Study of CeP_5O_{14}:Mn Crystal

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(Received May 25, 1985; revised August 20, 1985)

Abstract

A series of CeP_5O_{14}:Mn(II) crystals have been grown from phosphoric acid solution by the evaporation method. The structure of crystal was measured. CeP_5O_{14}:Mn belongs to monoclinic system, space group $P2_1/c$ and the lattice parameters were calculated. The EPR results show the manganese ion has a valency of two in CeP_5O_{14}:Mn. The excitation and emission spectra show there is an energy transfer from Ce^{3+} to Mn^{2+} in CeP_5O_{14}:Mn(II).

Introduction

Cerium pentaphosphate, CeP_5O_{14}, is an ultrafast scintillator [1], which has a UV-emission band with an extremely short lifetime (about $\tau_1 = 12$ ns). Ce^{3+} in cerium pentaphosphate has a broad UV-absorption band [2], so it can be used as sensitization ion [3, 4]. We have synthesized a new non-stoichiometric compound, CeP_5O_{14}:Mn, and investigated its structure and properties. We have found that CeP_5O_{14}:Mn can emit strong green light. It might be used as a new crystal material for laser or luminescence purposes.

Results and Discussion

Crystal Growth

A series of CeP_5O_{14}:Mn crystals were grown from phosphoric acid by the evaporation solution method [5]. The usual experimental procedures were as follows. The manganese carbonate (purity, A.R.) was added to a gold crucible, to which G.R.-grade commercial orthophosphoric acid, H_3PO_4, containing 15% by weight of water, was added. When the manganese carbonate had been dissolved completely, the cerium oxide (purity: 99.99%) was added into the solution. The mixture was heated in the crucible to about 250 °C and kept for about two days until the excess water was evaporated out and the CeO_2 was dissolved. Subsequently, the temperature was raised to about 550 °C. After two weeks the crucible was taken out and the mother liquor was poured out of the crucible. The crystals were rinsed with hot water repeatedly. The CeP_5O_{14}:Mn crystals, colourless or with a pale yellow colour, were obtained.

TABLE I. Typical Results of CeP_5O_{14}:Mn Crystal Growth

	Ratio of the raw material (g)			Temperature of growth (°C)	Mn% in crystal
	Phosphoric acid	$MnCO_3$	CeO_2		
1	60	0.05	1.0	559	
2	60	0.1	1.0	559	0.0067
3	60	0.2	1.0	559	0.015
4	60	0.4	1.0	564	0.018
5	60	1.5	1.0	559	0.066
6	60	2.5	1.0	553	
7	60	3.5	1.0	560	0.47
8	60	4.0	1.0	568	

Some typical results of CeP_5O_{14}:Mn crystal growth are shown in Table I. From Table I we can see that under the conditions of phosphoric acid 60 g, CeO_2 1 g, $MnCO_3$ from 0.05 g to 4.0 g and the temperatures of growth at 553–568 °C, a series of CeP_5O_{14}:Mn crystals of different Mn% were obtained. As the amount of manganese carbonate added was increased, Mn% in crystal increased, too.

Structure of Crystals

X-ray diffraction patterns of CeP_5O_{14}:Mn and CeP_5O_{14} crystals were measured. The diffraction patterns of CeP_5O_{14}:Mn are much the same as that of CeP_5O_{14} [6]. All of them belong to the same structure type, monoclinic system, space group $P2_1/c$. The diffraction patterns were indexed by the principle of isomorphic displacement. According to the formula regarding monoclinic interplanar distances:

$$D_{hkl}^{-2} = \left(\frac{h}{a \sin\beta}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c \sin\beta}\right)^2 + \frac{2hl\cos\beta}{ac\sin^2\beta}$$

the lattice parameters of CeP_5O_{14}:Mn and CeP_5O_{14} can be calculated. The results are listed in Table II.

0020-1693/86/$3.50

TABLE II. Structure Parameters of CeP_5O_{14}:Mn Crystals

	Mn% in crystal	Crystal system	Space group	Lattice parameters				Z
				a (Å)	b (Å)	c (Å)	β (°)	
0	0	Monoclinic	$P2_1/c$	8.797	9.074	13.124	90.4	4
4	0.018	Monoclinic	$P2_1/c$	8.75(2)	9.16(4)	13.1(3)	90.8(4)	4
5	0.066	Monoclinic	$P2_1/c$	8.77(2)	9.26(4)	13.2(3)	90.5(4)	4
7	0.47	Monoclinic	$P2_1/c$	8.81(2)	9.38(4)	12.7(4)	92.1(4)	4

Fig. 1. The electron paramagnetic resonance of CeP_5O_{14}:Mn.

From Table II we can see when the percent of Mn% in the crystal was lower, the lattice parameters of CeP_5O_{14}:Mn are the same or nearly the same as that of CeP_5O_{14}. The radius of Mn^{2+} is 0.8 Å and is smaller than that of Ce^{3+} (1.03 Å), so we suggest that the manganese ion might enter into the interstitial site of CeP_5O_{14} cell.

The infrared spectra of CeP_5O_{14}:Mn are the same as that of undoped CeP_5O_{14}.

Valency State of Manganese Ion

Cerium ion has a valency of three in CeP_5O_{14}. Ce^{3+} should be substituted by Mn^{3+} according to the principle of charge balance, but since Mn^{3+} is very unstable in acidic solution, it will be changed to Mn^{2+} and Mn^{4+}. So the valency state of manganese ion in CeP_5O_{14}:Mn crystal is a problem which must be discussed. In the synthetic process of the crystal, the manganese ion in $MnCO_3$ has a valency of two, and Mn^{2+} is stable in acidic solution. $MnCO_3$ was dissolved in H_3PO_4 to appear pale red, which is the characteristic colour of Mn^{2+}. So the Mn ion has a valency of two in the solution of crystal growth. The valency of the manganese ion can be determined by EPR. The result is shown in Fig. 1.

From the EPR spectrum of CeP_5O_{14}:Mn crystal we can see six lines, the distance between 3 and 4 is 67 G and the DPPH ($g = 2.0036$) line lies between 3 and 4. This is the characteristic spectrum of Mn^{2+}. It can show that the manganese ion in the CeP_5O_{14}:Mn crystal has a valency of two.

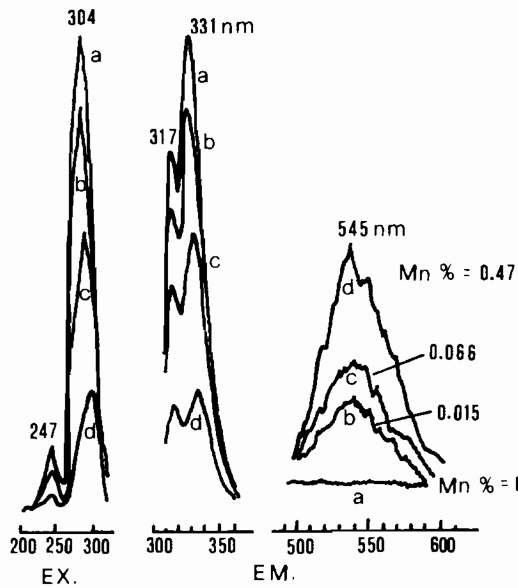

Fig. 2. The excitation and emission spectra of CeP_5O_{14}:Mn(II).

Luminescence of CeP_5O_{14}:Mn(II)

CeP_5O_{14}:Mn(II) crystals emit strong green light when excited by 254 nm ultraviolet light. The luminescence intensity increases with the increase of Mn% content. CeP_5O_{14} emits ultraviolet light, and no luminescence of LaP_5O_{14}:Mn was observed. The results indicate that there is an energy transfer from Ce^{3+} to Mn^{2+}.

The excitation spectra of CeP_5O_{14}:Mn(II) have been measured (see Fig. 2). The excitation peak of CeP_5O_{14}:Mn(II) located at 247 nm and 304 nm is the same as that of CeP_5O_{14} and the intensity of 304 nm peak is stronger than 247 nm. They belong to 5d–4f transition of Ce^{3+}. The intensity of the Ce^{3+} excitation peak decreases as the content of Mn% increases. It shows that the energy absorbed by Ce^{3+} transfers to Mn^{2+}.

The emission spectra of CeP_5O_{14}:Mn(II) under the excitation of 304 nm was shown in Fig. 2. There are three groups of emission peak at about 317 nm, 331 nm and 545 nm. The peaks at 317 nm and 331 nm belong to Ce^{3+} emission peak, which exist also in the case of CeP_5O_{14}. The peak at 545 nm belongs to Mn^{2+} emission, which is the characteristic emission of Mn^{2+}. It is the reason that CeP_5O_{14}:Mn(II) appeared green. An interesting phenomenon was observed, *i.e.*, as the content of Mn% was increased the emission intensity at 545 nm was increased, while that at 317 nm and 331 nm were decreased. It indicates the energy transfer from Ce^{3+} to Mn^{2+} exists in CeP_5O_{14}:Mn(II).

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