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Study of zinc borophosphate compositions doped with samarium and manganese

G. I. Patronov*, I. P. Kostova, D. T. Tonchev

Dept. Chem. Technology, Plovdiv University "Paisii Hilendarski", 4000 Plovdiv, Bulgaria

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Synthesis and characterisation studies of samarium and manganese doped ZnO-rich borophosphate material of composition 0.5M – 71.8ZnO – yP_2O_5 – (27.7 – y)B_2O_3 where: M = Sm_2O_3 or MnO, y = 9.7, 13.85, 18 mol% were presented. The compositions were prepared by a typical high-temperature ceramic syntheses where ZnO, $NH_4H_2PO_4$, H_3BO_3 and Sm_2O_3 (or MnO) of pre-determined ratios were powdered, mixed and placed in alumina crucibles. The synthesis was performed at 950 °C for 3 hours in a muffle furnace. Samples were quenched out of the melt to room temperatures and after that annealed at 250 °C for 2 hours.

Samarium and manganese doped ZnO-rich zinc borophosphate compositions were investigated by powder X-ray diffraction, differential scanning calorimetry, temperature – modulated differential scanning calorimetry, Raman spectra analysis and photoluminescence spectroscopy. The results obtained show that the samples are predominantly amorphous, with the presence of crystalline structure in some of them. The main crystalline phases are zinc borate phosphate $Zn_3(BO_3)(PO_4)$ and zinc borate α-$Zn_5B_4O_{11}$. While samarium doped samples exhibit strong visible (orange to red) immediate photoluminescence (scintillation) signal under UV light, manganese doped samples do not exhibit visible scintillation signal.

Key words: doped zinc borophosphates, samarium, manganese, crystal structure.

INTRODUCTION

Compositions based on ZnO and P_2O_5 are both scientifically and technologically important materials because of their interesting characteristics. Having in view that the addition of rare earth and transition metal ions to such materials usually induces significant changes in their optical, electrical and magnetic behaviour, opening thus opportunities in the finding of new applications, careful structural investigations of compositions containing rare earth and transition metal ions become necessary [1–5].

In this work we present synthesis and characterisation studies of samarium and manganese doped ZnO-rich borophosphate material of composition 0.5M – 71.8ZnO – yP_2O_5 – (27.7 – y)B_2O_3 where: M = Sm_2O_3 or MnO, y = 9.7 mol%, 13.85 mol%, 18 mol%.

Samarium and manganese doped ZnO-rich borophosphate compositions were investigated by powder X-ray diffraction, differential scanning calorimetry (DSC), temperature – modulated DSC (TMDSC), Raman spectra analysis and photoluminescence spectroscopy.

EXPERIMENTAL

Sample preparation

All samples were prepared by high-temperature ceramic methods using ZnO, $NH_4H_2PO_4$, H_3BO_3 and Sm_2O_3 (or MnO) as starting materials. The reagents were thoroughly mixed, placed in alumina crucibles and heated at 950 °C for 3 hours in a muffle furnace. The obtained homogeneous melts were then poured onto a graphite plate and by manual pressing have reached a suitable thickness (1–2 mm). Then the samples were annealed at 250 °C for two hours. Synthesized compositions are homogeneous, not hygroscopic and transparent glass. They are easily reproducible. List of the samples is presented in Table 1.

* To whom all correspondence should be sent:
E-mail: patron@uni-plovdiv.bg

Table 1. List of the non-doped and Sm or Mn doped zinc borophosphate samples

Sample, №	Composition				
	ZnO, mol%	B_2O_3, mol%	P_2O_5, mol%	Sm_2O_3, mol%	MnO, mol%
1	72.31	9.69	18.00	–	–
2	72.31	13.84	13.85	–	–
3	72.31	18.00	9.69	–	–
4	71.81	9.69	18.00	0.50	–
5	71.81	13.84	13.85	0.50	–
6	71.81	18.00	9.69	0.50	–
7	71.81	9.69	18.00	–	0.50
8	71.81	13.84	13.85	–	0.50
9	71.81	18.00	9.69	–	0.50

Density measurements

Density measurements were carried out according to the Archimedes method using deionised water of density 1 gm cm^{-3} as an immersion liquid.

Powder X-ray diffraction analysis

Powder X-ray diffraction data were collected on Bruker diffractometer operating with a Cu –Kα radiation source (λ = 1.5406 nm), in steps of 0.02° over the range of 10–80° 2θ, with a time per step of 2.8 s. The crystalline phases were identified using the powder diffraction files PDF 19-1455 and PDF 86-2017 from database JCPDS – International Centre for Diffraction Data PCPDFWIN v.2.2 (2001) [6–8].

Raman spectroscopy analysis

The Raman studies were conducted using the 1064 nm Nd:YAG laser line at a power of 700 mW and a RAM II spectrometer (Bruker Optics) having a resolution of 2 cm^{-1}.

Differential Scanning Calorimetric and Temperature Modulated DSC analysis

DSC and TMDSC measurements were performed using TA Instruments DSC Q100 and DSC 2910 with attached Fast Air Cooling System (FACS) and Refrigerating Cooling System (RCS). The samples (20–22 mg) were placed in aluminium hermetic pans. A heating rate of 10 K/min was used.

Photoluminescence measurements

The photoluminescence spectra were measured by optical CCD Avantes spectrometer Avaspec 2048, operating at 25 MW in the range 250–1100 nm at room temperature. As a light source was used 450 nm wavelength laser diode.

RESULTS AND DISCUSSION

Density measurements

The data obtained from density measurements of the samples are presented in Table 2. There are some variations in the density as a function of the B_2O_3 content. Addition of B_2O_3 in zinc phosphate glasses causes an increase in oxygen-packing density that may squeeze the structure of the sample. This may be due to the replacement of an equal amount of low bond strength glass former P_2O_5 with B_2O_3, which has high bond strength [9]. Moreover, the doped agents (Sm_2O_3 or MnO) act as a glass modifier, which increases the fraction of non-bridging oxygen atoms and leads to increased porosity and reduced density of the glass.

Table 2. Density of the non-doped and Sm or Mn doped zinc borophosphate samples

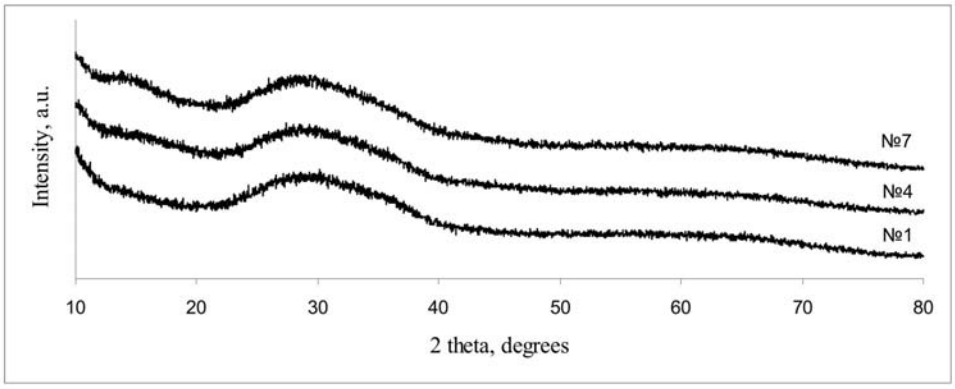
Undoped samples			Samples doped with Sm			Samples doped with Mn		
Sample, №	B_2O_3, mol%	Density (ρ), gm cm^{-3}	Sample, №	B_2O_3, mol%	Density (ρ), gm cm^{-3}	Sample, №	B_2O_3, mol%	Density (ρ), gm cm^{-3}
1	9.69	2.035	4	9.69	1.861	7	9.69	1.842
2	13.84	2.157	5	13.84	1.887	8	13.84	1.916
3	18.00	2.023	6	18.00	1.888	9	18.00	1.961

Powder X-ray diffraction data

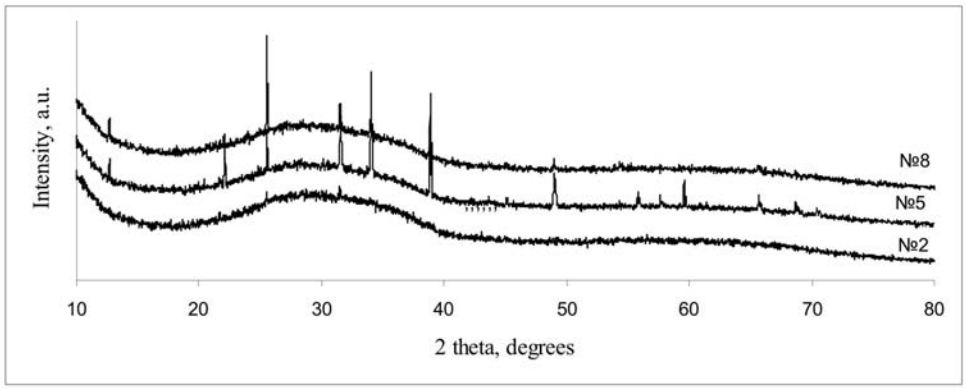
The results obtained show that the samples are predominantly amorphous, with the presence of crystalline structure in some of them (Fig. 1). The main crystalline phases are zinc borate phosphate $Zn_3(BO_3)(PO_4)$ and zinc borate α-$Zn_5B_4O_{11}$ (Fig. 2). The appearance of borate and phosphate in the crystallization products shows the important role of PO_4 and BO_4 structural units in the structural network of borophosphate glasses. It is possible to suggest based on other authors' studies that these borophosphate glasses contain B–O–P linkages within their structural network [2, 10].

Raman spectroscopy data

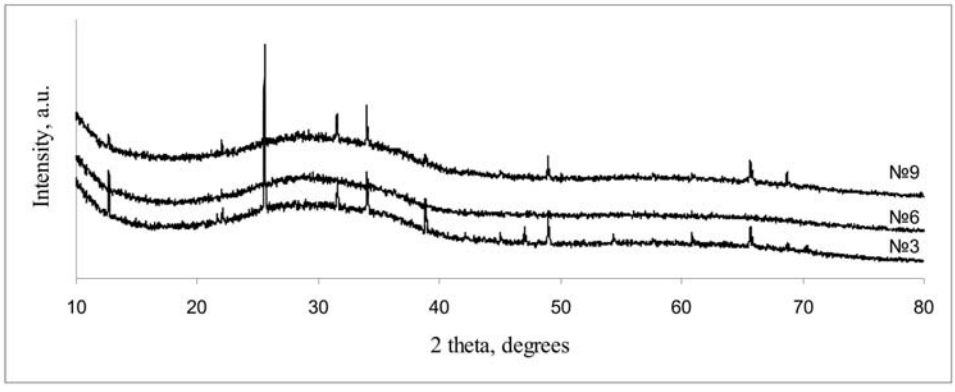
Raman spectra of the glass samples are presented in Fig. 3. They contain a vibrational band at 968 cm^{-1} ascribed to the vibrations of isolated PO_4 units in the



a. Powder X-ray diffraction patterns for samples № 1, 4, 7 (B_2O_3:P_2O_5=1:2)



b. Powder X-ray diffraction patterns for samples № 2, 5, 8 (B_2O_3:P_2O_5=1:1)



c. Powder X-ray diffraction patterns for samples № 3, 6, 9 (B_2O_3:P_2O_5=2:1)

Fig. 1. Powder X-ray diffraction patterns for synthesized samples

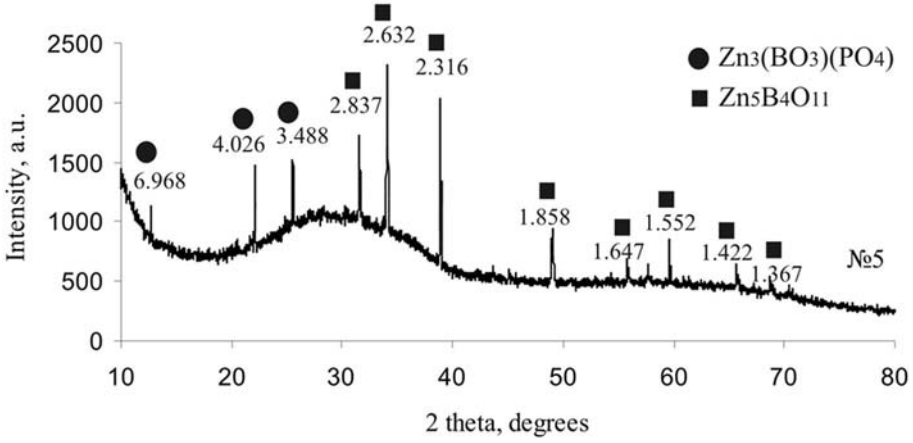


Fig. 2. Powder X-ray diffraction pattern for sample № 5

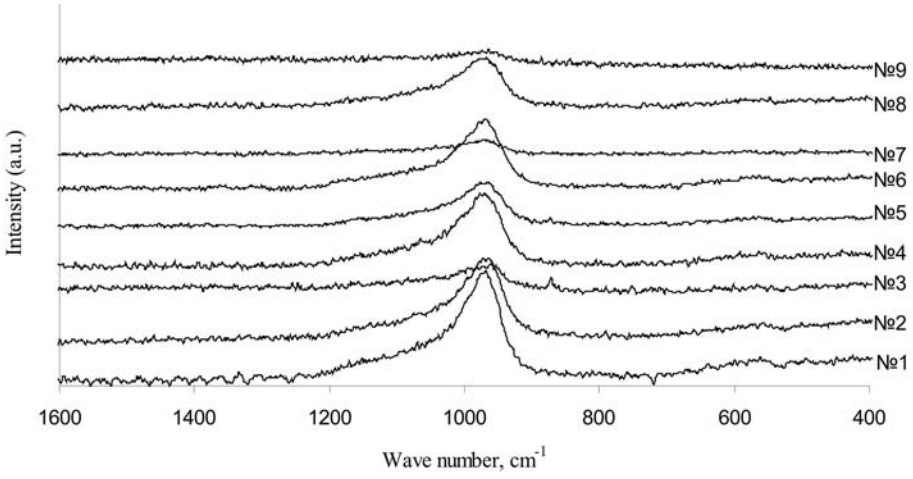


Fig. 3. Raman spectra of the glass samples

structural network of borophosphate glasses at the B_2O_3 – rich side [2].

Differential Scanning Calorimetric and Temperature Modulated DSC data

Figure 4 reveals typical examples of scanning with DSC and TMDSC. Figure 5 presents the dependence of the glass transition temperature obtained by DSC and TMDSC versus the content of B_2O_3. Increasing the content of B_2O_3 is associated with increased glass transition point, indicating a higher stability of the glass.

Values of the glass transition temperature for the same composition as measured by the heat flow (DSC) and the specific heat (TMDSC) differ minimally as shown in Fig. 5. The difference due to the fact that these values characterize the different areas of the same viscosity curve at Tg for the glassy material according to previous studies [11].

Photoluminescence measurements

Representative emission spectra for synthesized samples are illustrated in Figure 6. All of Sm-doped samples display photoluminescence in contrast to undoped samples and those with manganese. Typical photoluminescence of Sm^{3+} ions is observed with three emission bands corresponding to transitions:

564 nm – $^4G_{5/2} \rightarrow {}^6H_{5/2}$
600 nm – $^4G_{5/2} \rightarrow {}^6H_{7/2}$
645 nm – $^4G_{5/2} \rightarrow {}^6H_{9/2}$

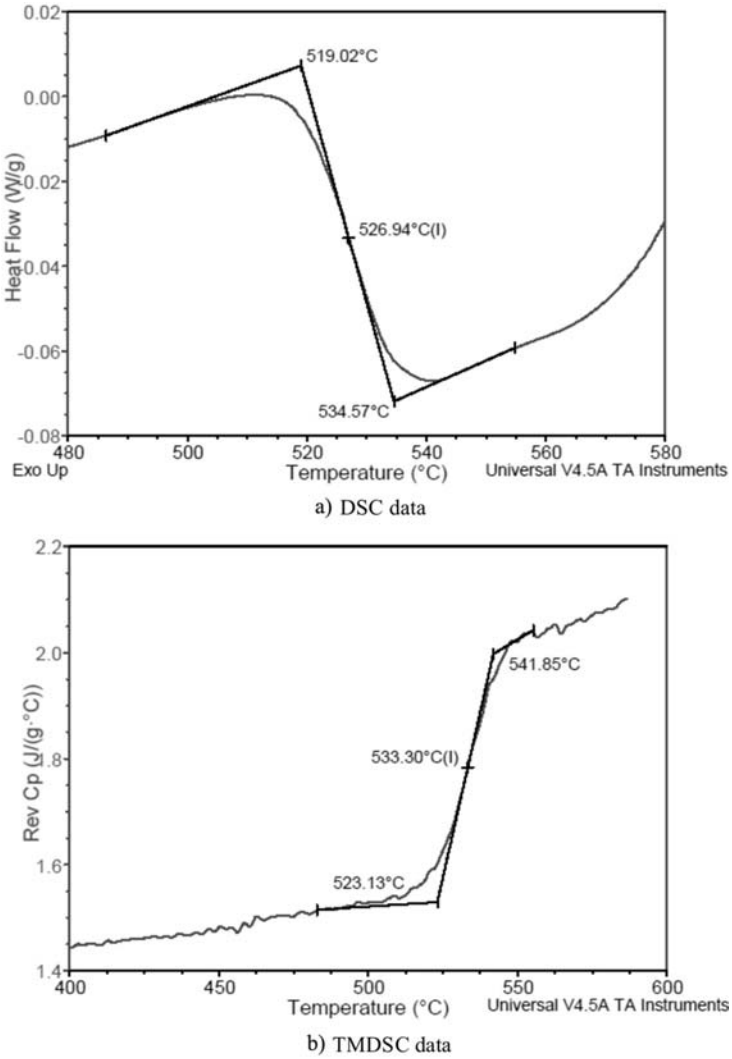


Fig. 4. DSC and TMDSC data of the glass sample № 4

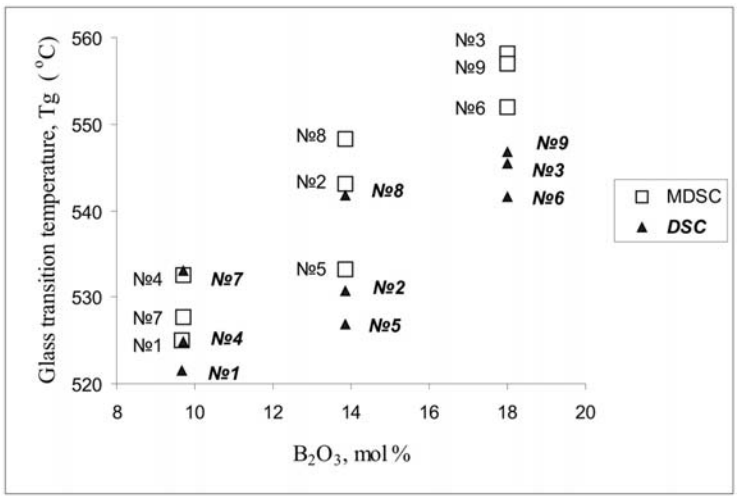
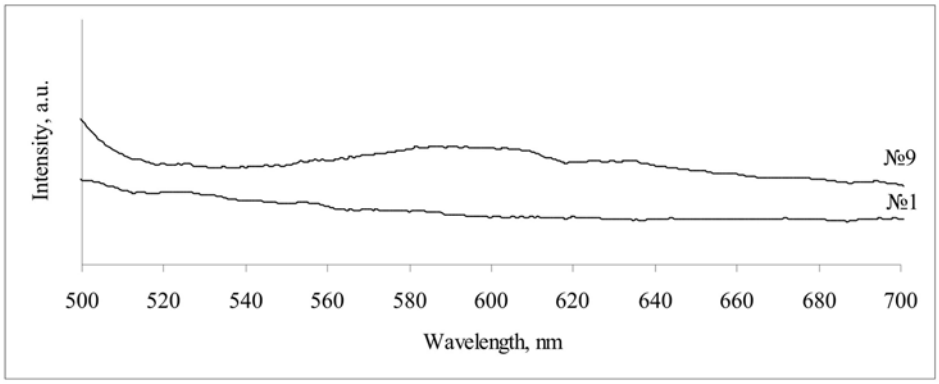
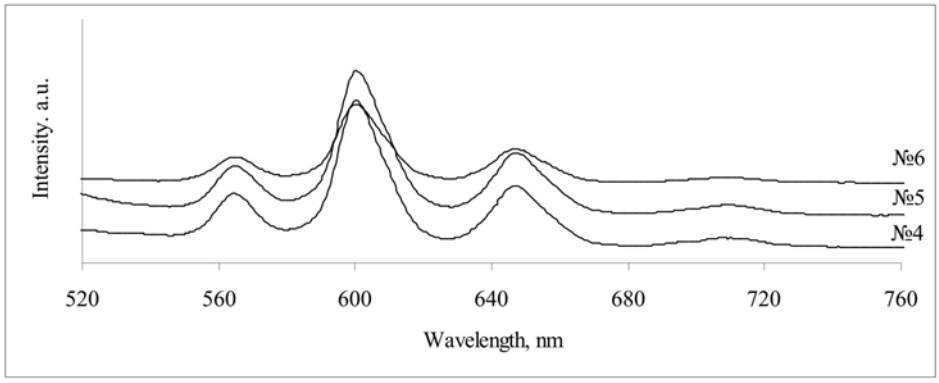


Fig. 5. Dependence of the glass transition temperature obtained by DSC and TMDSC versus the content of B_2O_3



a) Typical photoluminescence spectra of undoped samples (№1) and Mn-doped samples (№9)



b) Photoluminescence spectra of Sm-doped samples (№4-6)

Fig. 6. Photoluminescence spectra of samples №1, 4–6, 9 at excitation wavelength 450 nm

The band at 600 nm, which corresponds to orange emission, is the most intense [12, 13].

CONCLUSIONS

Samarium and manganese doped ZnO-rich borophosphate compositions were investigated by powder X-ray diffraction, differential scanning calorimetry (DSC), temperature – modulated DSC, Raman spectra analysis and photoluminescence spectroscopy.

The results obtained show that the samples are predominantly amorphous, with the presence of crystalline structure in some of them. The main crystallization phases are zinc borate phosphate $Zn_3(BO_3)(PO_4)$ and zinc borate α-$Zn_5B_4O_{11}$.

When samarium doped samples exhibit strong visible (orange to red) immediate photoluminescence (scintillation) signal under UV light, manganese doped samples do not exhibit visible scintillation signal in glass-ceramics materials we have prepared (Mn doped materials need extra work to reveal their potential).

Synthesized glassy and glass-ceramic materials are all transparent, stable, and strong to mechanical damage. In addition, these materials are not hygroscopic what made them a good candidate for a number of sensing, optical security etc. applications.

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ИЗСЛЕДВАНЕ НА ЦИНК-БОР-ФОСФАТНИ КОМПОЗИЦИИ, ДОТИРАНИ СЪС САМАРИЙ И МАНГАН

Г. И. Патронов, И. П. Костова, Д. Т. Тончев

Катедра Химична технология, Пловдивски Университет „Паисий Хилендарски“, 4000 Пловдив, България

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(Резюме)

Настоящото изследване представя синтез и характеристика на богати на ZnO борфасфатни материали, дотирани със Sm и Mn, със състав 0.5M – 71.8ZnO – уP_2O_5 – (27.7-у)B_2O_3, където M = Sm_2O_3 или MnO, у = 9.7, 13.85, 18 mol%. Композициите са получени чрез високотемпературен синтез от ZnO, $NH_4H_2PO_4$, H_3BO_3 и Sm_2O_3 (или MnO) в определено съотношение, които са стрити, смесени и поставени в керамичен тигел. Синтезът е извършен при температура от 950 °C за 3 часа в муфелна пещ. Пробите са охладени до стайна температура и след това темперирани при 250 °C за 2 часа.

Богатите на ZnO борфасфатни композиции, дотирани със Sm и Mn, са изследвани чрез рентгеноструктурен анализ, диференциална сканираща калориметрия, температурно – модулирана диференциална сканираща калориметрия, Раман спектрален анализ и фотолуминесцентна спектроскопия. Получените резултати показват преимуществено аморфния характер на пробите, с наличие на кристална структура в някои от тях. Основните кристални фази са $Zn_3(BO_3)(PO_4)$ и α-$Zn_5B_4O_{11}$. Докато дотираните със Sm проби показват силен видим (оранжев до червен) фотолуминесцентен (сцинтилационен) сигнал под ултравиолетова светлина, дотираните с Mn проби не показват видим сцинтилационен сигнал.