

# APPLICATION OF CALCIUM ALUMINATE DOPED WITH Mn AND Cr IN OPTICAL THERMOMETRY

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Optical thermometers are advantageous for temperature measurement in electromagnetic fields and aggressive environments; however, their composition mostly relies on materials doped with expensive and resource-limited rare earth ions.

In this article, we describe the application of calcium aluminate doped with transition metal ions ( $Mn^{2+}$  and  $Cr^{3+}$ ) in optical thermometry, employing optical fibres for signal transmission. Upon excitation with 450 nm laser diode radiation, changes in the luminescence of  $Mn^{2+}$  ions in the 500–550 nm band are followed along with changes in the  $Cr^{3+}$  band at 750–800 nm.

The application has been tested in the temperature range from 20 °C to 800 °C. The temperature dependence of  $Cr^{3+}$  luminescence encompasses the high-temperature range, whereas the luminescence band of  $Mn^{2+}$  ions gives an increase in the total intensity and provides a more consistent change in the range from 400 °C to 550 °C.

**Keywords:** Calcium aluminate, electron paramagnetic resonance (EPR),  $Mn^{2+}$  and  $Cr^{3+}$  ions, luminescence, optical thermometry.

## 1. INTRODUCTION

Temperature sensors (thermometers) are widely used in science, industry and everyday life [1]. Physical phenomena used in thermometers are related to thermal expansion, thermoelectric effects (thermocouples) and changes in optical signals due

to temperature [1], [2]. Thermal expansion thermometers often have difficulty with electrical readings of temperature. Thermocouples have a broad range of applications, but face limitations in aggressive environments and electromagnetic fields. In con-

trast, optical temperature sensors are the most suitable for operation in electromagnetic fields and aggressive environments.

Optical temperature sensors process the optical signal of absorption, reflection, Rayleigh or Raman scattering, or luminescence [2]. Luminescent temperature sensors can use luminescence intensity or band parameters, decay time, or luminescence polarization [3]. Among these, sensors using changes in the luminescence signal and decay times are the most popular. There is a widespread method of determining the relative intensity ratio of luminescence (fluorescence) bands (fluorescence intensity ratio – FIR, also luminescence intensity ratio – LIR) depending on temperature [4]–[6]. So far, the applicability of rare earth elements for optical temperature detection has been widely studied [4], [5], [7], [8]. The luminescence spectra of rare earth ions are characterised by a wide distribution of bands in the ranges of ultraviolet radiation, visible light, and infrared radiation.

## 2. EXPERIMENTAL

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**A. Samples.** Polycrystalline hexaaluminate  $\text{CaA}_{12}\text{O}_{19}$  samples doped with 5 mol% of  $\text{Mn}^{2+}$  ( $\text{CA}_6\text{:Mn}$ ) and 2 mol% of  $\text{Cr}^{3+}$  ( $\text{CA}_6\text{:Cr}$ ) were produced using the high temperature solid state synthesis method. Stoichiometric amounts of  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}_2$ , and  $\text{Cr}_2\text{O}_3$  were mixed in agate mortar. Obtained homogeneous mixtures were heat treated at high temperature: 1500 °C in air for the  $\text{Cr}^{3+}$  doped sample and 1300 °C in reducing atmosphere for the  $\text{Mn}^{2+}$  doped sample until the reaction was completed. A mixture of polycrystalline  $\text{CA}_6\text{:Mn}$  and  $\text{CA}_6\text{:Cr}$  was pelletized with the 2:1 ratio to obtain the material for optical temperature sensing.

**B. EPR measurements.** The Bruker

Transition metal ions are less used in optical temperature sensors, and the range of their application temperatures discussed in the literature is not so wide, especially for applications in the highest temperature range from 400 up to 800 °C [4], [7], [8]. The most suitable transition metals in optical temperature sensor materials are Mn and Cr [4], [7], [8], constituting approximately 96 % of all proposed transition metal activators [3]. The use of transition metal activators in the sensor makes it possible to abandon the use of expensive and resource-limited rare earth ions. The use of  $\text{Mn}^{2+}$  ions in luminescence thermometry has been described for temperatures up to 400 °C, and  $\text{Cr}^{3+}$  ions – for temperatures up to 500 °C [4], [7].

In this study, we present a combination of  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  in calcium aluminate, which enables us to achieve changes in the total intensity of luminescence of the material in the temperature range of 20–800 °C.

ELEXSYS-II E500 CW-EPR spectrometer was used for EPR spectra measurements at room temperature. Powdered  $\text{CA}_6\text{:Mn}$  and/or  $\text{CA}_6\text{:Cr}$  samples were filled into EPR tubes with an outer diameter of 5 mm. Magnetic field modulation parameters were 100 kHz and 0.2 mT, while microwaves were generated at 9.835 GHz frequency and 10 mW power. Normalisation of signal intensities to sample mass was performed for a relative comparison of the paramagnetic ion concentration.

**B. Luminescence measurements.** The emission and excitation spectra of polycrystalline samples at room temperature were obtained using an FLS1000 spectrometer manufactured by Edinburgh Instruments

(model: FLS1000-DD-stm). The spectrometer was equipped with a CW 450 W Xenon lamp (model: Xe2) and a red photomultiplier tube (model: R928P, cooled for better detection). The spectra were corrected to the instrumental response.

**D. Optical fibres and temperature dependence.** The temperature dependence measurements were carried out using an Andor SR-303i-B spectrometer with DU401-BV CCD camera to measure spectra in the range from 430 to 1000 nm. Excitation was performed using a 450 nm laser diode with a power of 1.0 W. To filter out the

excitation light, a 500 nm long-pass filter from Thorlabs was employed. Temperature was stabilized using the LUMEL RE19 PID controller. The temperature dependence was investigated in 50 °C increments, starting from room temperature up to 850 °C. Both excitation and luminescence light were transmitted through an appropriate light guide bundle manufactured by Light Guide Optics International Ltd in Latvia. To obtain integral intensities, 50 nm wide ranges were selected, centred at 525 nm for the green band and 775 nm for the red band.

### 3. RESULTS AND DISCUSSION

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The incorporation of  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  activators in the  $\text{CA}_6$  lattice is confirmed by the EPR spectra presented in Fig. 1. Due to the differences in electronic configurations, each transition metal ion exhibits a distinct EPR signal.  $\text{Cr}^{3+}$  is a  $d^3$  electronic configuration ion with three unpaired electrons, which gives rise to the zero-field splitting of the ground state and the emergence of EPR spectra fine structure. In  $\text{CA}_6:\text{Cr}^{3+}$ , we observe a signal at 355 mT, low field structure in the range of 100–230 mT and several resonances in the high field region, which is in line with the previous investigation of the host [9]. As a result, multi-site incorporation of  $\text{Cr}^{3+}$  ions in the  $\text{CA}_6$  lattice can be implied. Analysis of the Mn-doped samples is more challenging as the activators can have both  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  oxidation states each with unique magnetic and optical characteristics [10]. Moreover, hyperfine structure due to electronic spin interaction with the 100 % abundant nuclear spin of  $^{55}\text{Mn}$  nucleus typically complicates and broadens EPR spectra. However, considering the number of fine structure components in the EPR spectrum and the reducing syn-

thesis conditions of the Mn-doped sample, the dominant contribution can be attributed to  $\text{Mn}^{2+}$  centres. It is noteworthy to highlight that the EPR spectrum of  $\text{CA}_6:\text{Mn}^{2+}$  notably differs from that of  $\text{CA}_6:\text{Mn}^{2+}$  [11], implying variations in the local structure of  $\text{Mn}^{2+}$  ions in the two materials, which are also reflected in the luminescence spectra. Finally, the determined relative weights of  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  EPR signals of 1.94:1.00 in the mixed  $\text{CA}_6$  material are consistent with the intended 2:1 ratio.

For use in an optical temperature sensor, we investigated the luminescence properties of  $\text{CA}_6$  poly-crystals doped by  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  ions. Figure 2 shows the luminescence spectra of  $\text{CA}_6$  polycrystalline samples doped by  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  ions, excited by 450 nm Xe lamp excitation. A luminescence band of  $\text{Mn}^{2+}$  ions is observed in the 500–550 nm spectral range, with the maximal intensity at 518 nm (Fig. 2(a-b)). The observed green luminescence band occurs due to the transition  ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$  of  $\text{Mn}^{2+}$  ions in the  $\text{CA}_6$  structure [12], [13]. The valence of manganese ions in the  $\text{CA}_6$  can be controlled with the preparation con-

ditions. The reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{2+}$  ions in  $\text{CA}_6$  is promoted by using a reducing atmosphere during the sample synthesis [12]. In the red and near-infrared spectral range, luminescence bands of  $\text{Cr}^{3+}$  ions have been observed (Fig. 2(a-b)). The narrow luminescence band at 689 nm with the phonon side-bands in the 660–730 nm range is attributed to the  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  transition of  $\text{Cr}^{3+}$  ions (spin-forbidden transition), and the

broad luminescence band in the 750–850 nm range is assigned to the  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  transition (spin-allowed transition) [14]. The two  $\text{Cr}^{3+}$  luminescence bands arise from the incorporation of  $\text{Cr}^{3+}$  ions in several non-equivalent sites in the  $\text{CA}_6$  structure, possessing different coordination environments and crystal field strengths affecting the luminescence properties of  $\text{Cr}^{3+}$  ions [14].

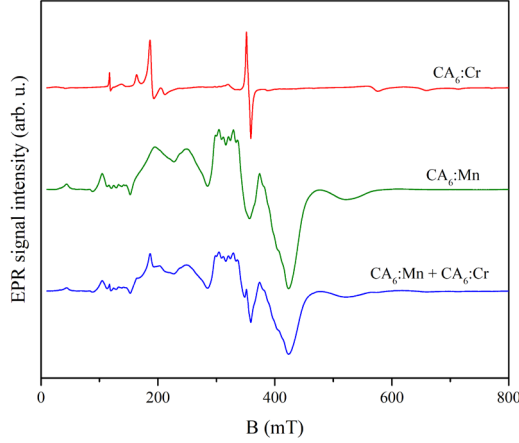


Fig. 1. EPR spectra of the investigated  $\text{CA}_6$  samples.

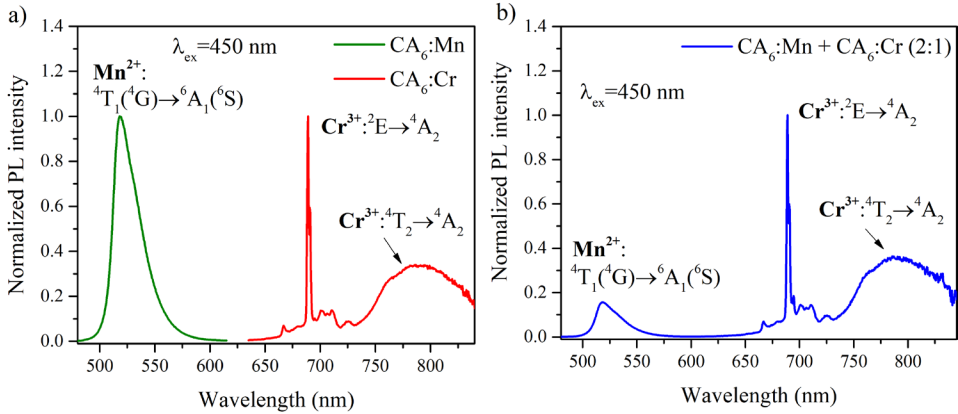


Fig. 2. The luminescence spectra of  $\text{Mn}^{2+}$ - and  $\text{Cr}^{3+}$ -doped  $\text{CA}_6$  powders with 450 nm excitation. a)  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  singly-doped samples, b)  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  doubly-doped sample.

The luminescence excitation spectra of  $\text{Mn}^{2+}$  (at 518 nm) and  $\text{Cr}^{3+}$  (at 760 nm) ions depicted in Fig. 3 show that 450 nm is suitable for the excitation of both  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  ions. The  $\text{Cr}^{3+}$  excitation bands of 760 nm emission are assigned to

${}^4\text{A}_2 \rightarrow {}^4\text{T}_1({}^4\text{P})$  (225–300 nm),  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1({}^4\text{F})$  (330–490 nm), and  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2({}^4\text{F})$  (490–650 nm) with the maximal excitation intensity around 390 nm ( ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1({}^4\text{F})$ ) [14]. The excitation spectrum of  $\text{Mn}^{2+}$  ions ( $\lambda_{\text{em}} = 518$  nm) consists of relatively narrower bands

at 358 nm ( ${}^6A_1({}^6S) \rightarrow {}^4E_g({}^4D)$ ), 386 nm ( ${}^6A_1({}^6S) \rightarrow {}^4T_{2g}({}^4D)$ ), 426 nm ( ${}^6A_1({}^6S) \rightarrow {}^4A_{1g}({}^4G)$ ), and 450 nm ( ${}^6A_1({}^6S) \rightarrow {}^4T_2({}^4G)$ )

[13]. Thus, Fig. 3 shows that 450 nm radiation overlaps with the most intense excitation bands of  $Cr^{3+}$  and  $Mn^{2+}$  ions in  $CA_6$ .

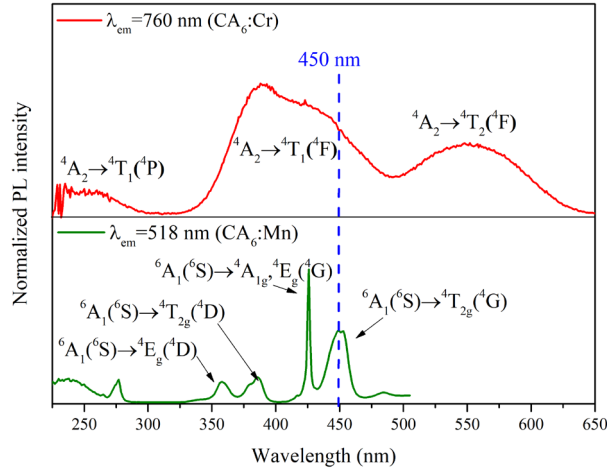


Fig. 3. Luminescence excitation spectra of  $Cr^{3+}$  ( $\lambda_{em}=760$  nm) and  $Mn^{2+}$  ( $\lambda_{em}=518$  nm) ions in  $CA_6$  powders.

To obtain temperature dependences of luminescence, we chose 450 nm as the optimal excitation wavelength, using which luminescence of both  $Mn^{2+}$  and  $Cr^{3+}$  centres is excited at comparable intensities. As a result of the experiments, it was determined that 450 nm excitation provides the most monotonous temperature dependence of the total  $Mn^{2+}$  (500 – 550 nm) and  $Cr^{3+}$  (750–

800 nm) luminescence in the entire studied temperature range from 20 °C to 800 °C (see Fig. 4). The temperature dependence of the  $Cr^{3+}$  ion covers the high temperature range, while the  $Mn^{2+}$  ion luminescence band gives an increase in the total intensity and provides a more uniform change in the range from 400 °C to 550 °C.

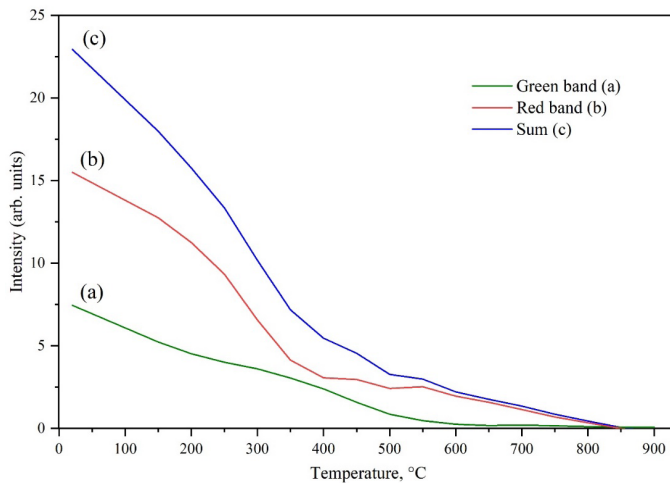


Fig. 4. Temperature dependence of the luminescence intensities of  $CA_6:Mn + Cr$  sample: a)  $Mn^{2+}$  luminescence (Green band, 500–550 nm), b)  $Cr^{3+}$  luminescence (Red band, 750–800 nm), c)  $Mn^{2+}$  luminescence +  $Cr^{3+}$  luminescence (Sum).

For optimal input and transmission of luminescence excitation radiation (450 nm) and emission bands of  $\text{Mn}^{2+}$  (green) and  $\text{Cr}^{3+}$  (red), we suggest using the scheme shown in Fig. 5. The optical bundle is made of 100  $\mu\text{m}$  fused silica fibres with fluorine doped fused silica cladding. Polyimide coat-

ing withstand temperatures up to 385 °C, but since the optical bundle end is not in a direct contact with hot surface, it can be used to measure temperatures up to 800 °C. The sample holding probe (Fig. 5, part No. 5) is made of stainless steel with calcium aluminate phosphor containing capsule.

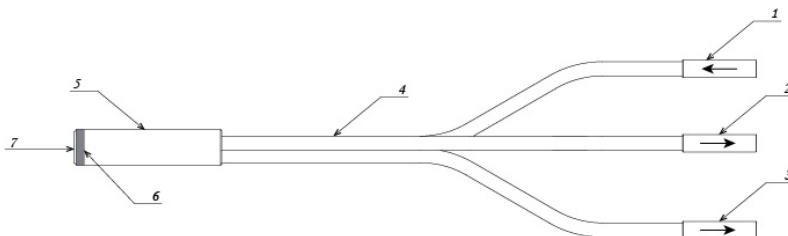


Fig. 5. The operating principle of the optical temperature sensor, using optical fibres to transmit light: 1) exciting light input – 450 nm laser diode, 2) filtered green light (500-550 nm) output, 3) filtered red light (750–800 nm) output, 4) optical fibre bundle, 5) temperature measuring probe body, 6) phosphor in the form of a tablet made from with  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  of doped calcium aluminate material, 7) temperature measurement point.

The thermal resistance of the active end of the temperature sensor design must also reach the mentioned 800 °C. In the temper-

ature range above 600 °C, light modulation and a lock-in detector can be used to separate the thermal radiation background.

## 4. CONCLUSIONS

The application of  $\text{CA}_6$  material doped with Mn and Cr in optical thermometry was investigated. The incorporation of  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  ions in  $\text{CA}_6$  was confirmed by EPR and luminescence spectroscopy techniques. In the Mn-doped material, a single luminescence band at 518 nm was detected, whereas the luminescence spectrum of the Cr-doped sample comprised of overlapping  $\text{Cr}^{3+}$  signals in the 660–850 nm range. An

excitation wavelength of 450 nm provided optimal results for simultaneous luminescence excitation in the mixed Mn- and Cr-doped  $\text{CA}_6$  material. Using a specially designed optical fibre bundle and filtering  $\text{Mn}^{2+}$  (500–550 nm) and  $\text{Cr}^{3+}$  (750–800 nm) luminescence signals, a proof-of-concept optical temperature sensor was successfully demonstrated, operating within a temperature range of 20–800 °C.

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