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DTA INVESTIGATIONS ON THE SYNTHESIS OF HALOPHOSPHATE-TYPE PHOSPHORS

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ABSTRACT

The effects of temperature, heating rate and the protective atmosphere used during synthesis on the luminous properties of the Polish halophosphate phosphor H_{11} were studied. From the results, optimum synthetic conditions are suggested.

INTRODUCTION

The synthesis of halophosphate-type phosphors involves a series of chemical reactions, which are not characterised completely. For Sb/Mn doped Ca halophosphates, several substrates are reacted in the solid state at 1100–1200 °C for 2 h in a reducing, protective atmosphere. The probable mechanism of phosphor formation is [1]

$$2CaHPO_4 \xrightarrow{723^\circ C} Ca_2P_2O_7 + H_2O \tag{1}$$

$$CaCO_3 \xrightarrow{1073^\circ C} CaO + CO_2 \tag{2}$$

$$Ca_2P_2O_7 + CaO \xrightarrow{1073^\circ C} Ca_3(PO_4)_2 \tag{3}$$

$$Ca_3(PO_4)_2 + CaF_2/NH_4Cl \xrightarrow{1473^\circ C} Ca_3(PO_4)_2Ca(F/Cl) + NH_3 + HF \tag{4}$$

The luminous properties of the product (e.g. intensity or stability of light emission) are dependent on many factors [2,3] such as proper substrate

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composition, suitable oxidation state of Sb and Mn in the apatite lattice, side reactions leading to loss of activators, and equivalent stoichiometric ratio of both Ca/P and F/P. If the substrate mixture contains excess Ca, or is deficient in fluorine, this inhibits incorporation of Sb^{3+} cations into the apatite structure. Moreover, inadequate reaction conditions may cause oxidation of Sb^{3+} or Mn^{2+} cations to higher oxidation numbers, or reduction of Sb^{3+} to elementary antimony, or formation of antimonates, all of which make the luminous quality worse. The synthesis is carried out under a reducing, protective atmosphere since an oxidising atmosphere favours calcium antimonate formation. The duration of reaction, the number of heating cycles and the heating or cooling rate may also influence the quality of the phosphor formed.

In the present work, the effects of component composition, temperature, heating rate and protective atmosphere were studied. The luminous and surface properties of the phosphors formed were determined and optimum conditions of the synthesis suggested.

EXPERIMENTAL

Mixtures for synthesis of Sb/Mn-doped Ca halophosphate phosphors were obtained from COBR (Research and Development Centre; Warsaw) and are identified as (a) H_{11}, a white powder (3500 K) containing $CaHPO_4$, NH_4Cl, $CaCO_3$, CaF_2, $MnCO_3$, Sb_2O_4, La_2O_3 and CdO; (b) M-I, a white powder (6500 K); (c) M-II, containing Al; (d) M-III, not containing La or Cd, and (e) M-IV, containing La and Cd. The investigations were carried out on a Derivatograph Q-1500 D (MOM, Hungary) with heating rates of 3.75, 7.5 and 15 °C min^{-1}, over the temperature range 20–1500 °C. Temperature, TG, DTA and DTG curves were recorded [4].

The luminous properties of the phosphors were examined in a home-made photometer consisting of a mercury-vapour lamp, photoelement, amplifier and microammeter. For testing, each phosphor was suspended in a nitrocellulose–butyl acetate solution (75 mg ml^{-1}) then deposited on a microscope cover glass. After drying, the glass was placed in the photometer chamber and the total luminous flux measured.

The specific surface area of the phosphors was determined by the thermal nitrogen-desorption method of Nelsen and Eggersten [5].

RESULTS AND DISCUSSION

Figure 1 shows DTG and DTA curves recorded for the substrate mixture used to prepare phosphor H_{11} at a heating rate of 15° C min^{-1} over the temperature range 20–1500 °C. These curves show that during phosphor

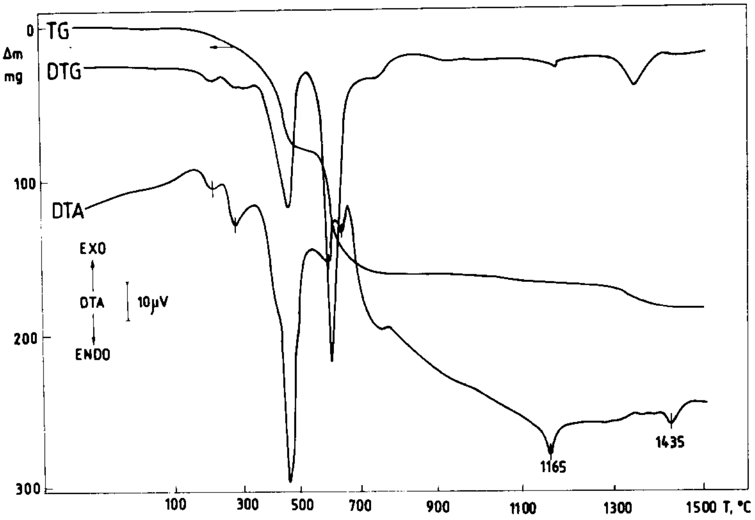

Fig. 1. The TG, DTG and DTA curves for the synthesis of the phosphor H_{11} heated at 15 ° C min^{-1}

synthesis at least five endothermic reactions take place at 190, 270, 480, 610 and 650 ° C, respectively. The TG curve shows the largest weight loss (about 17%) occurs at up to 1000 ° C, but at this temperature the phosphor is not formed, as shown by the grey colour of the sample. The DTA curve also shows two endotherms at 1165 ° C and 1435 ° C, where the actual phosphor synthesis occurs. It should be emphasized that the temperatures recorded during phosphor synthesis are different from those indicated in eqns.

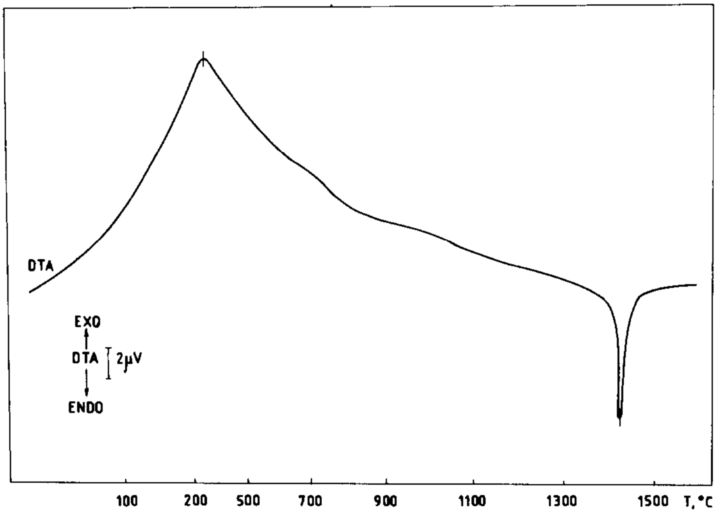

Fig. 2. The DTA curve for the second heating cycle of a phosphor sample heated at 15 ° C min^{-1}.

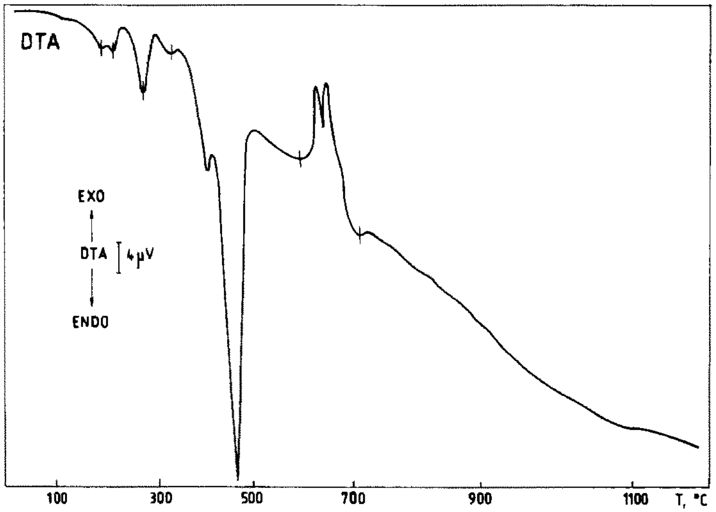

Fig. 3. The DTA curve for the synthesis of the phosphor H_{11} heated at 3.75 °C min^{-1}.

(1)–(4), which are taken from ref. 1. These discrepancies are probably caused by different synthesis conditions and also by some qualitative and quantitative differences in the substrate mixtures used.

Figure 2 shows DTA curves recorded during the second heating cycle of the same phosphor sample at a heating rate of 15° min^{-1}. No weight loss was observed, although the DTA curve shows one exotherm at 320 °C and one endotherm at 1430 °C. These suggest structural changes which may have great influence on the luminous properties of the phosphor [6].

At lower heating rates (7.5 and 3.75 °C min^{-1}, respectively), the DTA peaks observed at a heating rate of 15 °C min^{-1} were shifted to lower temperature. The DTA curve obtained at 3.75 °C min^{-1} shows additional peaks (Fig. 3) which were not present in Fig. 1. These results confirm published data about the very complex nature of halophosphate synthesis.

To test the effect of various protective atmospheres on the formation of phosphor H_{11}, the synthesis was carried out in an NH_3 atmosphere produced by the decomposition of NH_4Cl included in the mixture. A second protective atmosphere was made by passing pure nitrogen, dried by molecular sieves, through the measuring chamber. Depending on the experimental conditions the phosphor samples obtained differed from one another in colour and hardness. Luminous properties and surface areas were measured as described earlier. The dependence of weight loss ($\%U$) (which is related to the reaction rate) for each peak on the heating rate (ϕ) and other measurement conditions was also examined. The results are presented in Fig. 4 as the function $\%U = f(\phi)$ for peak III (480 °C), recorded for phosphors synthesis carried out in the NH_3 protective atmosphere or with N_2 passed through the measuring chamber. As expected, the reaction rate

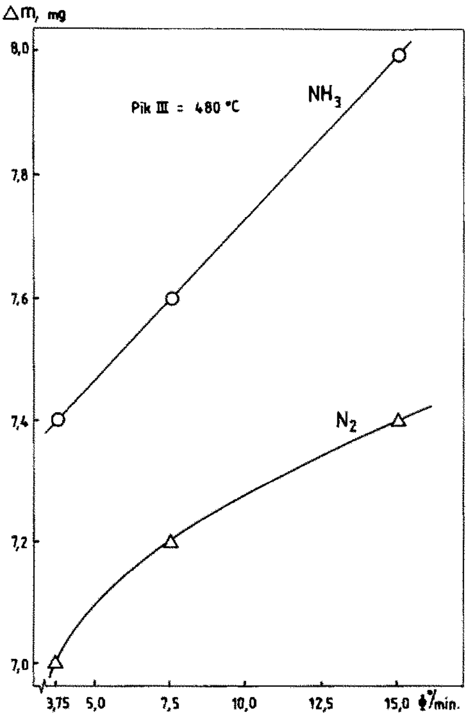

Fig. 4. The relationships between weight loss and heating rate for the temperature peak III (480 °C) in the synthesis of phosphor H_{11} in atmospheres of NH_3 or N_2.

increases at higher heating rates. Moreover, the synthesis is more rapid in the reducing NH_3 atmosphere (the upper curve in Fig. 4). The specific surface areas (S, $m^2\ g^{-1}$) and visible emission intensities (E, %) of the phosphors obtained at a heating rate of $15\,^\circ C\ min^{-1}$ were also investigated.

As a result of heating the substrate mixture for phosphor H_{11} production, the specific surface area decreases markedly, from 1.38 to about $0.5\ m^2\ g^{-1}$, but it does not reach the value for the Sylvania phosphor ($0.28\ m^2\ g^{-1}$). For synthesis of the phosphor H_{11} the optimum values of S and E were obtained for samples synthesized at $\phi = 15\,^\circ C\ min^{-1}$, where the reaction rate is maximum. The value of E corresponds to 90% of the emission of the Sylvania phosphor, while the specific surface area $S = 0.49\ m^2\ g^{-1}$ is intermediate between those obtained at $\phi = 3.75$ and $7.5\,^\circ C\ min^{-1}$. Therefore further investigations of phosphor synthesis were carried out with $\phi = 15\,^\circ C\ min^{-1}$.

Figure 5 shows the results of measurements of S and E for phosphor H_{11} synthesized at various temperatures, with the samples being heated for only a short time—about 15 min. It appears from Fig. 5 that at 1160° the curve $S = f(T)$ shows a minimum, while the second curve, $E = f(T)$, shows a maximum. This proves that the best luminous quality of the phosphor is obtained in this series ($S = 0.49\ m^2\ g^{-1}$, $E = 90\%$) at 1160 °C.

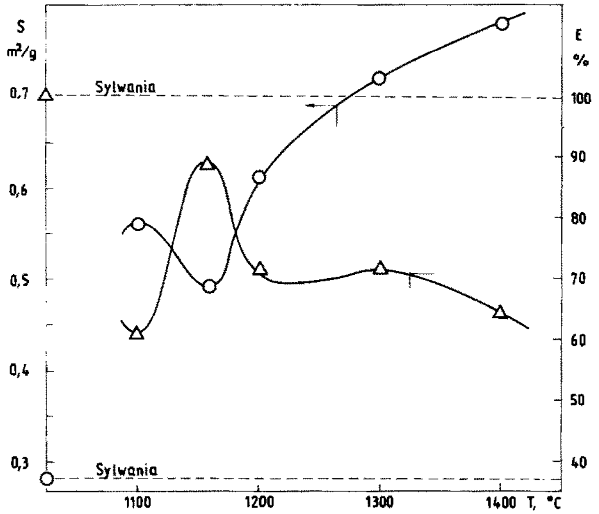

Fig. 5. The specific surface area (S) and emission intensity (E) for samples synthesized at various temperatures in NH_3 atmosphere.

Further investigations were carried out by increasing the temperature of the measuring chamber to 1160 °C, heating the samples at this temperature for 1, 2 or 3 h and also by making two or three measuring cycles in the NH_3 protective atmosphere.

The data showed that halophosphates with the best luminous properties were obtained by heating the mixture to $T = 1160\,°C$ ($E = 90\%$), followed by heating for 2 h at this temperature in the NH_3 protective atmosphere.

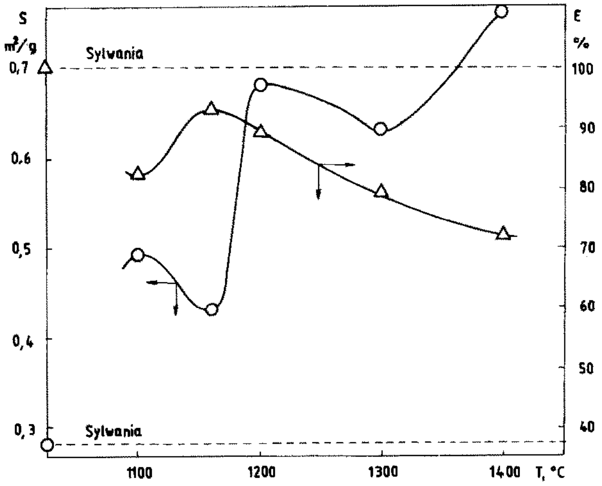

Fig. 6. The specific surface area (S) and emission intensity (E) for samples synthesized at various temperatures in N_2 atmosphere.

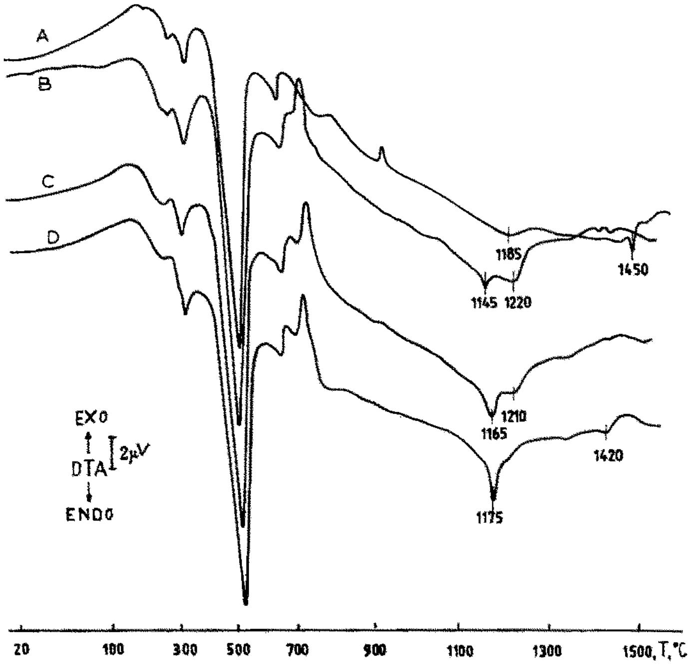

Fig. 7. The DTA curves for the synthesis of halophosphate phosphors obtained from the mixtures M-I, M-II, M-III and M-IV.

Similar syntheses were carried out in a pure N_2 atmosphere at $\phi = 15\,°C\ min^{-1}$. The values of S and E obtained at various temperatures are presented in Fig. 6.

It appears from these data, that the sample of phosphors H_{11} which was most similar to the Sylvania phosphor was obtained at 1160 °C, with heating at this temperature for about 15 min ($E = 92.8\%$). In these experiments, the N_2 flow provided complete removal of air and at high temperatures reducing compounds (e.g. radicals) might be formed by reaction between nitrogen and gases generated during the synthesis. This suggestion needs to be confirmed by further investigations.

The synthesis of phosphors from other substrate mixtures (M-I, M-II, M-III, M-IV) obtained from COBR was examined at 20–1500 °C. The measurements were carried out in the NH_3 protective atmosphere at $\phi = 15\,°C\ min^{-1}$. Figure 7 shows DTA curves of synthesis of the Sb/Mn doped Ca halophosphate 6500K (curve A—mixture M-I), a halophosphate containing Al (curve B—mixture M-II), a halophosphate of the M-IV type but without La and Cd (curve C—mixture M-III) and a halophosphate containing both La and Cd (curve D—mixture M-IV). Comparison of these DTA curves with the data in Fig. 1 suggests that no fundamental differences in the synthesis reactions (i.e. number, shape and temperature of DTA peaks) occur up to 1000 °C. However, above 1100 °C the DTA endotherms do differ from each other in shape and temperature.

It can be seen from Fig. 7, that the course of synthesis from mixtures M-II and M-III are rather different from that of phosphor H_{11}, because the last endotherms occur at about 1200 °C. Addition of La and Cd (M-IV) has no significant effect on the synthesis, compared with that of H_{11}. Only the endotherm at 1175 °C is somewhat larger, possibly caused by stabilization of the lattice structure.

Phosphor synthesis was also carried out at $\phi = 15\,°C\ min^{-1}$ in the N_2 protective atmosphere, stopping the temperature increase at 1160 °C for 1, 2 and 3 h. Specific surface areas and luminous properties of the samples obtained were then measured. From these experiments it appears that the best luminous quality is shown by phosphors M-I ($S = 0.62\ m^2\ g^{-1}$, $E = 78.6\%$) and M-IV ($S = 0.41\ m^2\ g^{-1}$, $E = 82.1\%$) after 1 h, and by phosphors M-II ($S = 0.38\ m^2\ g^{-1}$, $E = 85.7\%$) and M-III ($S = 0.39\ m^2\ g^{-1}$, $E = 85.7\%$) after 2 h of heating at 1160 °C.

These results are comparable with those obtained for the synthesis of H_{11}. It appears that an increase in the heating time of the phosphor sample leads to a decrease in both E and S values. In other experiments (see ref. 6) it was found that higher temperatures and longer heating times applied to porous boron-containing glasses produce glasses of a larger pore diameter (i.e. reduced porosity) and to enrichment of boron at the surface because of boron diffusion from the bulk solid phase. The dependence between pore radius and thermal treatment conditions is expressed by the equation [6]

$$r^n = k \cdot t_t \cdot e^{-m/T} \tag{5}$$

where r is the pore radius, k, m and n are constants; T is the thermal treatment temperature and t_t is the thermal treatment time.

From these relationships it is clear that the increase in pore magnitude is directly proportional to the heating time. Moreover, the diffusion of atoms to the surface at high temperature is caused by either a high migration rate of atoms (e.g. on catalysts surfaces, about $10\ m\ s^{-1}$ [7]) or a decrease in the coordination number of atoms or ions on the surface [8]. It seems that 'adjustment' of Sb^{3+} and Mn^{2+}, and of impurity atoms, to the apatite lattice is very significant for the migration process. This leads to removal of these atoms and ions from the bulk to the surface. This process is intensified by increasing the time and temperature of heating, and may degrade the luminous properties because impurities on the surface can cause damping and worsening of luminescence (decreasing $\%E$). The migration of atoms and ions in phosphors confirms phase change processes, i.e. occurrence of metastable phases in the bulk solid [9].

Heating of the phosphors also eliminates OH^- groups, which can absorb IR and visible light of some wavelengths, leading to an increase in light damping in fiber optics [8].

CONCLUSIONS

DTA results show that synthesis of phosphor H_{11} is a very complex process, with the largest weight loss of substrates taking place at up to 1000 °C, although the phosphor is not produced at this temperature. The DTA curve shows two endotherms at 1165 °C and 1435 °C (with only small weight loss) and synthesis of Sb/Mn doped Ca halophosphate phosphors should be done at 1160 °C.

During the second heating cycle, no weight loss was observed, but the DTA curve shows an exotherm at about 320 °C and an endotherm at about 1430 °C. These indicate phase changes (lattice recrystallizations) occurring at these temperatures.

Synthesis of H_{11} is most rapid in the NH_3 reducing atmosphere and at the highest heating rate (15 °C min^{-1}) tested. The best luminous properties were obtained by heating for about 15 min in the nitrogen ($E = 92.8\%$) or NH_3 ($E = 90\%$) atmospheres, and also by heating for 2 h in NH_3 ($E = 95.7\%$), probably because prolonged heating causes migration of Sb^{3+} and Mn^{2+} ions from the bulk solid phase to the surface.

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