

Determination of manganese in thermoluminescent materials by inductively coupled plasma atomic emission spectrometry and spectrophotometry

Aime Lust^a, Lilli Paama^{a*}, Mihkel Kerikmäe^a, Mare Must^a,
and Paavo Perämäki^b

^a Institute of Chemical Physics, University of Tartu, Jakobi 2, 51014 Tartu, Estonia

^b Department of Chemistry, University of Oulu, FIN- 90401 Oulu, Finland

Received 15 October 2001, in revised form 7 December 2001

Abstract. The content of manganese in the mixed fluorides $\text{CaF}_2:\text{MnF}_2$ and $\text{CaF}_2:\text{Mn}$ thermoluminophors was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and spectrophotometry. The various Mn emission lines were compared and the manganese emission line at 257.610 nm was used for ICP-AES analysis. For the spectrophotometric determination the manganese(II) ions were oxidized to intensively coloured permanganate ions using potassium periodate. No statistically significant differences were found between the results of ICP-AES and spectrophotometric methods of analysis. The thermoluminophors were synthesized by coprecipitation of manganese with CaF_2 , varying the concentration of manganese in the initial solutions in the range of 0.01–2.0% (m/m). The coprecipitated mixed fluorides $\text{CaF}_2:\text{MnF}_2$ were heated at 1423 K. The glow curves of synthesized $\text{CaF}_2:\text{Mn}$ thermoluminophors were measured.

Key words: manganese determination, ICP-AES spectrophotometry, thermoluminophors $\text{CaF}_2:\text{Mn}$, glow curves.

INTRODUCTION

Chemical characterization of advanced materials such as thermoluminophors, semiconductors, and conducting materials requires highly accurate methods for the determination of main and trace elements [1–3]. The large acceptance of

* Corresponding author, lilli@chem.ut.ee

inductively coupled plasma atomic emission spectrometry (ICP-AES) can be explained by some excellent characteristics such as high precision, high sensitivity as well as low limit of detection, a large linear dynamic range, and low matrix effects [4–6].

The thermoluminophor $\text{CaF}_2:\text{Mn}$ is used in environmental dosimetry [7–11]. It is applied in accident dosimetry because of the linear response of the thermoluminescence intensity in the large range of the radiation dose (0.5 mGy to 10^3 Gy) [12–14]. The fading of these thermoluminophors is low due to the relatively deep electron traps of $\text{CaF}_2:\text{Mn}$, and the luminophors are not sensitive to daylight [15, 16]. The thermoluminescence properties of $\text{CaF}_2:\text{Mn}$ thermoluminophor depend mainly on the concentration of manganese.

The content of manganese in the semimagnetic semiconductors, bulk crystals, and epitaxially grown layers was examined by X-ray spectrometry [17]. A simple and fast analytical procedure was proposed for simultaneous spectrophotometric determination of manganese, lanthanum, and holmium in synthetic ceramics by using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) [18]. Small quantities of manganese are readily determined photometrically by the oxidation of Mn(II) to the coloured permanganate ion. Potassium periodate is an effective oxidizing reagent for this purpose and permanganate solutions that contain excess of periodate are quite stable.

In earlier reports we discussed photoluminescence of $\text{CaF}_2:\text{Mn}$ phosphors excited by vacuum ultraviolet (VUV) radiation. Spectra of emission, excitation of steady-state luminescence, and phosphorescence of samples excited by monochromatic VUV radiation with quantum energies up to 14 eV at 293 K and up to 12 eV at 85 K were measured [19]. The conditions of coprecipitation of manganese with CaF_2 and the synthesis of $\text{CaF}_2:\text{Mn}$ thermoluminophor at high temperature were worked out earlier [20, 21].

In the present study the content of the activator (manganese) was determined spectrophotometrically and using the ICP-AES method. The aim of the study reported here was to develop spectrochemical and spectrophotometric methods for the analyses of different powders of $\text{CaF}_2:\text{MnF}_2$ and $\text{CaF}_2:\text{Mn}$ thermoluminophors and to find suitable concentrations of the activator.

EXPERIMENTAL

Instrumentation and operating technique

A sequential PU 7000 Philips (Unicam Analytical Systems, Cambridge, UK) inductive plasma atomic emission spectrometer was used for the measurements. The design of this spectrometer includes a 40.68-MHz free-running oscillator for driving the plasma, an echelle grating for wavelength separation, and a grid nebulizer for sample introduction. The system is equipped with a Gilson 221 autosampler and is controlled by a Philips P3230 computer. The ICP-AES instrumental parameters are summarized in Table 1.

Table 1. Instrumental parameters of ICP-AES

| | |
|--------------------------|------------------|
| Injector tube (quartz) | 1.50 mm i.d. |
| Plasma power | 1.0 kW |
| Coolant argon flow | 13.0 L/min |
| Nebulizer argon pressure | 280 kPa (40 psi) |
| Sample uptake | 1.0 mL/min |
| Sample read delay | 40 s |
| Autosampler wash delay | 20 s |
| Integration time | 3 s |
| Number of integrations | 3 |
| Mn(II) ^a | 257.610 nm |

^a ion line

A spectrometer Lambda 2S Perkin Elmer UV/Vis was used for spectrophotometric measurements.

The glow curves of thermoluminophors were measured by a thermoluminescence reader (TLD reader) UPF-02 (Moscow, Russia).

Reagents and standards

All reagents were of analytical grade (Merck). The sulphuric, nitric, and hydrochloric acids were ultrapure (Merck). Deionized water (18 M Ω /cm) was used for the preparation of the solutions for ICP-AES analysis.

The stock solution, containing 1000 mg/L of manganese, was prepared from MnSO₄ · 5H₂O (anal. gr., Merck). The working standard solutions for ICP-AES were obtained by serial dilution of stock solution with deionized water (18 M Ω /cm). The concentrated HNO₃ (5% v/v) and concentrated H₂SO₄ (2% v/v) were added to the working standard solutions.

The calibration standards for spectrophotometric determination were prepared by serial dilution of the stock solution with deionized water. Six standard solutions in the range of 0.01–0.25 mg manganese in 50 mL were prepared for spectrophotometric measurements.

Samples, their decomposition and procedures

The powders of CaF₂: MnF₂ were synthesized by coprecipitation using CaCl₂, HF, and MnCl₂ solutions. The MnCl₂ was added into solution of CaCl₂ and the excess of fluoride ions was used. The heating of powders was carried out at 1323 K during 30 min in special quartz apparatus in the argon atmosphere [20, 21].

The samples (0.05–0.06 ± 0.0002 g) were weighed into a fluoroplastic crucible and 5 mL concentrated H₂SO₄ (Suprapur, Merck) was added. The samples were heated until HF vapours separated. For ICP-AES analysis 5 mL HNO₃ (65% v/v, Suprapur, Merck) was added. The solution was allowed to cool and then transferred into a 100 mL calibrated flask and coupled to volume with deionized water.

For spectrophotometric analysis the samples (after heating with concentrated H₂SO₄ on a hot plate) were transferred into a 100 mL baker. Then 14 mL of concentrated H₂SO₄ was added, diluted to 70 mL, and heated to dissolve the precipitate. After cooling the solution was transferred into a 100 mL calibrated flask and coupled to volume 100 mL with deionized water. For oxidation of manganese(II) to permanganate ions 25 mL aliquot part of sample solution was transferred into a 100 mL baker, 25 mL H₃PO₄ (85% v/v) and 1 g KJO₄ were added. The solution was heated to boiling and kept at 95 °C during 15 min. The solution was allowed to cool and transferred into a 50 mL calibrated flask and coupled to volume with deionized water. The absorbance of the solutions was measured at 545 nm to blank solution.

RESULTS AND DISCUSSION

Spectral lines for ICP-AES measurements were selected on the basis of minimum spectral line interferences and maximum sensitivity. Three emission lines Mn(II) at 257.610 nm, Mn(II) at 259.373 nm, and Mn(II) at 293.306 nm were compared. The Mn emission line Mn(II) at 257.610 nm was found to be the most suitable for source peaking (to find an optimum viewing position in the ICP discharge) and the detection limits (3 s of the blank prepared as samples) were all in the 0.007–0.01 mg/L range (Table 2). The concentration of Ca in the analysed solution can affect the determination of Mn by ICP-AES. The matrix effects due to calcium were tested by measuring analyte intensities of 1.0 mg/L of manganese in solutions containing 500 mg/L of calcium. The actual concentration of Ca in the decomposed samples was about 200–300 mg/L. The influence of calcium matrix on the Mn emission signal at 257.610 nm was <1%. The precision of determination (RSD) ranged from 0.5% to 0.9% (Table 2). On the basis of optimized experimental conditions the Mn(II) emission line at 257.610 nm was selected for the spectrochemical determination of manganese in the samples of thermoluminescence materials. The following five manganese calibration standards were used: 0.05, 0.1, 1.0, 5.0, 10.0 mg/L. A scan of the

Table 2. Wavelength, excitation potentials (EP), ionization potential (IP), and detection limits (DL) of determination of Mn in solutions containing 1.0 mg/L manganese and 500 mg/L calcium

| Manganese line | Wavelength, nm | EP, eV | IP ^a + EP, eV | DL, mg/L | Found ^b , mg/L | |
|---------------------|----------------|--------|--------------------------|----------|---------------------------|--------|
| | | | | | $\bar{c} \pm s$ | RSD, % |
| Mn(II) ^c | 257.610 | 4.813 | 12.248 | 0.007 | 0.994 ± 0.0054 | 0.54 |
| Mn(II) | 259.373 | 4.784 | 12.222 | 0.009 | 0.983 ± 0.0076 | 0.77 |
| Mn(II) | 293.306 | 4.228 | 11.663 | 0.010 | 1.052 ± 0.0096 | 0.92 |

^a IP Mn(II) = 7.435

^b four replicates

^c ion line

measurement lines showed neither background shifts nor sloped background, and therefore it was not necessary to introduce background correction (Fig. 1).

The results of analysis of laboratory synthesized powders of $\text{CaF}_2:\text{MnF}_2$ and $\text{CaF}_2:\text{Mn}$ thermoluminophors by ICP-AES and spectrophotometry are shown in Table 3. Statistical tests applied (*t*-test, *F*-test) showed no significant differences between the results of ICP-AES and spectrophotometric analysis [22]. The RSD ranged from 0.63% to 1.0% for ICP-AES and from 0.96% to 2.3% for the spectrophotometric method.

Luminescence properties of thermoluminophors are determined by their glow curves. The glow curves measured by a TLD reader UPF-02 with rising the temperature 2°C/s are shown in Fig. 2. The shape of the glow curves, the temperature, and the intensity of the thermoluminescence peak depend mainly on the concentration of manganese in luminophors and the heating conditions. The increasing of the concentration of manganese reduces the intensity of the low-temperature thermoluminescence peak and increases the intensity of the high-temperature thermoluminescence peak. The most suitable concentration of the activator in the thermoluminophors seems to be in the range of 1.5–2.0% m/m. These thermoluminophors and detectors have only one thermoluminescence peak at 290°C . A higher concentration than 2.0% m/m is not recommended because of oxidation of Mn(II) in the case of reuse of detectors. These detectors are not sensitive to visible light and the fading is also very low because no low-temperature thermoluminescence peaks occur and the maximum of the high-

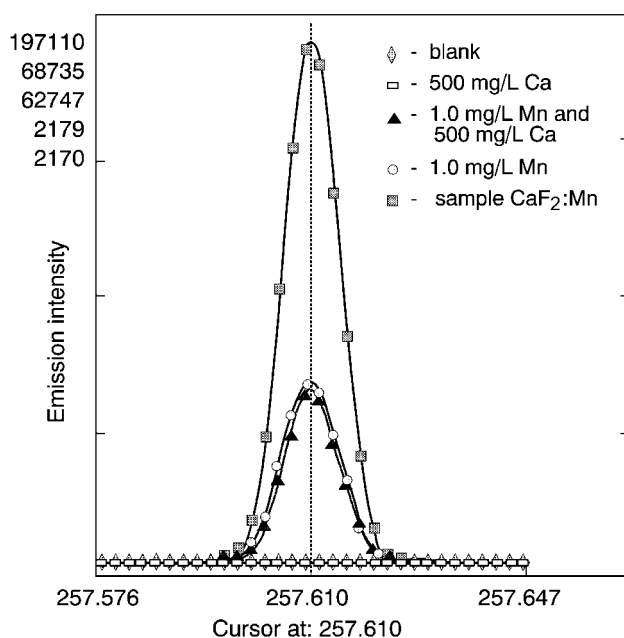


Fig. 1. Scan of manganese line Mn(II) at 257.610 nm.

Table 3. Results of ICP-AES and spectrophotometric analyses of powder of CaF₂: MnF₂ and CaF₂: Mn thermoluminophor (four replicates) with precision of determination (RSD)

| Sample | Mn, % (m/m) | | | | |
|---|----------------------|-----------------|--------|-------------------|--------|
| | In initial solutions | ICP-AES | | Spectrophotometry | |
| | | $\bar{c} \pm s$ | RSD, % | $\bar{c} \pm s$ | RSD, % |
| CaF₂: MnF₂ | | | | | |
| 1 | 0.01 | 0.12 ± 0.0012 | 1.00 | 0.10 ± 0.0018 | 1.8 |
| 2 | 0.05 | 0.27 ± 0.0026 | 0.98 | 0.28 ± 0.0027 | 0.96 |
| 3 | 0.1 | 0.51 ± 0.0049 | 0.96 | 0.49 ± 0.0098 | 2.0 |
| 4 | 0.2 | 0.62 ± 0.0055 | 0.88 | 0.59 ± 0.012 | 2.0 |
| 5 | 0.4 | 1.49 ± 0.0044 | 0.90 | 1.54 ± 0.028 | 1.8 |
| 6 | 0.8 | 2.20 ± 0.0094 | 0.63 | 2.12 ± 0.044 | 2.1 |
| 7 | 1.0 | 2.53 ± 0.017 | 0.69 | 2.50 ± 0.048 | 1.92 |
| 8 | 1.2 | 2.39 ± 0.019 | 0.80 | 2.46 ± 0.042 | 1.71 |
| 9 | 1.6 | 1.63 ± 0.011 | 0.65 | 1.55 ± 0.029 | 1.87 |
| 10 | 2.0 | 1.78 ± 0.016 | 0.65 | 1.73 ± 0.04 | 2.3 |
| CaF₂: Mn | | | | | |
| 1 | 0.1 | 0.58 ± 0.0042 | 0.72 | 0.62 ± 0.014 | 2.2 |
| 2 | 0.2 | 0.68 ± 0.0051 | 0.76 | 0.73 ± 0.013 | 1.7 |
| 3 | 0.4 | 1.46 ± 0.010 | 0.68 | 1.44 ± 0.028 | 1.9 |
| 4 | 0.8 | 1.66 ± 0.012 | 0.70 | 1.56 ± 0.031 | 2.0 |

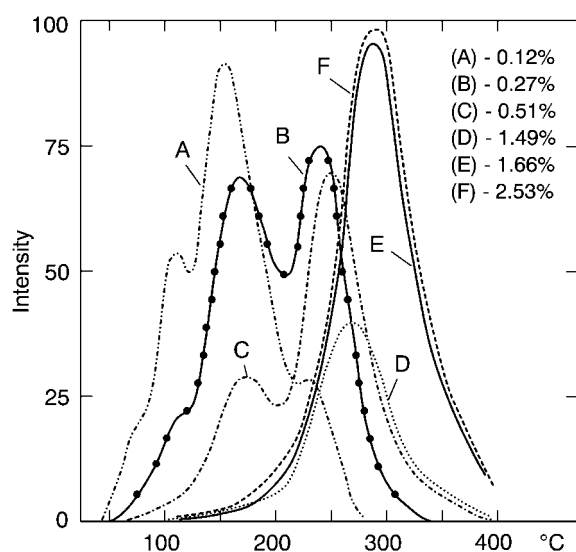


Fig. 2. Effects of the concentration of manganese on the intensity of glow curves. A–F, concentration of Mn (% m/m) in synthesized powders CaF₂: MnF₂.

temperature thermoluminescence peak is at quite a high temperature (290 °C). The response of thermoluminescence intensity is linear up to 10³ Gy and the sensitivity of the detectors does not change after radiation with high doses.

Therefore they are suitable as extreme detectors. These detectors may be reused many times (up to 50) and all measurements may be carried out in air.

CONCLUSIONS

The ICP-AES method is rapid and simple when compared to the spectrophotometric method, which is more complicated and time consuming. The manganese content has significant effects on the thermoluminescence properties of $\text{CaF}_2:\text{Mn}$ thermoluminophors. Thermoluminophors containing 1.7–2.0% (m/m) of manganese are the most suitable materials for the preparation of thermoluminescence detectors.

ACKNOWLEDGEMENTS

Financial support from the Estonian Science Foundation (grants Nos. 4587 and 3371) and Estonian Innovation Foundation (contract 29 it/97) is gratefully acknowledged. Thanks are due to Professor Risto Laitinen, University of Oulu, for the instrumental facilities that were used in this study.

REFERENCES

1. Fairman, B., Hinds, M. W., Nelms, S. M., Penny, D. M. & Goodall, P. Atomic spectrometry update – industrial analysis: metals, chemicals and advanced materials. *J. Anal. At. Spectrom.*, 1998, **13**, 233–266.
2. Fairman, B., Hinds, M. W., Nelms, S. M., Penny, D. M. & Goodall, P. Atomic spectrometry update – industrial analysis: metals, chemicals and advanced materials. *J. Anal. At. Spectrom.*, 1999, **14**, 1937–1969.
3. Gupta, R. K., Al-Ammar, A. & Barnes, R. M. Sample standard interaction during trace analysis of semiconductorgrade trimethylindium by inductively coupled plasma emission spectrometry. *J. Anal. At. Spectrom.*, 1999, **14**, 839–844.
4. Nickel, H. & Broekaert, J. A. C. Some topical applications of plasma atomic spectrochemical methods for the analysis of ceramic powders. *Fresenius' J. Anal. Chem.*, 1999, **363**, 145–155.
5. Paama, L., Pärnoja, E. & Perämäki, P. Trace element analysis of superconductor oxides by ICP-AES. *J. Anal. At. Spectrom.*, 2000, **15**, 571–572.
6. Paama, L., Perämäki, P. & Lajunen, L. H. J. Analysis of superconductor oxides $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ by inductively coupled plasma atomic emission spectrometry and complexometric titration. *Anal. Chim. Acta*, 1996, **330**, 259–263.
7. Zarate-Morales, A. & Buentil, A. E. Environmental gamma dose measurements in Mexico City using TLD. *Health Phys.*, 1996, **71**, 358–361.
8. Vehl, D. L., Muron, D. I., Suijka, R. R., Vehar, D. W., Lorence, L. I., Westfall, R. L., Jones, S. C., Sweet, I. A. & Braunlich, P. Characterization of a two-dimensional thermoluminescent, dose-mapping system: uniformity, reproducibility and calibrations. *Rev. Sci. Instrum.*, 1994, **65**, 3243–3251.
9. Nicolae, M. & Lazar, M. Thermoluminescent dosimeter for monitoring of the environment around nuclear power plants. *Rev. Roum. Phys.*, 1985, **30**, 207.

10. Environmental Radiation Data. Report 75, July–September 1993, United States Environmental Protection Agency, Office of Radiation and Indoor Air. <http://www.epa.gov/narel/erd75g.htm>.
11. Miller, S. D. Environmental Radiation Detection via Thermoluminescence. PCT WO94/15227 (1994).
12. Schulman, J. R., Ginther, R. F., Kirk, K. D. & Goulart, H. S. Thermoluminescent dosimeter. Storage. Stability. Linearity. *Nucleonics*, 1960, **18**, 92–102.
13. Puute, K. J. & Arends, J. Trapping centers in CaF₂: Mn from thermoluminescence and thermally stimulated exoelectron emission measurements on undoped CaF₂ samples. In *Proceedings of the III International Conference on Luminescence Dosimetry, Resö Rept.*, 1971, **249**, 680.
14. Prokert, K. & Sommer, M. A new hypersensitive thermoluminophor based on the CaF₂. *Radiat. Prot. Dosim.*, 1998, **78**, 249–252.
15. Chakrabarti, K., Sharma, J. & Mathur, V. K. Laser bleaching of deep traps and reduction of zero dose problem in CaF₂: Mn dosimeters. *Radiat. Prot. Dosim.*, 1993, **47**, 155–158.
16. Miller, S. D., McDonald, J. C., Eichner, F. N. & Tomeraasen, P. L. System for Use with Solid State Dosimeter. US Patent No 4954707 (1990).
17. Lawniczak-Jablonska, K., Kachniarz, J., Spolnik, Z., Libera, J., Dynowska, E., Nadoln, A. & Sadowski, J. The use of Mn L α line chemical effects in X-ray analysis to probe sample homogeneity. *J. Anal. At. Spectrom.*, 1999, **14**, 461–464.
18. Ferreyra, R. E., Camina, J. M., Marchevsky, E. & Luco, J. M. Simultaneous spectrophotometric determination of La, Ho, Mn 5-Br-PADAP complexes using multivariate calibration with partial least-squares (PLS) data evaluation. *Fresenius' J. Anal. Chem.*, 2000, **368**, 595–600.
19. Denks, V. P., Kerikmyae, M. P., Lust, A. L. & Savikhina, T. I. Photoluminescence of concentration series of CaF₂: Mn phosphors excited by VUV radiation. *Phys. Solid State*, 2000, **42**, 261–270.
20. Allsalu, M.-L., Kilk, I., Kuus, H., Lust, A. & Pedak, E. Method of Preparation of Thermoluminophor CaF₂, Activated with Manganese. Author's Certificate SU No 749095 (1980) (in Russian).
21. Lust, A. CaF₂: Mn termoluminofoori ja detektorite sünteesimeetodika. M.Sc. thesis, University of Tartu, Estonia, 1996.
22. Miller, J. C. & Miller, J. N. *Statistics for Analytical Chemistry*. Ellis Horwood, UK, 1984.

Mangaani määramine termoluminestsentsmaterjalides induktiivse plasma aatomiemissioonspektromeetrilisel ja spektrofotomeetrilisel meetodil

Aime Lust, Lilli Paama, Mihkel Kerikmäe, Mare Must ja Paavo Perämäki

Mangaani sisaldus fluoriidide CaF₂: MnF₂ segus ja CaF₂: Mn termoluminofoorides määrati induktiivse plasma aatomiemissioonspektromeetria (ICP-AES) ja spektrofotomeetria meetodil. Võrreldi erinevaid mangaani emissioonijooni ja ICP-AES analüüs tehti kasutades emissioonijooni 257,610 nm juures. Spektrofotomeetrilise analüüsi puhul oksüdeeriti Mn(II)-ioonid permanganaatioonideks kaaliumperjodaadi abil. Olulisi erinevusi kahel meetodil saadud tulemuste vahel ei täheldatud. Termoluminofoorid sünteesiti mangaani kaasasadamisel CaF₂-ga, varieerides Mn kontsentratsiooni vahemikus 0,01–2,0% (m/m). Kaasasades-tatud fluoriidide segu kuumutati 1423 K juures inertse gaasi atmosfääris. Sünteesitud termoluminofooridel mõõdeti ka termovälja kiirguskõverad.