fluorescence bands are originated in the electron transitions

from the lowest vibrational level of the first excited election state to the different vibrational levels of ground state.

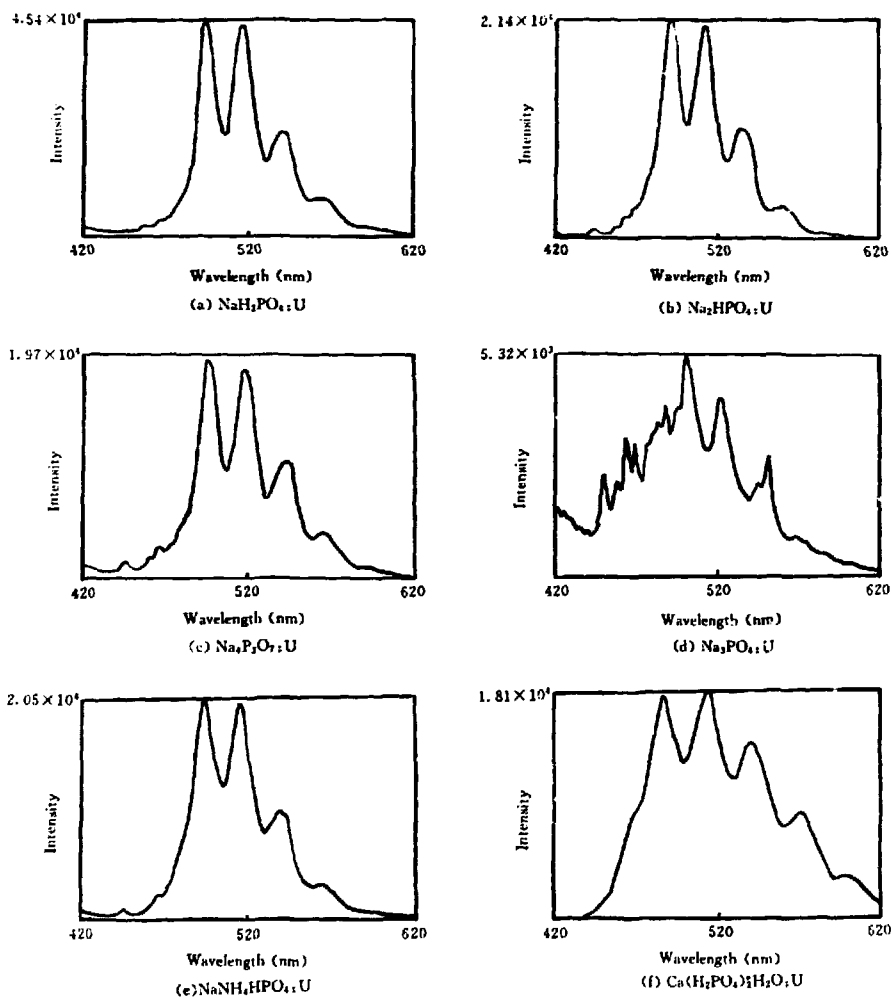


Fig. 2 Fluorescence emission spectra of uranium in phosphates

The experimental results (Fig. 2) also show that different phosphates affect slightly the position of luminescence lines, but make significant differences in fluorescence intensity. $\text{NaH}_2\text{PO}_4 : \text{U}$ gives the highest fluorescence efficiency among these phosphates.

The fluorescence emission levels of uranyl ion in NaH_2PO_4 are shown in Fig. 3. the data are from Table 1.

Table 1 Emission lines of uranium in several phosphates (at room temperature)

line No.		1	2	3	4	5	optimal excitation wavelength (nm)
NaH_2PO_4 $\text{Na}_2\text{NH}_4\text{HPO}_4$	λ_e (nm)	496	517	540	565	592	330
	ν_e (cm^{-1})	20161	19342	18519	17699	16892	
	$\Delta\nu_e$ (cm^{-1})		819	823	820	807	
$\text{Na}_4\text{P}_2\text{O}_7$ Na_6HPO_4	λ_e (nm)	494	515	538	563		322
	ν_e (cm^{-1})	20243	19417	18587	17762		
	$\Delta\nu_e$ (cm^{-1})		826	830	825		
Na_2PO_4	λ_e (nm)		503	525	553		328
	ν_e (cm^{-1})		19881	19048	18083		
	$\Delta\nu_e$ (cm^{-1})			833	965		
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	λ_e (nm)	494	516	540	567	596	337
	ν_e (cm^{-1})	20243	19380	18519	17637	16779	
	$\Delta\nu_e$ (cm^{-1})		863	861	882	858	

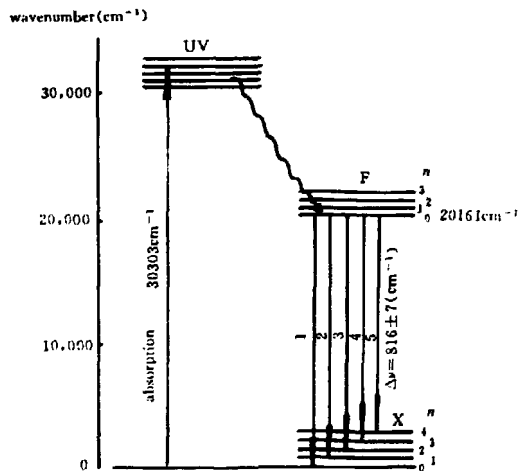


Fig. 3 Fluorescence emission level scheme of $\text{NaH}_2\text{PO}_4 : \text{U}$

2.2 Analysis of Crystal Structure for Forming Luminescence Center at Differ-

ent Ignition Temperature

Uranyl ion as impurity must be ignited at certain temperature and doped in matrix to form the luminescence center. Our experimental result shows that when the ignition temperature below 200 °C, the fluorescence intensity of $\text{NaH}_2\text{PO}_4 : \text{U}$ is weak and unstable.

The relationship between fluorescence intensity of $\text{NaH}_2\text{PO}_4 : \text{U}$ (the mass ratio of $\text{U}/\text{NaH}_2\text{PO}_4$ is 10^{-5}) and ignition temperature is shown in Fig. 4.

The result shows that the resulting fluorescence intensity of $\text{NaH}_2\text{PO}_4 : \text{U}$ is strong and stable over a wide range of ignition temperature (200~600 °C). Over 600 °C, the resulting fluorescence decreases.

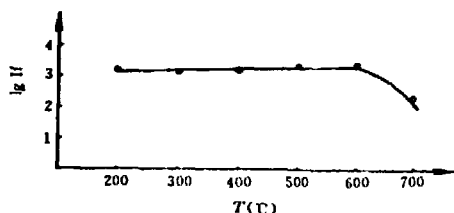


Fig. 4 The relationship between the fluorescence intensity of $\text{NaH}_2\text{PO}_4 : \text{U}$ and ignition temperature

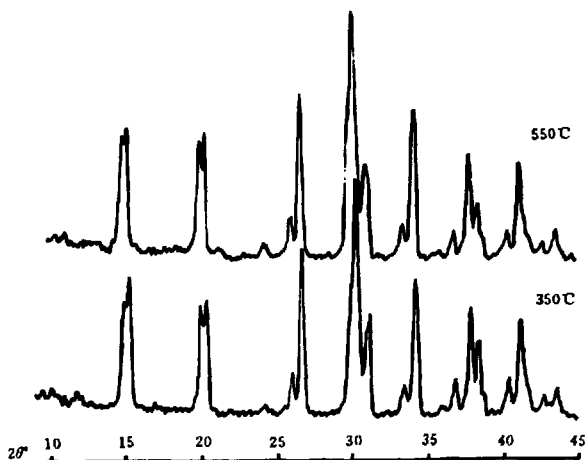


Fig. 5 X-ray diffraction patterns of $\text{NaH}_2\text{PO}_4 : \text{U}$ ignited at 350 °C and 550 °C

It is obvious that the formation of luminescence center in $\text{NaH}_2\text{PO}_4 : \text{U}$ is interrelated with its host lattice. Several $\text{NaH}_2\text{PO}_4 : \text{U}$ samples (the mass ratio of

$\text{U}/\text{NaH}_2\text{PO}_4$ is 10^{-5}) subjected to different ignition temperature were checked with X-ray diffraction analysis. The samples ignited at 350°C and 550°C are crystalline orthorhombic sodium metaphosphate (NaPO_3) (Fig. 5). The crystal lattice constants are $a=7.928 \text{ \AA}$, $b=13.220 \text{ \AA}$ and $c=7.703 \text{ \AA}$ [20]. The samples ignited at 650°C and 750°C become non-crystalline (Fig. 6). A dried sample (below 200°C) can't be transformed into NaPO_3 (Fig. 7).

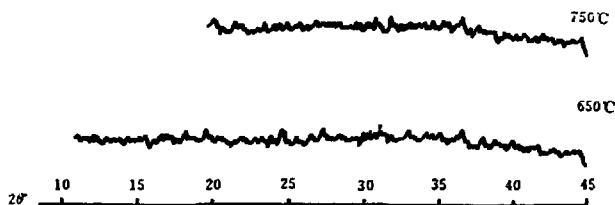


Fig. 6 X-ray diffraction patterns of $\text{NaH}_2\text{PO}_4 : \text{U}$ ignited at 650°C and 750°C

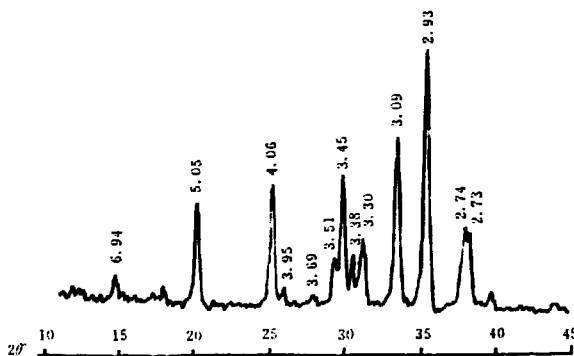


Fig. 7 X-ray diffraction patterns of $\text{NaH}_2\text{PO}_4 : \text{U}$ which was dried below 200°C

Basing on above experimental results we may lead to the following conclusions :

a. Luminescence of uranyl ion in phosphates depends on the crystal structure of matrix. As the ignition temperature is in the range of 200°C to 600°C, for NaH_2PO_4 matrix, uranyl ions doped into orthorhombic sodium metaphosphate crystal, and thus brings about strong fluorescence. The fluorescence intensity is stable at this temperature range.

b. When ignition temperature is higher than 650°C, the sample becomes non-crystalline. There are almost not the characteristic host lattices for most uranyl ions

to form luminescence center, and hence the fluorescence intensity is decreasing.

c. If the sample is not ignited up to 200 °C, the $\text{NaH}_2\text{PO}_4 : \text{U}$ system can not transform into $\text{NaPO}_3 : \text{U}$ system, and uranyl ions can not diffuse into their host lattices, the resulting fluorescence intensity is unstable.

2.3 Effect of Uranium Concentration on Crystal Structure

X-ray diffraction patterns of $\text{NaH}_2\text{PO}_4 : \text{U}$ with different uranium concentrations are shown in Fig 8.

As the weight ratio of $\text{U}/\text{NaH}_2\text{PO}_4$ below 10^{-3} , the crystal structure are not changed. But when the ratio increase to 10^{-2} , three new diffraction peaks appeared, i.e. $d_1 = 5.28 \text{ \AA}$, $d_2 = 4.12 \text{ \AA}$ and $d_3 = 4.06 \text{ \AA}$. As the ratio increases, the intensity of these new peaks increases but the characteristic diffraction peaks 5.11, 5.02, 3.95 and 3.85 \AA broaden and their intensities decrease. It shows that the host lattice in sodium metaphosphate has distorted when the mass ratio of $\text{U}/\text{NaH}_2\text{PO}_4$ is greater than 10^{-2} . It may be due to the excess uranium which can not integrate into the host lattices, and then causes the appearance of fluorescence saturation. The introduction of new lines with excess UO_2^{2+} addition could indicate interstitial incorporation of the activator.

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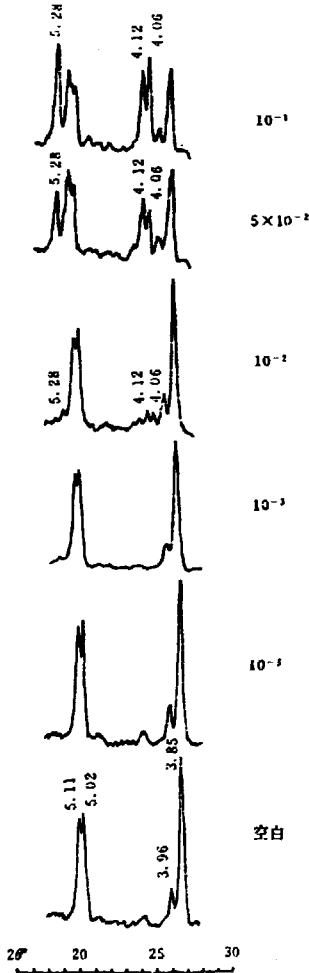


Fig. 8 X-ray diffraction patterns of $\text{NaH}_2\text{PO}_4 : \text{U}$ with different uranium concentrations (Ignition temperature is 300 °C)

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