

INFRARED SPECTRA, DIFFERENTIAL SCANNING CALORIMETRY AND MECHANICAL PROPERTIES OF POLYETHYLENE DOPED WITH $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$

T.D. IBRAGIMOV, O.B. TAGIEV, I.S. RAMAZANOVA, T.Sh. IBRAHIMOVA,
A.F. NURALIYEV, E.G. ASADOV, B.H. IBRAGIMOV

*Institute of Physics, Azerbaijan National Academy of Sciences, Azerbaijan
131, H. Javid ave., Baku, AZ 1143, Azerbaijan
e-mail:tdibragimov@mail.ru*

High-density polyethylene with the additive of $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ particles of different concentrations is investigated by infrared spectroscopy, differential scanning calorimetry and strength testing methods. It was shown that the presence of particles leads to an increase in the effective infrared absorption associated with an increase in scattering, a decrease in the heat of transition, and an increase in the ordering of the system. In this case, the yield threshold decreases with a simultaneous increase in the elastic modulus.

Keywords: phosphor, high density polyethylene, composite material.

PACS: 77.55.-f, 77.84. s , 77.84.Dy, 77.84.Lf, 81.07.Pr , 82.35.Np

INTRODUCTION

Production of high-performance devices for imaging and lighting, which are capable of competing with conventional systems, requires the obtaining of phosphors with specific properties. This necessity promoted the development of new materials and the optimization of existing phosphors. One of such promising materials is $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$. Its monocrystal and polycrystal emits a broad yellow luminescence band is centered at 562 and 565 nm, respectively, under both 420 nm and 337.1 nm excitation wavelengths [1-2].

The spectroscopic properties of the phosphor $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ provide high performance. However, it is not only requirement for the respective devices. Active luminescent elements must be resistant to water, solar radiation and temperature. The phosphor cannot meet these requirements by itself. Its encapsulation is required. Typically, a polymer is used as the matrix. To predict the most optimal conditions for encapsulation, it is necessary to determine the interaction between the filler particles and the matrix.

The aim of present work is the study of high-density polyethylene with the additive of $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ particles by infrared spectroscopy, differential scanning calorimetry and strength testing methods.

EXPERIMENTAL

$\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ (5 mol %) polycrystals were prepared from stoichiometric amounts of CaS and Ga_2S_3 powders. EuF_3 was used for the activation by europium. The synthesis of this material was done by a solid-state reaction in a graphite crucible covered with graphite powder at temperature of 1000°C and vacuum of 10^{-4} Torr for 4 hours. After the synthesis, a 4-hour annealing was carried out at 700°C in an argon atmosphere with hydrogen sulfide.

Powder was obtained by grinding in the planetary micro mill (the model Pulverisette 7, firm Fritsch, Germany).

The powder obtained was separated according to sedimentation time τ in a column with hexane according to the relation:

$$\tau = \frac{18h\eta}{(\rho_1 - \rho_2)gd^2} \quad (1)$$

where h is the height of the column; η is the viscosity coefficient of the liquid; ρ_1 and ρ_2 are the densities of this material and hexane; g is the acceleration of gravity; d is the transverse dimension of the particles. The fractions obtained were dried under a vacuum of 10^{-2} torr at $T = 50^\circ\text{C}$ for a week. This method produced a powder with an average particle size of 500 nm.

We used high density polyethylene (HDPE) as a matrix. Melting and softening points of polymer are 130-135°C and 80-90°C, correspondingly. Then obtained mixture was shaken in a vortex mixer for 1 hour at room temperature, followed by sonication with dispergator Ultrasonic Cleaner NATO CD-4800 (China) for 4 hours. Disc-shaped samples of composites were obtained by hot pressing at temperature of 165°C and pressure of 15 MPa. Pressing time after reaching the selected temperature is 15-20 minutes. The diameter and thickness of the obtained films were 4 cm and 80-90 μm , respectively. Aluminum electrodes with diameter of 3 cm and thickness of 10 μm are pressed on both sides of the films.

The infrared spectra of the samples were obtained using an FTIR 7600 Fourier spectrometer in the range of 7800-375 cm^{-1} with a resolution no worse than 0.5 cm^{-1} .

Thermal analysis of the samples is carried out in the inert gas (argon) by differential scanning calorimeter NETZSCH DSC 204 F1 (Germany). Liquid nitrogen is used as a protective gas and sample cooling. A sample with weight of 40 mg is placed in an aluminum pan. In the same way, a sapphire as reference sample is placed in another pan, and under exactly the same conditions, both panes are heated at

the rate of 10 K/min. The flow rate of the inert gas is chosen to be 20 ml/min and the studies are carried out in the temperature range from -10°C to 600°C.

The Tinius Olsen H5KS Benchtop Tester from Advanced Test Equipment Corporation with 50 N

probes was used for definition of mechanical parameters.

RESULTS AND DISCUSSION

Figure 1 and 2 show the infrared spectra of both pure polyethylene and composites.

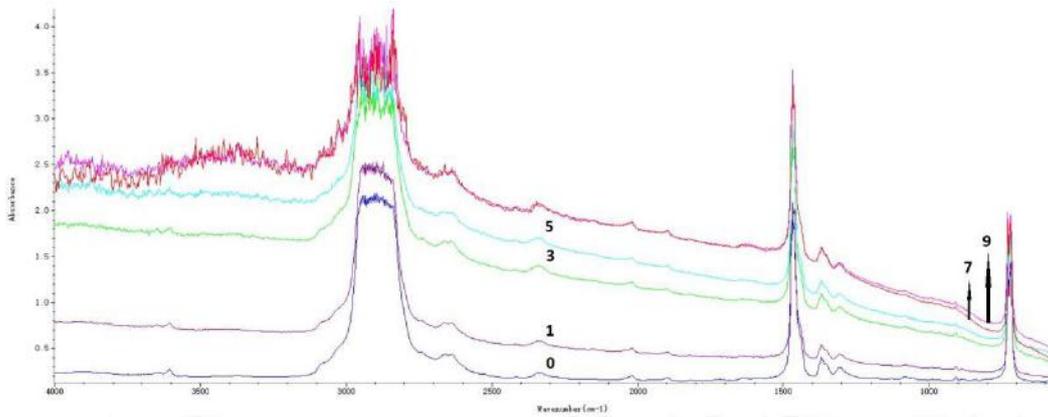


Fig. 1. Infrared spectra of the pure polyethylene and composites.

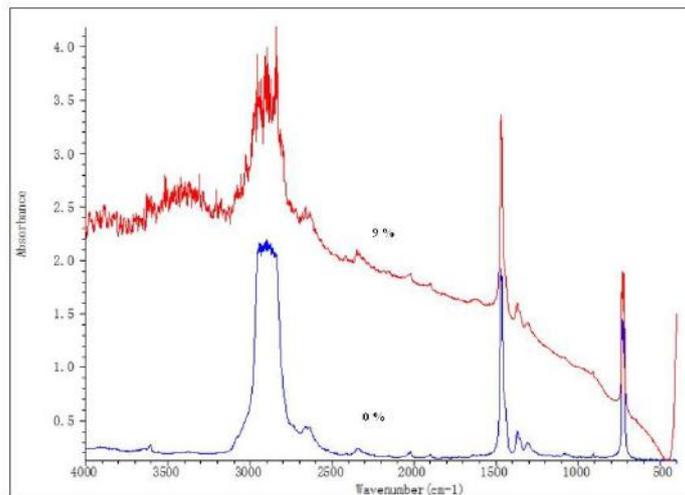


Fig. 2. Infrared spectra of the pure polyethylene and the composite with 9 vol.% filler.

All samples exhibit pronounced absorption peaks which correspond to different types of CH₂ vibrations: a) the wide band 3100-2700 cm⁻¹ which is manifestation of asymmetric stretching vibrations with symmetry B_{1u} (2924 cm⁻¹) and B_{2u} (2899 cm⁻¹); symmetric stretching vibrations B_{1u} (2850 cm⁻¹) and B_{2u} (2857 cm⁻¹); b) rather narrow split band 1500-1400 cm⁻¹ which corresponds to B_{1u} (1473 cm⁻¹) and B_{2u} (1463 cm⁻¹) deformation vibrations; c) 650-750 cm⁻¹ band corresponding to B_{1u} (731cm⁻¹) and B_{2u} (720 cm⁻¹) pendulum vibrations. In addition, a number of narrow peaks of low intensity are observed.

As can be seen, there are no noticeable changes in the positions of the absorption bands upon addition of the filler. It indicates that the particles have almost

no effect on various types of vibrations in polymer chains. However, in this case, the band 3100–2700 cm⁻¹ broadens and the total absorption increases. The latter fact is related to the scattering of infrared radiation in a heterogeneous medium [3].

Figures 3-8 show heat flow versus temperature (DSC) for both the pure polyethylene and composites at heating and cooling regimes. These dependences exhibit peaks at certain temperatures T_c, the areas under which correspond to the enthalpy characterizing the heat of transition from the solid state to the liquid one. At the same time, in the heating regime, this transition is endothermic, that is, heat is required, and when cooled, it is exothermic, in which heat is released.

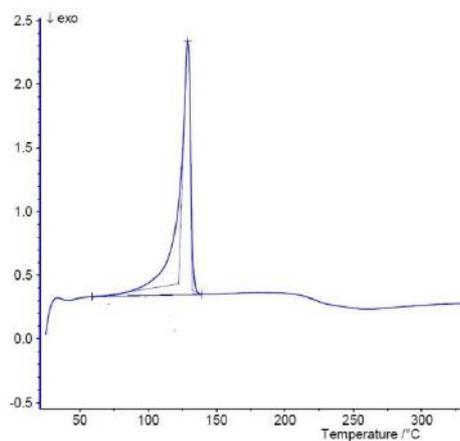


Fig.3. Temperature dependence of heat flow for the pure polyethylene.

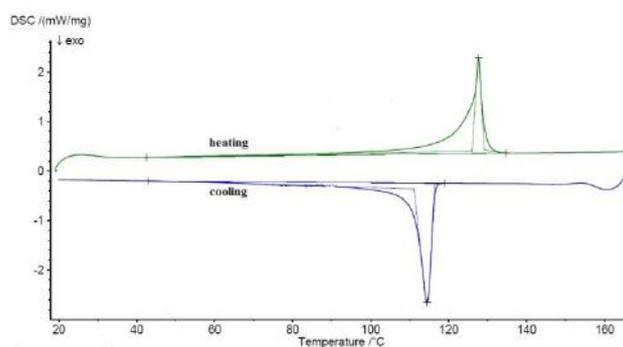


Fig. 4. Temperature dependence of heat flow for the pure polyethylene doped with 1vol.% of CaGa₂S₄:Eu⁺²

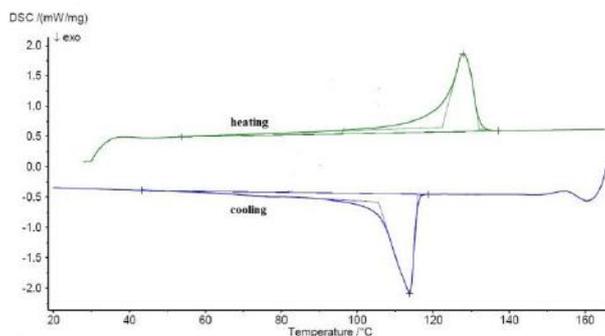


Fig.5. Temperature dependence of heat flow for the pure polyethylene doped with 3vol.% of CaGa₂S₄:Eu⁺²

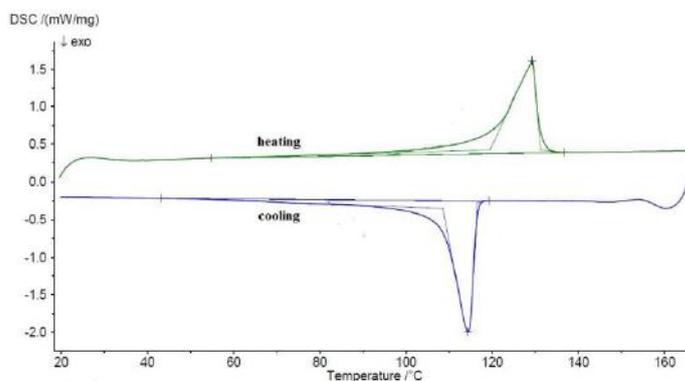


Fig.6. Temperature dependence of heat flow for the pure polyethylene doped with 5vol.% of CaGa₂S₄:Eu⁺²

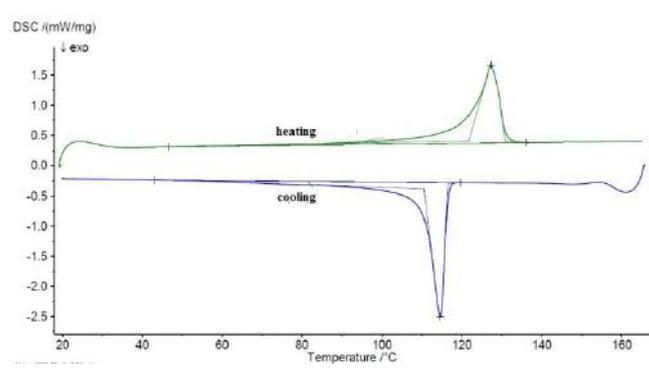


Fig.7. Temperature dependence of heat flow for the pure polyethylene doped with 7 vol.% of CaGa₂S₄:Eu²⁺

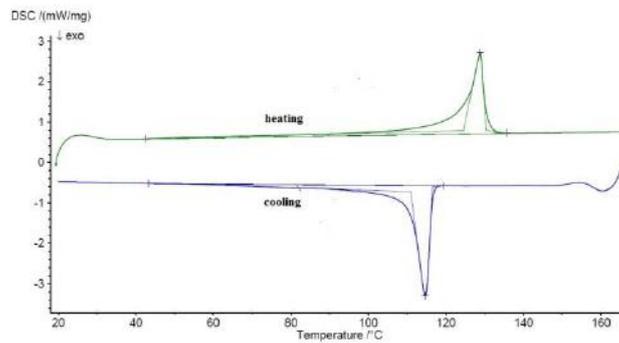


Fig.8. Temperature dependence of heat flow for the pure polyethylene doped with 9 vol.% of CaGa₂S₄:Eu²⁺

Table 1 shows the transition temperatures T_c , the change in enthalpy ΔH , and the change in entropy ΔS defined by the formula $\Delta S = \Delta H/T_c$.

Table 1.

The transition temperatures T_c , the change in enthalpy ΔH and entropy ΔS at this transition for the pure polyethylene and composites with different concentration of filler.

%	heating			cooling		
	T°C	ΔH , J/q	ΔS , J/q	T°C	ΔH , J/q	ΔS , J/q
0	128.9	125.2	0.97			
1	127.7	72.59	0.57	114.5	81.62	0.71
3	127.8	82.17	0.64	113.8	89.97	0.79
5	129.3	70.25	0.54	114.5	79.09	0.69
7	127.3	71.46	0.56	114.6	82.3	0.72
9	128.8	91.81	0.71	114.7	98.15	0.86

As can be seen, with the addition of particles even at concentration of 1%, the enthalpy, that is, the heat of transition sharply decreases. It indicates on weakening of intermolecular bonds in polymer chains due to the inclusion of particles. In this case, entropy (the measure of disorder) also decreases. It indicates on an increase in the ordering of the structure. The

addition of particles has little effect on the melting and solidification temperatures themselves. In this case, the curing temperature is shifted to low temperatures with respect to the melting temperature.

The results of some measurements of mechanical parameters are shown in Table 2.

Table 2.

Mechanical parameters of the pure polyethylene and composite with 9 vol.% of CaGa₂S₄ Eu²⁺.

Specimen	Thickness (mm)	Width (mm)	Ultimate force (N)	Ultimate stress (MPa)	Modulus (MPa)
pure HDPE	0.075	12.4	16.7	18.1	512
HDPE+9 vol.% CaGa ₂ S ₄ Eu ²⁺ .	0.075	12.4	11.8	12.7	585

In this table, ultimate stress is the stress at the yield point and modulus is the elastic modulus. As seen, the ultimate force and stress decrease. It indicates on a decrease in intermolecular interaction in the presence of particles and is consistent with thermal analysis data. But on the other hand, the elastic properties increase due to the incorporation of particles into the polymer chains.

CONCLUSIONS

It is known that the additive of CaGa_2S_4 Eu^{2+} particles into high-density polyethylene leads to light scattering in the composites, weakening of intermolecular bonds in polymer chains and an increase of elastic properties.

-
- [1] *C. Ronda, T. Justel, H. Nikol.* Rare earth phosphors: fundamentals and applications. *J. of Alloys and Compounds.* 1998, 669, 275–277.
- [2] *P. Benalloul, C. Barthou, C. Fouassier, A.N. Georgobiani, L.S. Lepnev, Yu.N. Emirov, A.N. Gruzintsev, B.G. Tagiev, O.B. Tagiev,*
- R.B. Jabbarov.* Luminescence of Eu^{2+} in Calcium Thiogallate. *Journal of The Electrochemical Society,* 2003,150, G62-G65.
- [3] *C.F. Bohren & D.R. Huffman.* 1983. *Absorption and Scattering of Light by Small Particles,* John wiley & Sons. New York 530 p.

Received: 17.06.2022