

Phosphor plasters of CaSO₄:Dy on the courtyard wall of Djehuty's tomb (Luxor, Egypt)

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Abstract

The X-ray diffraction (XRD) and environmental scanning electron microscopy (ESEM) analyses of plasters collected from the courtyard walls of Djehuty's tomb show anhydrite, calcite, dolomite, quartz, alkali feldspars and accessory amounts of halite and illite. The external outer bed is mainly composed by anhydrite, since the original hydrous phases of gypsum plaster were desiccated during thirty centuries in the dry land environment of the Luxor area, under low relative humidity and high temperatures. The luminescence analyses by thermoluminescence (TL) and cathodoluminescence (CL) demonstrate as one plaster sample (m8), i.e., 95% anhydrite, displays a gigantic TL emission of 33 555 a.u. and a SEM/CL emission of 2319 a.u. maxima peak. The spectra CL also exhibits a 484 nm peak attributable to the classic $^4F_{9/2} \rightarrow ^6H_{15/2}$ transition circa 490 nm of Dy³⁺ and a 573 nm emission of Dy³⁺ masked in a broad emission band centered at 620 nm. The common presence of sodium minerals such as halite or albite together with the probable presence of sodium in waters points to Na⁺ ions acting as compensators of Dy³⁺ to maintain the electrical neutrality of the CaSO₄:Dy phosphor lattice. Further analyses of more plaster CaSO₄ micro-samples could demonstrate if this observation is just an isolated mineralogical chance or an intentional archaeological handling.

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1. Introduction

The painting procedures of ancient Egyptian funeral objects used very fragile techniques throughout centuries and delicate methods for modifying the hue of pigment colors (Rinuy, 2001). Ancient Egyptian pigments have been extensively analyzed by several techniques (e.g. Nagashima et al., 1996; David et al., 2001). Papers specifically dealing with ancient plasters on Egyptian tomb walls from the Luxor area are scarce and they report that plasters are mainly composed by anhydrite, calcite and quartz. (e.g., Uda, 2004; Noll, 1981). A Spanish–Egyptian archaeological team has been working at the rock-cut tomb of Djehuty (Luxor, Egypt) since January 2002. Djehuty was

“overseer of the Treasury” and “overseer of craftsmen” under the female pharaoh Hatshepsut of the XVIIIth Dynasty (ca. 1480 BC.). He registered the products brought to Thebes from foreign lands, and he managed to gather the resources to make a nice tomb for him, decorated in relief of a high quality. One of the objectives of the 2006 archaeological campaign was the identification of building materials such as stuccoes and mortars, originally placed as gypsum plasters in different tomb spots. The thermal decomposition of gypsum (CaSO₄·2H₂O) to bassanite (CaSO₄·0.5H₂O) occurs circa 107 °C but incomplete changes can be observed from 50 °C. In addition, the thermal decomposition from bassanite to anhydrite in laboratory driven experiments ranges from 200 to 250 °C. The gypsum dehydration involves: (a) breaking of bonds of water molecules, (b) water self-diffusion through the pore spaces, (c) reordering of Ca cations and SO₄ ions (Garcia-Guinea et al., 2001).

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Anhydrite [CaSO₄] can be formed in environmental conditions of dry lands with low relative humidity; high temperatures and time enough to keep the kinetic processes. Moreover, a CaSO₄ phase grown-up with additional little amounts of dysprosium element, i.e., a CaSO₄:Dy phosphor, is an essential material for use in thermoluminescence (TL) dosimetry because of its ease of preparation, high TL sensitivity and climatic stability; it is widely used for personal and environmental radiation monitoring. The trapped states involved in the TL process are characteristics of the host matrix while the luminescence is facilitated by the impurity related states. According to the redox model hole traps are related to sulphate radicals of the CaSO₄ matrix and electron traps are related to Dy³⁺ impurities. Under X-irradiation Dy³⁺ changes to Dy²⁺ by taking the electron, while during the TL recording process, holes are released from the hole traps and recombine with trapped electrons at the Dy²⁺ sites. It has been observed from X-ray diffraction (XRD) studies that there is no change in the long range order in the CaSO₄ matrix due to repeated cycles of annealing and hence the observed decrease in TL sensitivity might be due to some change in the local environment of Dy³⁺ ions in CaSO₄ matrix (Bhattacharyya et al., 2006). The physicochemical characterization of the micro-samples collected on the courtyard walls of the Djehuty tomb was performed by XRD, scanning electron microscopy (SEM-EDS), differential thermal analysis (DTA), TL and cathodoluminescence (CL) techniques.

2. Experimental

The morphology and composition of plaster powders were observed under the environmental scanning electron microscope (ESEM) Philips XL30/40 ESEM-EDS Oxford-WDS. The powder XRD analyses were recorded on a X'Pert PRO MPD diffractometer using Cu K α radiation from 5° to 80° 2 θ with a scan step size of 0.017° using a fast X'Celerator detector with a divergence slit of 1/8°, i.e., 11 min per XRD profile, with secondary Ni filter without monochromator. Sample spinning and atmospheric air were used during the measurements. DTA of 50 ± 1 mg of plaster samples were recorded with a simultaneous TG-DTA-DSC thermal analyser (Setaram, Labsys CS 32-CS 332 Controller) in nitrogen atmosphere. Thermal treatments were performed at a heating rate of 10 °C min⁻¹ from RT up to 1000 °C. The sample was held in an alumina sample crucible and the reference material was also alumina. The TL measurements were performed using an automated Risø TL system model TL DA-12 (Botter-Jensen et al., 1999), this reader is provided with an EMI 9635 QA photomultiplier and the emission was observed through a blue filter (a FIB002 of the Melles-Griot Company) where the wavelength is peaked at 320–480 nm; full-width at half-maximum (FWHM) value is 80 ± 16 nm and peak transmittance (minimum) is 60%. It is also provided with a ⁹⁰Sr/⁹⁰Y source with a dose rate of 0.020 Gy s⁻¹ calibrated against a ⁶⁰Co photon source in a secondary standards laboratory (Correcher and Delgado, 1998). All the TL measurements were performed using a linear heating rate of 5 °C s⁻¹ from room temperature up to 550 °C in a N₂ atmosphere. Several aliquots of 5.0 ± 0.1 mg

each of plaster sample were used for each measurement. The CL spectrum of a 4 mm chip of the m8 plaster was obtained by SEM-CL in a Hitachi S2500 electron microscope. Light emissions were collected in a parabolic mirror and focused on a slip of 100 mm with lens attached to the microscope window and a light guide used to feed the light in the CCD camera. The CL spectra were recorded with a Hamamatsu PMA-11 CCD camera.

3. Results and discussion

Plaster micro-samples, i.e., circa 3 × 3 × 4 mm each, were collected by authors Galan and Sanchez-Moral from the tomb walls of the Djehuty tomb at 2006 (Fig. 1a. The mineralogical characterization of micro-samples by XRD) and environmental scanning electron microscopy (ESEM) of plaster samples had shown anhydrite, i.e., CaSO₄, (Fig. 1b). Plasters on the courtyard walls of the tombs display a multilayer structure with frequent calcite (CaCO₃), dolomite (CaMg(CO₃)₂), anhydrite (CaSO₄), quartz (SiO₂) and alkali feldspars ((Na, K)AlSi₃O₈ and minor amounts of accessory minerals such as huntite, gypsum, halite, etc., detectable by XRD and the EDS probe of the SEM (Table 1). The courtyard walls were originally covered in a thin coating of hydrous gypsum plaster [CaSO₄.2H₂O]. Nowadays, 3500 years later, the plasters are anhydrite phase (CaSO₄) by the scarce precipitation, high temperatures and low humidity in the Luxor area. In addition, during the custom DTA-TG and TL measurements of the plaster samples (Figs. 2 and 3), we observed as the m8 sample, mainly composed by CaSO₄ (Fig. 1, Table 1) displayed a gigantic TL emission of 32 000 arbitrary units (Fig. 3), very different to the other anhydrite samples analyzed and we decide to perform the CL spectrum (Fig. 4). The DTA analysis of m8 sample (Fig. 2) shows an endothermic peak at 124 °C which can be explained by dehydration from minor amounts of bassanite (CaSO₄.0.5H₂O) or adsorbed water. Beyond this temperature we observe minor endothermic and exothermic peaks, e.g., at 243 and 380 °C, framed in a general weight loss (coupled TG analysis) in which some dehydroxylation processes cannot be disregarded. The large DTA endothermic peak at 815 °C and the end of the TG mass variation of -36% obviously represent the CaSO₄ dissociation in gas SO₂ and calcium oxide CaO. The TL glow curve of the as received CaSO₄ plaster m8 (Fig. 3) displays three thermoluminescent peaks at 186, 243 and 380 °C. In addition the TL glow curve of the same plaster aliquot after the TL analysis preheating and the additional irradiation under the ⁹⁰Sr/⁹⁰Y source only shows the 186 °C peak being reduced its initial gigantic emission at from the 33 555 a.u. to only 2319 a.u. in the same aliquot after the preheating up to 500 °C and further irradiation of short wavelength. This observation is in good agreement with the DTA-TG analysis since we could attribute the 85 °C to TL lattice defects linked to dehydration processes and the minor 243 and 380 °C maxima peaks to structural defects associated with possible dehydroxylation features. Conversely, this thermal destruction of the anhydrite hydrous-super-structure and the original textures, reduces the gigantic peak from the 33 555 a.u. to 2319 a.u. This

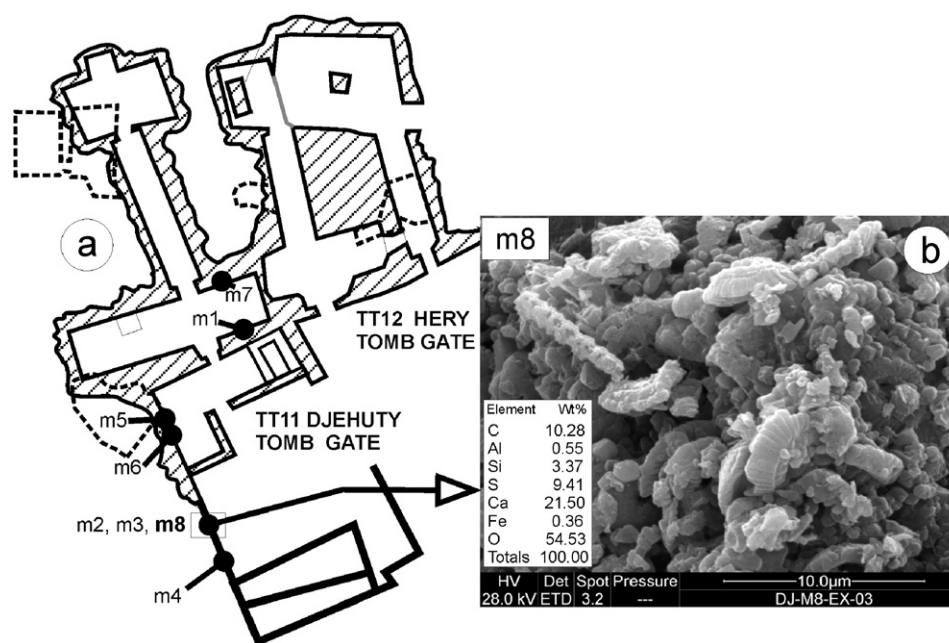


Fig. 1. (a) Sampling plasters in Djehuty's tomb courtyard. Note the chosen m8 sample of CaSO_4 was used as external coating in the courtyard wall of Djehuty's tomb (Luxor, Egypt). (b) Petrographic detail of m8 sample under the ESEM and chemical composition including additional calcite CaCO_3 and quartz SiO_2 .

Table 1
X-ray diffraction semi-quantitative analyses of sampled plasters in the Djehuty's tomb courtyard

Sample	CaSO_4	CaCO_3	NaSi_3O_8	SiO_2	$\text{CaMg}(\text{CO}_3)_2$
m1	85%	10%	–	5%	–
m1x	20%	65%	5%	15%	–
m2	60%	–	–	30%	5%
m3	–	90%	–	–	5%
m4	–	90%	–	5%	5%
m4a	10%	30%	25%	35%	–
m4c	5%	70%	–	–	25%
m4q	–	90%	–	10%	–
m5	90%	5%	–	5%	–
m6	90%	5%	–	5%	–
m7	90%	5%	–	5%	–
m8	95%	5%	–	–	–

Plasters are mainly composed by CaSO_4 , CaCO_3 and SiO_2 .

peak could be linked with the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition at 580 nm of Dy^{3+} or to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition circa 490 nm. Barkyoumb et al. (1997) suggest that a portion of the luminescence observed in $\text{CaSO}_4:\text{Dy}$ is an “athermal” tunneling luminescence with TL from shallow traps superimposed on top of this athermal component. This luminescence may be due to a temperature-independent tunneling process. Furthermore, we here analyze the spectra CL under the scanning electron microscope in several areas of the m8 sample to obtain additional information on possible rare earth elements which play a role as dopants in the CaSO_4 lattice (Fig. 4a). The experimental CL spectrum of the CaSO_4 plaster exhibits an intense light emission up to 2000 arbitrary units (Fig. 4a). The unusual peak at 484 nm can be associated with the existence of minor amounts of Dy in sample following the Gaft et al. (1984) assignments (Fig. 4b). The experimental spectra CL show the well-known

(Salah et al., 2006; Lakshmanan, 2001) band at 484 nm, clearly detached, and the 573 nm band masked in a broad band around 620 nm which can also be attributed to Mn^{2+} point defects in Ca^{2+} positions of both phases CaSO_4 and the accessorial CaCO_3 . Assuming the surrounding existence of sodium in the plaster's walls observed in halite traces, in albite feldspar and in the same sulphate, together with the calcium ion; we could take for granted the mechanism of enhancement of luminescence output of $\text{CaSO}_4:\text{Dy}$ by trace of charge compensator Na^+ proposed by Mulla and Pawar (1984) who describe that the incorporation of Dy^{3+} in the lattice CaSO_4 is likely to be substitutional as ionic radius of Dy^{3+} is close to ionic radius of Ca^{2+} . The charge neutrality demands removal of three Ca^{2+} ions to incorporate two Dy^{3+} ions, during the preparation of the phosphors plasters. This creates Ca^{2+} ion vacancies. Large amount of energy is required to create such Ca^{2+} vacancies,

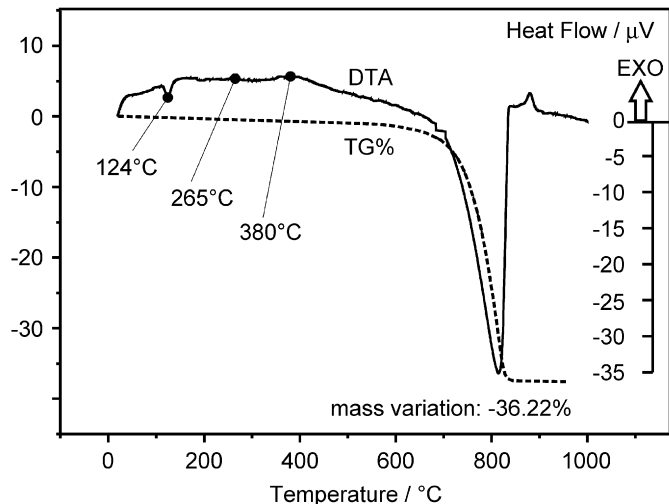


Fig. 2. Differential thermal and thermogravimetric analysis of the m8 sample collected in the Djehuty's tomb courtyard.

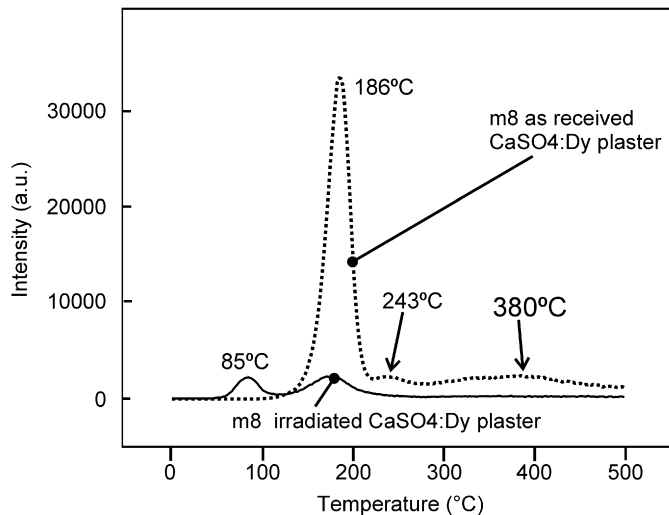


Fig. 3. Thermoluminescence analysis of the m8 CaSO₄:Dy phosphor plaster collected from the Djehuty's tomb courtyard.

which restrict the entry of Dy³⁺ ions after a certain limit. However, the presence of charge compensating ion Na⁺ removes such Ca²⁺ ion vacancies and helps to incorporate more number of Dy³⁺ ions in the host lattice on account of charge balancing: $2\text{Ca}^{2+} \rightarrow \text{Dy}^{3+} + \text{Na}^{+}$. The increased number of Dy³⁺ ions, which also act as active luminescent centers, causes enhancement of TL. The effect of the climatic conditions and sunlight on the stability of the TL emission in CaSO₄ was studied by Pradhan (1993), in Luxor area case we must consider the following features: (a) plasters are mainly CaSO₄ anhydrite but not the hydrous phases gypsum or bassanite; (b) the special environmental conditions with very low relative humidity, high temperature and long time to complete the kinetics processes; (c) it is important to consider that the open courtyards of the tombs were covered by more than 5 m of rubble that had accumulated over the years. At the end of the fifth work season

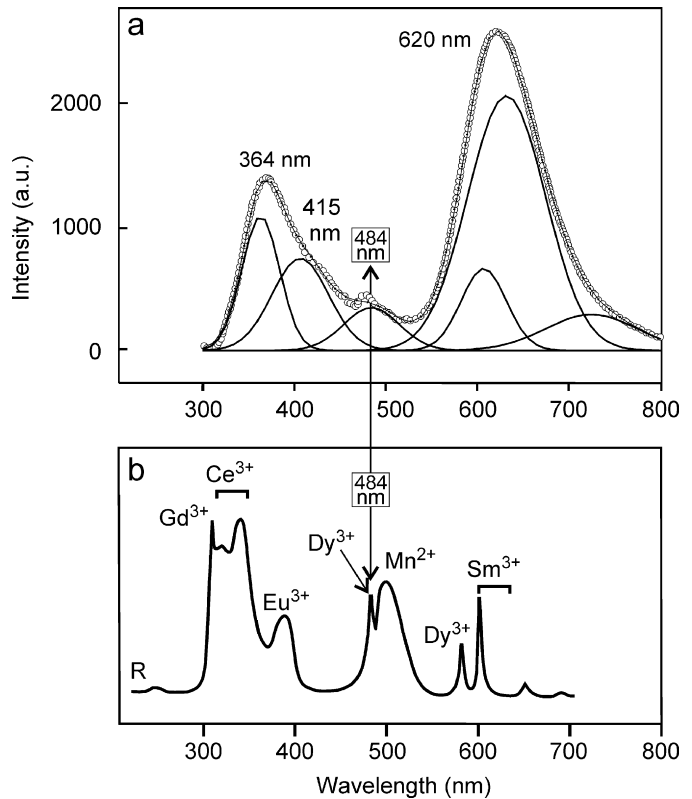


Fig. 4. (a) X-spatially-resolved spectra cathodoluminescence under the scanning electron microscope. (b) For comparison a spectra plot of a CaSO₄ specimen containing several rare elements from Gaft et al. (1984).

of the archaeological project (2006), the mud brick entrance to the open courtyard of Djehuty's tomb (TT11) was discovered, thus exposing the whole court. It is exceptionally large compared to the standard of the period, measuring 34 m long. The courtyard walls are coated with white mortar, which has been preserved in several areas. The crucial question is to explain the origin of this plaster of CaSO₄:Dy phosphor on the walls of the Djehuty's tomb courtyard. Further analyses on additional CaSO₄ plaster micro-samples taken during the sixth work season of the archaeological project (2007) could demonstrate two possible scenarios: (a) an isolated mineralogical chance or, (b) a deliberate constructive treatment.

4. Summary

The XRD and environmental scanning electron microscopy analyses of plasters collected from the courtyard walls of the Djehuty's tomb show anhydrite, calcite, dolomite, quartz, alkali feldspars and accessory amounts of halite, illite and other minerals. The external outer bed is mainly composed by anhydrite, since the original hydrous phases of gypsum and bassanite were desiccated after more than three centuries in the dry land environment of the Luxor area under low relative humidity and high temperature. The luminescence analyses by TL and CL found one plaster sample, i.e., 95% anhydrite displaying a gigantic TL emission of 33 555 a.u. and a SEM/CL emission of

2319 a.u. maxima peaks. The spectra CL also exhibits a clear 484 nm peak attributable to the classic ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition circa 490 nm of Dy^{3+} and the 573 nm Dy^{3+} masked in a broad emission band centered at 620 nm. The common presence of sodium minerals such as halite or albite together with the probable presence of sodium in waters points to Na^+ ions acting as compensators of Dy^{3+} to maintain the electrical neutrality of the $CaSO_4:Dy$ phosphor lattice. Further analyses of more plaster $CaSO_4$ micro-samples could demonstrate if our finding is just an isolated mineralogical chance or an intentional handling.

Acknowledgments

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References

- Barkyoumb, J.H., Mathur, V.K., Lewandowski, A.C., Tookey, A., Townsend, P.D., Giblin, I., 1997. *J. Lumin.* 72–74, 629.
- Bhattacharyya, D., Bakshi, A.K., Ciatto, G., Aquilanti, G., Pradhan, A.S., Pascarelli, S., 2006. *Solid State Commun.* 137, 650.
- Botter-Jensen, L., Duller, G.A.T., Murray, A.S., Banerjee, D., 1999. *Radiat. Prot. Dosim.* 84, 335–340.
- Correcher, V., Delgado, A., 1998. *Radiat. Meas.* 29, 411.
- David, A.R., Edwards, H.G.M., Farwell, D.W., DeFaria, D.L.A., 2001. *Archaeometry* 43, 461.
- Gaft, M.L., Gorobets, B.S., Nikolaeva, E.P., Pankratova, Z.S., 1984. *Proc. All Russ. Mineral. Soc. (Zapiskii)* 3, 332.
- Garcia-Guinea, J., Sanchez-Moral, S., Martin-Ramos, D., Palomo, A., 2001. *ZKG Int.* 54, 404.
- Lakshmanan, A.R., 2001. *Phys. Status Solidi (a)* 186, 153.
- Mulla, M.R., Pawar, S.H., 1984. *J. Lumin.* 31–32, 239.
- Nagashima, S., Kato, M., Kotani, T., Morito, K., Miyazawa, M., Kondo, J., Yoshimura, S., Sasa, Y., Uda, M., 1996. *Nucl. Instrum. Methods Phys. Res. B* 109, 658.
- Noll, W., 1981. *Neues Jahrb. Mineral. Monatsh.* 9, 416.
- Pradhan, A.S., 1993. *Radiat. Prot. Dosim.* 47, 151–154.
- Rinuy, A., 2001. *Chimia* 55, 938.
- Salah, N., Sahar, P.D., Lochab, S.P., Kumar, P., 2006. *Radiat. Meas.* 41, 40.
- Uda, M., 2004. *Nucl. Instrum. Methods Phys. Res. B* 226, 75.