مجلة جامعة تشرين للدراسات والبحوث العلمية _ سلسلة العلوم الأساسية المجلد (29) العدد (1) 2007
Tishreen University Journal for Studies and Scientific Research- Basic Sciences Series Vol. (29) No. (1) 2007

Studying Properties of the Scintillation Spectra for some Solid Solutions under the X-Rays Excitation

Dr. Yahia M. Suleiman*
Dr. Ahmad Hamed Khadro**

(Received 4 / 10 / 2006. Accepted 4/3/2007)

□ ABSTRACT □

Scintillation characteristics such as spectra, decay times and yields of Cu- and Ag-doped ZnS_XSe_{1-X} solid solutions, and some other compounds have been measured under X-rays excitation. Certain investigated materials show a high light yield in the long wavelength region and adequate kinetic properties. It is shown that the light yield can be increased for compounds synthesized at optimal conditions.

The measurements have been held in St. Petersburg State Polytechnical University, Petersburg, Russia

Key Words: Luminescent characteristic, Emission bands.

***Professor, Department of Radiation Physics, Faculty of Mechanical and Electronic Engineering, Tishreen University, Lattakia, Syria.**
****Associate Professor, Department of Physics, Faculty of Sciences. Tishreen University, Lattakia, Syria.**

مجلة جامعة تشرين للدراسات والبحوث العلمية _ سلسلة العلوم الأساسية المجلد (29) العدد (1) 2007
Tishreen University Journal for Studies and Scientific Research- Basic Sciences Series Vol. (29) No. (1) 2007

دراسة مميزات أطياف التألق لبعض المحاليل الصلبة المتألقة تحت تأثير الأشعة السينية

الدكتور يحيى مصطفى سليمان*
الدكتور أحمد حميد خضرو **

(تاريخ الإيداع 4 / 10 / 2006. قُبِل للنشر في 2007/3/4)

□ الملخّص □

تحت تأثير الأشعة السينية، تم قياس مميزات أطياف التألق وأزمنة التفكك لعناصر النحاس والفضة المضافة إلى المحاليل الصلبة $ZnS_X Se_{1-X}$ وكذلك بعض المركبات الأخرى المستخدمة.

أظهرت الدراسة على بعض المواد حدوث (تحرر) تألق ضمن مجال طول موجي واسع وبميزات طاقية كافية. وتبين أن طاقة الضوء المتحرر يمكن زيادتها في بعض المركبات المصنعة (المحضرة) عند شروط تركيبية مثالية.

أجريت القياسات في جامعة بطرس بورغ التكنولوجية الحكومية – بطرس بورغ – روسيا.

كلمات مفتاحية: مميزات التألق – الحزم الانبعاثية.

* أستاذ الفيزياء الإشعاعية – كلية الميكانيك والكهرباء – جامعة تشرين – اللاذقية –سورية.
** أستاذ مساعد قسم الفيزياء – كلية العلوم – جامعة تشرين – اللاذقية – سورية.

Introduction

Commonly used silicon photodiodes exhibit an efficient sensitivity in the range from 500 to 1000 nm. This generates a need for long wavelength scintillators (LWS) [1]. There is a rich variety of phosphors and laser materials suitable for use in the red or near-infrared range, while most of the conventional scintillators emit in the short wavelength region. Generally, the long wavelength scintillators (LWS) can show high yield; and small forbidden bandwidth of a crystal is required for long wavelength emission. The Number of electron-hole (e-h) pairs generated by incident particle or quantum is inversely proportional to the band width of the crystal [2]. A large number of e-h pairs would yield high scintillation efficiency. A wide range of potential scintillation materials has been studied by Moses et al [3]. The crystals containing other rare-earth ions show longer decay times. So, the problem is to find materials with a short decay time among the long wavelength phosphors.

The properties of currently used LWS_S, such as $CsI:Tl, CdWO_4, Gd_2O_{2S}:\mathrm{Pr},Ce$, $(YGd)_2O_3:Eu$ are a matter of common knowledge [4]. Some new compounds have been proposed as LWS_S $(\lambda m): Y_2W_2O_{12}:Eu\ (610nm), La_2O_2S:Eu\ (620nm)$ [5-7]

Aim and importance of this work

In the present work we study the luminescent characteristics of ZnS_XSe_{1-X} $(x=0.5)$ solid solutions doped with Cu or Ag as activators and Al as co-activator and prepared as large transparent polycrystalline pieces. The Cu-doped samples exhibit broad emission bands, peaking near 600 nm. The best scintillation properties have been detected for $ZnS-ZnSe:Cu,Al$ solid solutions.

Methods and Experiments

The $ZnS-ZnSe$ solid solutions were obtained by means of sublimation in the form of polycrystalline unitary bodies. The synthesis was carried out by the physical vapor deposition (PVD) method in a closed reactor placed in a two-zone vertical furnace. Initially, the $ZnS-ZnSe$ powder mixture was sintered at ~1000°C. Different Cu, Ag, and Al dopants and $BaCl_2, CsCl, and\ NaCl$ fluxes were added at this stage of the synthesis process. The Al content in the samples after PVD was about 0.01%. 35mm diameter and 5 mm thickness samples were obtained. After that the samples were cut and polished.

The emission spectra of the samples were measured under steady-state X-ray (35V, 15mA) excitation, fig 1. A short pulsed (~1 ns) X-ray source and photon counting method were used for decay time measurements [8]. The measurements were carried out essentially at room temperature and in case of need in a 80-500 k temperature range. The energy efficiency (η) of the scintillators was determined at pulsed X-ray excitation at $50\mu s$ shaping time. The (η) value of the studied compound was compared with that for $CsI:Tl$ crystal using it as a standard. The studied sample and $CsI:Tl$ were placed as far as possible in similar conditions.

Results and Discussion

In order to control the scintillation characteristics of the $ZnS_X Se_{1-X}$ samples, we varied the value of x, deposition temperature, concentration of the dopants (Cu), and type and concentration of the fluxes (Table 1).

Both these features can give high scintillation efficiency [2]. The band gaps E_g are 3.6 and 2.67 eV in ZnS and ZnSe, respectively. Since the gap of $ZnS_X Se_{1-X}$ is proportional to x [9], we can estimate that $E_g \approx 3.14eV$ for ZnS (0.5)-ZnSe (0.5) solid solution. Using similar considerations, we can assume that the density is ZnS (0.5)-ZnSe (0.5). The samples were reasonably transparent to self-emission. Absorption coefficient of ZnS-ZnSe: Cu, Al sample was $\approx 7.0cm^{-1}$ near 600 nm.

Table 1 Characteristics of some $ZnS_X Se_{1-X}$ mixed samples: maximum of emission band λ_m, energy efficiency η and decay time constant τ_1 (X-ray excitation, room temperature).

No	X	Dopant (wt %)	Flux	λ_m (nm)	η of (CsI:Tl)	τ_1 (ns)
1	0.5	Cu (5×10^{-3}), Al	CsCl	580	1.20	25
2	0.5	Cu (5×10^{-3}), Al	$BaCl_2$	604	0.38	200
3	0.5	Cu (5×10^{-2}), Al	NaCl	601	0.04	~1000

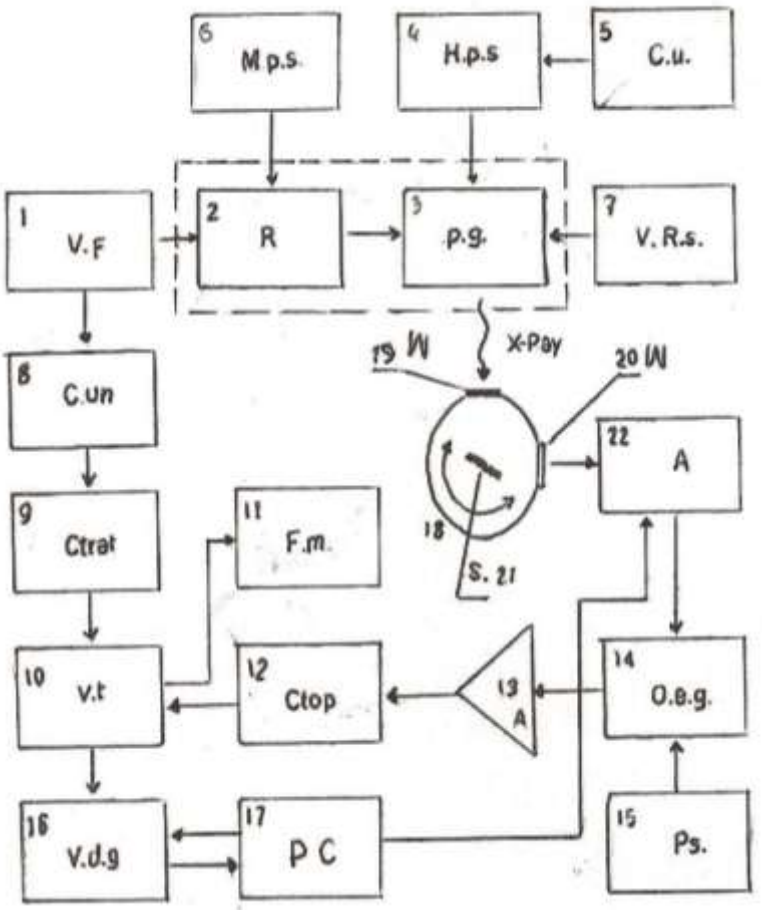

Fig 1: shows the instruments used for the measurement of the RL (X-Ray Luminescence), TSL (Thermoluminescence)

1- Variable frequency generator.	2- Rheostat.
3- X-Ray pulses generator.	4- High power supply
5- control unit.	6- Modulating power supply
7-Variable power supply.	8- Cut universal.
9-Time control connected to channel CYRAT.	10- Variable time modulator.
11- Frequency measuring.	12-Time control connected to channel CTOP.
13- Amplifier.	14- Optical electron generator.
15- Power supply for optical electron generator.	16- Variable digital analyzers.
17- IBM PC computer.	18- Cryostat.
19- Windows for cryostat of Beryllium.	20- Quarts windows.
21-Sample.	22- Analyzer.

The X-ray excited emission spectra of some samples are shown in Fig 2. The growing condition (flux) does not influence strongly the emission shape of the ZnS (0.5)-ZnSe (0.5): Cu, Al Samples, while the intensity changes greatly. That is why the spectra of Fig 2 are presented on a semi-logarithmic scale. The samples exhibit broad emission bands peaking near 600 nm (Fig 2, Table 1). This is not particularly surprising, since the ZnS: Cu films [10] as well as ZnSe: Cu crystal [11] offer similar emissions. Increasing the ZnS content in the solid solution, the emission band shifts to the short wavelength region (Table 1). Related emission has been associated with rediative recombination of a free electron with a hole located in acceptor Cu^{+} [12] or with a complex associative center [13]. Aluminum can play the role of a donor incorporated into associative luminescence centers [14]. An optimal content of Cu in in ZnS-ZnSe solid solution is about $5\times10^{-3} wt\%$. An increase of the Cu content leads to concentration quenching of the luminescence (curve 3, Fig 2).

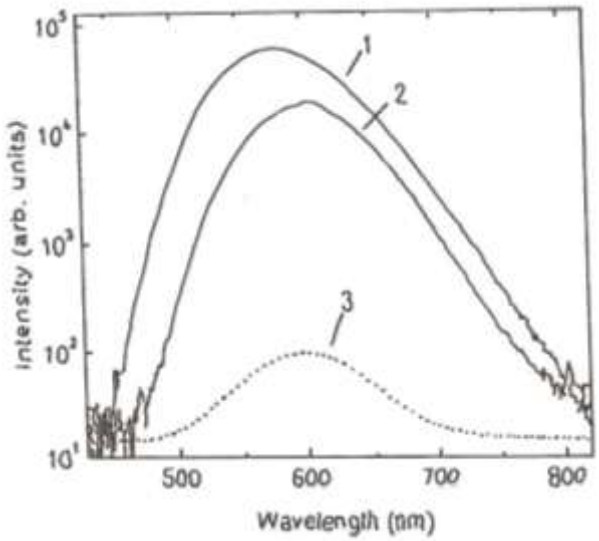

Fig 2: X-ray induced emission spectra of ZnS (0.5) ZnSe (0.5): Cu, Al compounds at room temperature (the curve number corresponds to the sample number in Table 1).

The scintillation efficiencies of the samples are presented in Table 1. The largest energy efficiency (120% of that of CsI:Tl) has been detected for ZnS (0.5)-ZnSe (0.5): Cu, Al growing with CsCl flux (Sample 1). The luminescence intensity of sample 1 (steady-state excitation) is about three times larger at (80K) compared with that at room temperature. Besides, a new emission band peaking at 525 nm appears at <140K.

Typical luminescence decay curves of some samples are presented in Fig. 3. The decay curves of the studied samples have usually complicated shapes. The initial parts of the curves may be approximated by exponents with decay constants τ_1, which are presented in Table 1. For sample 1 (ZnS-ZnSe: Cu, Al), one can make out a fast component $\tau_1 = 25$ ns and a slow component $\tau_2 = 1.7$ μs (curve 1, Fig 3). The last one has a high intensity and contributes significantly to the light yield of the sample. By contrast, sample 2 ($BaCl_2$ flux) exhibits one decay constant $\tau_1 = 200$ ns and the emission decays to noise level in about $10\,\mu s$ (curve 2, Fig. 3).

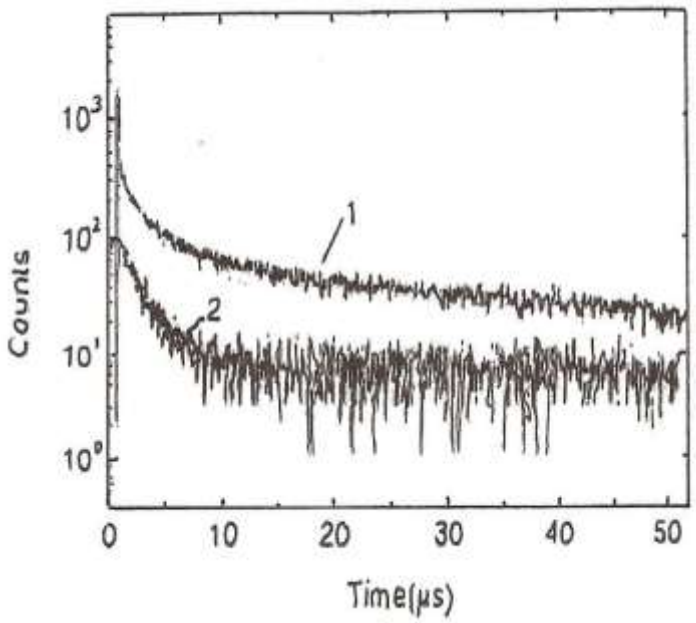

Fig. 3: Scintillation pulse shapes of X-ray excited samples:
ZnS (0.5)-ZnSe (0.5): Cu (0.005), Al/CsCl (sample 1) -1
ZnS (0.5)-ZnSe (0.5): Cu (0.01), Al/NaCl (sample 3) -2

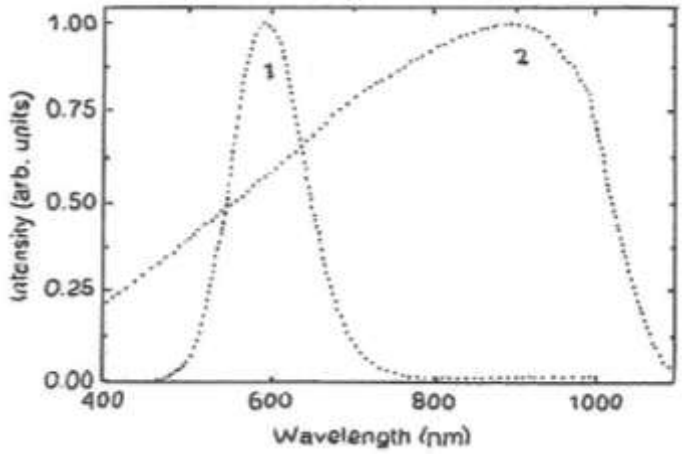

Fig. 4: X-ray excited emission spectra of ZnS/ZnSe: Cu, Al (1), and spectrum sensitivity of Si photodiode (2).

Table 2 Main scintillation characteristics of some compounds

Compound	$\lambda_{max}\ (nm)$	$\tau_1/\tau_2\ (\mu s)$	η of (CsI: Tl)
CsI: Tl	540	0.8	1
ZnS/ZnSe: Cu, Al	580-604	0.025/1.7	1.20
$LaMgAl_{11}O_{19}$: Nd, Cr	695, 709, 750	0.45	-
$Sr_2P_2O_7$: Pr	520, 594, 603, 640	0.3	-
CdI_2	505, 680	0.004	0.20
$CaMoO_4$	532	~0.004/16	0.20

Several others compounds have been investigated in assumption that they give long wavelength scintillations.

Main characteristics of the compounds are presented in Table 2 and spectra of some of them are shown in Fig.5. Unfortunately, CaF_2: Na and SrF_2: Na crystals, which show an efficient long wavelength luminescence of F_{2A} centers at optical (UV) excitation, do not scintillate at X-ray excitation. It means that the energy transfer from host to F_{2A} centers in the crystals is not efficient.

Conclusions

The present work shows that the characteristics of some studied scintillators can be improved. Therefore, we have to choose optimal growth conditions, concentration of activator and co-activator, and the type of flux. Besides, we plan to vary the post-growth conditions, particularly the cooling rate.

References

1- SCHOTANUS, P.; DORENBOS, P.; RYZHIKOV, V, D.; *Detection of CdS (Te) and ZnSe (Te) Scintillation ligh with silicon photodiodes,* IEEE trans. Nucl. Russia, Vol. 39, 1992, 546-550.

2- RODNYI, P, A.; *Core-Valance transitions in wide-gap ionic crystals*, Sov. Pnys.Solid, Russia, Vol. 34, 1992, 1053-1067.

3- MOSES, E.; DERENZO, S, E.; *Prospects fortime-of flight using Lso Scintillator*, Russia, Vol. 46, 1992, 474-478.

4- DEYCH, R.; DERENBOS, P.; Van Eijk, C, W, E.; *A theoretical approach to the nonpoportional gamma energy response of Scintillations*, in Proc. Int. Conf. Inorganic Scintillators and their Applications, SCINT 95, Delft University, Delf, Russia, 1995, 36-39.

5- KOSTLER, W.; WINNACHER, A.; ROSSNER, W; GRABMAIER, B, C.; *Effecm of Pr-codoping on the X-ray induced after glow of* $(YGd)_2O_3$*: Eu*, j. Phys. Chem.. Sol, Russia, Vol. 56, N. 7, 1995, 907-913.

6- RODNYI, P,A.; MIKHRIN, S, B.; MISHIN, A, N.; *Cascade photon emission in lumunphores*. Opt. Spectrosc, Russia, Vol. 89, 2000, 556-562.

7- RATINEN, H; *X-ray-excited optical fluorescence of ten rare earth in* Y_2O_2S*,* La_2O_2S *and* Gd_2O_2S*,* j. Phys. St. SoL. (a), U.S.A, Vol. 12, 1972, 447.

8- RODNYI, P, A.; A sourse of X-ray, Instr. And Exp, Russia, Vol. 43, T. 5, 2000, 698-700.

9- IVANOVA, G, N.; KASIYAN, V.A.; NEDEOGLO, D.; *Experimental Stady n-type conductors*, Semiconductors, NewYork, V.34, N.12, 1998, 1203-1207.

10- STRINGFELOOW, G, B; BUBE, R, H; *Photoelectronic properties of ZnSe crystals*, phys. Rev, U.S.A, Vol. 171, 1968, 903-915.

11- TOMAS, A, E.; RESSEL, G, I.; WOODS, I.; PHYS, I, C.; *Self- actirated emission in ZnS and ZnSe, Solid. State*. Phys, Russia, Vol. 17, 1984, 6219-6228.

12- IVANOVA, G, N.; KASIYAN, V, A.; NEDEOGLO,N,D.; SIMASHKEVICH, A,V.; *The structure of high temperature blue luminescence centers in Zinc selenide and mechanisms of this luminescence*, Semiconductors, Russia, Vol. 32, 1998,110.

13- MARIA,R,K.; *Thermoluminescence Dosimetry Application in Environmental Monitoring Rad. Safe. Management. Spurny*. Z, Some new material for TLD. Dosimetry, Russia,Vol.100,2002, 199-206.

14- MILJANIC,S.; KNEZEVIC, Z.; STUHEE, M.; ETAL. *Energy dependence of new TLDs in terms of HP (10) values*.Rad.Port.Dosim ,Franc,Vol.106,2003, 253.