

SOL-GEL-DERIVED THIN CERAMIC CoAl_2O_4 COATINGS FOR OPTICAL APPLICATIONS

TANKE KERAMIČNE OPTIČNOSELEKTIVNE PREVLEKE CoAl_2O_4 , PRIPRAVLJENE PO POSTOPKU SOL-GEL

Urška Lavrenčič Štangar¹, Boris Orel¹, Matjaž Krajnc², Romana Cerc Korošec²,
Peter Bukovec²

¹National Institute of Chemistry, Laboratory for Spectroscopy of Materials, Hajdrihova 19, 1000 Ljubljana, Slovenia

²University of Ljubljana, Faculty for Chemistry and Chemical Technology, Aškerčeva 5, 1000 Ljubljana, Slovenia
boris.orel@ki.si

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Optically selective thin films of CoAl_2O_4 with a spinel structure were produced for an automotive-lamps application via the sol-gel process using aluminum *sec*-butoxide, ethylacetoacetate chelating agent, cobalt nitrate hexahydrate and iso-propanol solvent. Dip-coated films annealed at 700 °C showed a characteristic bright blue color, providing that the cobalt-to-aluminum molar ratio in the precursor solution was decreased from 0.5 to 0.3. IR studies supported by thermal analysis and UV-VIS spectroscopy revealed the formation of a Co/Al-oxide solid solution below 600 °C, while above this temperature the spinel CoAl_2O_4 phase was formed.

Key words: blue CoAl_2O_4 coatings, optical thin solid films, sol-gel processing

Optičnoselektivne tanke prevleke CoAl_2O_4 za uporabo na halogenskih avtomobilskih žarnicah smo pripravili po postopku sol-gel iz aluminijevega *s*-butoksida, etilacetoacetata (zaradi sposobnosti kelatiranja aluminija ima vlogo stabilizatorja sola), kobaltovega nitrata heksahidrata in izopropanola kot topila. Prevleke, ki so bile žgane v peči pri 700 °C, so pridobile značilno svetlo modro obarvanje, če smo molsko razmerje kobalta proti aluminiju v izhodni raztopini znižali od nominalne vrednosti 0,5 na 0,3. IR spektroskopska analiza, podprta s termično analizo in UV-VIS spektroskopijo, je pokazala na tvorbo Co/Al-oksidge trdne raztopine pri žganju vzorcev pod 600 °C, medtem ko je nad to temperaturo že prišlo do pretvorbe v špinelno fazo CoAl_2O_4 .

Ključne besede: modre prevleke CoAl_2O_4 , optičnoselektivne tanke plasti, postopek sol-gel

1 INTRODUCTION

CoAl_2O_4 , the ceramic pigment known as Thénard's blue, has been known since ancient times, and has often attracted the interest of researchers ¹. Cobalt aluminates are also important materials for heterogeneous catalysis in areas such as the CO_2 reforming of methane ². In thin-film form, cobalt aluminates recently became interesting as a light filter for automotive lamps. Lamps with tungsten wire emit a yellowish light because the intensity of the emitted light peaks in the near-IR range (~1 μm) due to the relatively low temperature of the tungsten filament. To increase the visibility of vehicles it would be better if the emitted light exhibited a spectral distribution which resembles that of daylight. One way to achieve this is to block selectively, at least in part, the long wavelength radiation which is emitted from the hot tungsten wire. CoAl_2O_4 is quite suitable for this purpose because it exhibits a characteristic absorption in the 500-600-nm range, which gives the coating its typical bright blue color (royal blue). Consequently, the color temperature of the wire is shifted to higher temperatures, and the emitted light resembles daylight to the human eye.

Different chemical processing methods are used for the preparation of CoAl_2O_4 pigments. All of them

involve relatively high processing temperatures above 1000 °C ³⁻⁵. Temperatures this high are impractical for the deposition of CoAl_2O_4 in thin-film form onto automotive lamps, even though the lamp bodies are made from quartz. Severe oxidation of the metal contacts was often noted, and so lower processing temperatures are very much in demand. Sol-gel processing can offer an advantage for making materials at lower temperatures because precursors are mixed in the right proportion at the very beginning of the process, i.e. in solution. Zayat and Levy ⁶ reported on CoAl_2O_4 powders made in the temperature range 600-1000 °C. The blue color starts to develop at 600 °C, but more than 700 °C is needed to attain the bright blue color typical for the Thénard blue pigment.

While Al-alkoxide seems to be one of the most effective precursors for obtaining CoAl_2O_4 in combination with Co-salts ², CoAl_2O_4 powders were also made from sols obtained with the peptization of boehmite combined with Co-chloride ⁷ or Co-acetate ⁸. A more advanced synthesis based on bimetallic (Co/Al) alkoxide was also reported, but the temperatures needed to obtain the blue spinel phase are still over 800 °C ⁹. Highly porous CoAl_2O_4 powders were also synthesized from bimetallic alkoxide precursors (230-360 m^2/g) at 450 °C, but no studies of the color development in the

resulting material containing an excess of alumina phase were reported ¹⁰, and no attempts to make films from these sols are known. High-surface-area CoAl_2O_4 was prepared in a similar way by Platero et al. ¹¹, showing that spinels with a high surface area could be obtained without the need for severe sintering and the consequent loss of a high specific surface area.

In this paper, we first report on the synthesis of sols that have long-term (several months) stability under ambient conditions and are therefore appropriate for thin-film deposition over a long period of time. Ethylacetoacetate (EAA) is used as a sol stabilizer to avoid the undesirable precipitation of transition-metal hydroxides ^{12,13}. IR spectroscopy was used extensively to assess the structure of the xerogels, showing the bridging effect of NO_3^- ions which link together CoO_6 and AlO_4 species. We next investigated the formation of a spinel phase using IR spectroscopy combined with TG, DTA and XRD spectra analysis. Special attention was paid to elucidating the role of the solid solution of Co_3O_4 and Al_2O_3 which forms at annealing temperatures in the range 450-550 °C, i.e. before the CoAl_2O_4 is fully developed (>600 °C). IR spectroscopic analysis was combined with UV-VIS spectra analysis, showing the evolution of characteristic electronic absorptions with increasing annealing temperature that stemmed from the Co^{2+}O_4 species, which are responsible for the characteristic blue color of the spinel films.

2 EXPERIMENTAL DETAILS

2.1 Preparation of a dipping solution

An amount of 0.02 mole of aluminum-sec-butoxide ($\text{Al}(\text{O}i\text{Bu})_3$) (Gelest) was dissolved in 10 ml of iso-propanol (*i*-PrOH). An equimolar quantity of the chelating agent, ethylacetoacetate (EAA) (Fluka), diluted in 2 ml of *i*-PrOH, was mixed with the solution of $\text{Al}(\text{O}i\text{Bu})_3$. When the exothermic chelating reaction between $\text{Al}(\text{O}i\text{Bu})_3$ and EAA was completed, a solution of 0.006 mole of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Kemika, Zagreb) dissolved in 9 ml of *i*-PrOH, was added dropwise to a solution of the modified aluminum alkoxide precursor. The resulting clear sol is stable for several months at room temperature.

2.2 Thin film deposition

Thin films were deposited, using the dip-coating technique, on tempered flat-glass substrates and automotive halogen-lamp bodies made of quartz. The pulling speed was 10 cm/min for a freshly prepared sol, and 5 cm/min for an aged sol. The annealing temperature that leads to bright-blue-colored films was 700 °C. Two to three dipping and heat-treatment cycles were needed to obtain films with a sufficiently intense bright blue color that could be used as an optical filter for automotive lamps. The first dipping was followed by an annealing

time of 15 min while subsequent dipping(s) were followed with longer annealing times (30-60 min). An eventual oxidation of the lamp's metal contacts, which may occur after long annealing times (>30 min) at 700 °C, deteriorates the optical quality of the deposited films on automotive halogen lamps. This was solved either by using appropriate ceramic sockets or by soaking the coated lamp bodies in a solution of phosphoric acid (40 vol.%) in a water-ethanol system (30 vol.% H_2O , 30 vol.% EtOH) for 10 minutes. Cleaning the lamp bodies with this solution removed the deposited opaque overlayer and left the bright blue coating without a tarnished layer.

2.3 Preparation of powders

The powders were also prepared using a solvent-evaporation-based approach. The sols with various cobalt-to-aluminum molar ratios ($\text{Co}/\text{Al} = 0-1$) were cast in petri dishes, and left to gel and dry. The drying was completed under vacuum, generating xerogel powders. The xerogels were then annealed at various temperatures (450, 500, 550, 600 and 650) °C for 30 minutes and for different times of heat treatment at 650 °C (10-90 min). The overall preparation procedure is shown schematically on the processing flow chart (Figure 1).

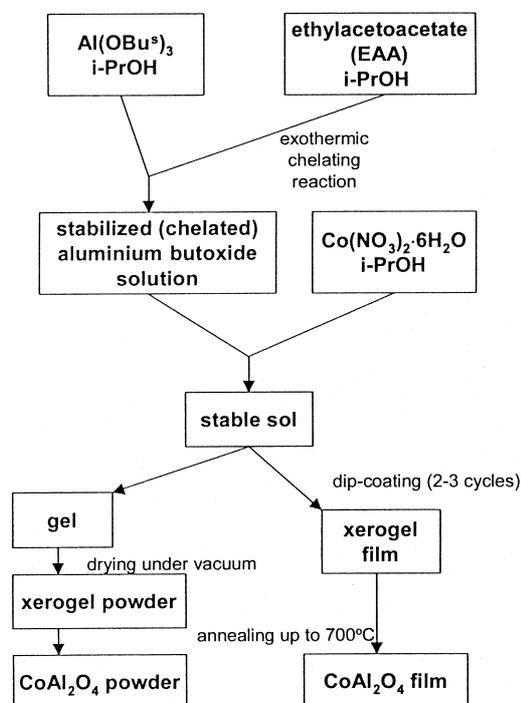


Figure 1: Sol-gel processing flow chart of CoAl_2O_4 films and powders

Slika 1: Shematski prikaz priprave tankih prevlek CoAl_2O_4 in prahov po postopku sol-gel

2.4 Instrumental

Ultraviolet-visible (UV-VIS) spectra of the cobalt aluminate films (Co/Al = 0.3, various annealing temperatures) deposited on tempered glass substrates were recorded using a HP8453 UV-visible system diode array spectrophotometer. The thickness of the films was measured with a Profilometer Talysurf (Taylor Hobson). *Infrared (IR) spectra* were measured using a FT-IR Perkin Elmer 2000 system spectrometer (the spectral range used was $4000\text{--}400\text{ cm}^{-1}$). The spectra of the Co/Al-xerogel and the oxide powders were recorded using KBr pellets. The *X-ray diffraction (XRD)* measurements of the cobalt aluminate powder (Co/Al = 0.3, annealing temperature $650\text{ }^\circ\text{C}$) were made using a Philips PW1710 automated X-ray diffractometer. The grain sizes were determined according to Scherrer's formula. *Thermogravimetric analysis (TG)* was performed on a Mettler Toledo TGA/SDTA851^e Module, while *differential thermal analysis (DTA)* on a Perkin Elmer DTA7 Analyzer.

3 RESULTS AND DISCUSSION

3.1 Infrared spectra

The IR spectra of the xerogels (Co/Al = 0.3) (**Figure 2, b**) exhibit bands that signal the presence of bridging ($1684, 1619\text{ cm}^{-1}$), bidentate ($1535, 1310$ and probably 1019 cm^{-1}) and ionic (1384 cm^{-1}) NO_3^- groups. Although the bands of the bridging NO_3^- units coincide with the

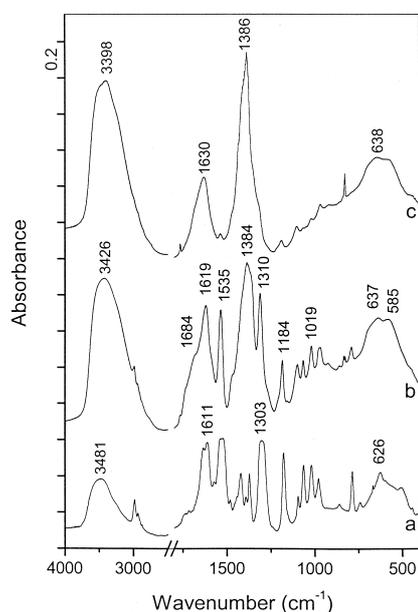


Figure 2: IR absorbance spectra of xerogel powders (KBr pellets) with various Co/Al molar ratio: Co/Al = 0 (a), Co/Al = 0.3 (b) and Co/Al = 0.5 (c) in the spectral ranges $4000\text{--}2500\text{ cm}^{-1}$ and $1800\text{--}400\text{ cm}^{-1}$

Slika 2: IR absorbančni spektri prahov kserogelov (v tabletkah KBr) z različnim molskim razmerjem: Co/Al = 0 (a), Co/Al = 0,3 (b) in Co/Al = 0,5 (c) v spektralnem območju $(4000\text{--}2500)\text{ cm}^{-1}$ in $(1800\text{--}400)\text{ cm}^{-1}$

bands of the COO groups of EAA, the spectrum of a xerogel made without $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ addition (**Figure 2, a**) differs markedly from the spectrum of a Co/Al-xerogel (Co/Al = 0.3) in the region where bands of coordinated NO_3^- groups are expected. Based on this argument and regarding the ability of nitrate counter ions to coordinate the metal ions in xerogels¹⁴, it is concluded that xerogel particles are connected via the NO_3^- units. When a larger amount of cobalt nitrate hexahydrate (Co/Al = 0.5) is introduced in the xerogel (**Figure 2, c**), the spectrum exhibits mainly bands for NO_3^- in the ionic form (1386 cm^{-1}) along with intense bands due to water ($3398, 1630\text{ cm}^{-1}$).

In the region of Al-O and Co-O stretching modes ($700\text{--}500\text{ cm}^{-1}$), two intense bands appear in the spectrum of Co/Al = 0.3 xerogel at 637 cm^{-1} and 585 cm^{-1} . With respect to the spectrum of pure Al-xerogel (Co/Al = 0), the band at 637 cm^{-1} is attributed to a O-Al-O mode coupled with the Co-O mode of CoO_6 groups at 585 cm^{-1} . The band at 631 cm^{-1} observed in the IR spectrum of the Co/Al = 1 sample remains broad, which indicates the continued presence of Al/Co-O coupled modes in the sample with the highest amount of Co in the Al_2O_3 host.

The spectra are changed upon heating the xerogel samples with different compositions (Co/Al = 0, Co/Al = 0.3 and Co/Al = 0.5) (**Figures 3a-c**). IR spectra of pure Al-oxide (Fig. 3A) exhibit two bands ($850, 640\text{ cm}^{-1}$) in the temperature range $450\text{--}550\text{ }^\circ\text{C}$. At $600\text{ }^\circ\text{C}$ the splitting of both bands is diminished ($780, 670\text{ cm}^{-1}$), and both bands degenerate to the single broad band at 710 cm^{-1} when annealing is performed at $650\text{ }^\circ\text{C}$.

The IR spectra of Co/Al = 0.5 oxide samples (**Figure 3c**) also do not exhibit drastic changes even in the whole annealing interval ($450\text{--}650\text{ }^\circ\text{C}$). Two bands centered at 672 cm^{-1} and $560\text{--}568\text{ cm}^{-1}$ that govern the IR spectra suggest that the Co-oxide phase is formed separately with respect to the Al-oxide phase. Cobalt aluminate spinel phase is not formed at such low temperatures, even though the "right" Co/Al molar ratio is used in the starting solution. Identification of the Co-oxide phase as Co_3O_4 is supported by the fact that the bands coincide well with the Co-O stretchings (667 and 580 cm^{-1}) observed for Co_3O_4 spinel¹⁵. The broad underlying absorption onto which both bands are superimposed is undoubtedly due to the Al-oxide phase, which forms in this temperature range (see **Figure 3a**).

In contrast to the Co/Al = 0 and Co/Al = 0.5 samples, IR spectra of the Co/Al = 0.3 oxide samples (**Figure 3b**) show different behavior in the temperature range $450\text{--}550\text{ }^\circ\text{C}$ and $550\text{--}650\text{ }^\circ\text{C}$. When annealed in the $450\text{--}550\text{ }^\circ\text{C}$ range, both bands attributed to the Co-oxide phase ($\nu_1: 696\text{ cm}^{-1}$, $\nu_2: 567\text{ cm}^{-1}$) remain nearly unchanged, showing small red shifts with heating at $550\text{ }^\circ\text{C}$ ($696\text{ cm}^{-1} \rightarrow 680\text{ cm}^{-1}$, $567\text{ cm}^{-1} \rightarrow 559\text{ cm}^{-1}$). This suggests the formation of a solid solution of Co- and Al-oxide phases, which is judged from the fact that the

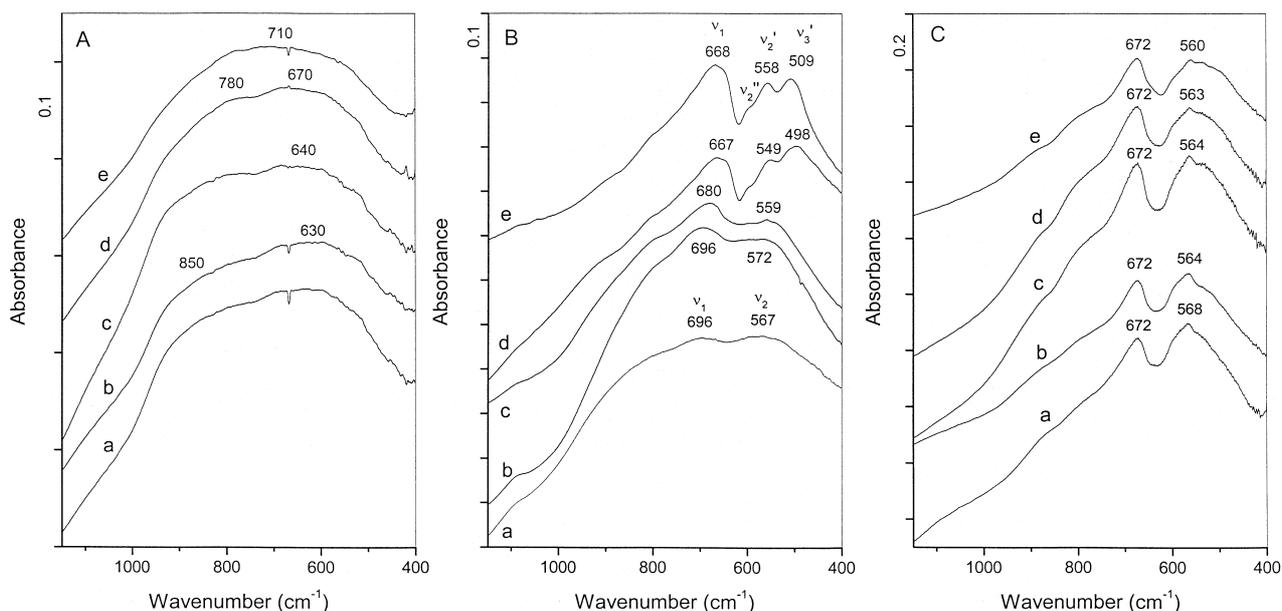


Figure 3: IR absorbance spectra between 1150 and 400 cm^{-1} (KBr pellets) of (A) $\text{Co/Al} = 0$, (B) $\text{Co/Al} = 0.3$ and (C) $\text{Co/Al} = 0.5$ oxide powders annealed at 450 (a), 500 (b), 550 (c), 600 (d) and 650 $^{\circ}\text{C}$ (e) for 0.5 hour.

Slika 3: IR absorbančni spektri oksidnih prahov (v tabletkah KBr) v območju med 1150 cm^{-1} in 400 cm^{-1} : (A) $\text{Co/Al} = 0$, (B) $\text{Co/Al} = 0,3$ in (C) $\text{Co/Al} = 0,5$. Prahovi kserogelov so bili žgani 30 min na 450 $^{\circ}\text{C}$ (a), 500 $^{\circ}\text{C}$ (b), 550 $^{\circ}\text{C}$ (c), 600 $^{\circ}\text{C}$ (d) in 650 $^{\circ}\text{C}$ (e)

ν_1 band appears at higher wavenumbers than in the $\text{Co/Al} = 0.5$ powder ($\sim 670 \text{ cm}^{-1}$) or pure Co_3O_4 spinel (667 cm^{-1}). The ν_2 band (567 cm^{-1}) is less affected by the presence of Al species, which agrees with the one-phonon-mode behavior of the ν_1 band ¹⁶.

Annealing of the $\text{Al/Co} = 0.3$ samples in the temperature range 550-650 $^{\circ}\text{C}$ brings about drastic changes that are reflected in the splitting of ν_2 band to ν_2' and ν_3' bands at 558 cm^{-1} and 509 cm^{-1} , and in the small but distinct red frequency shift of the ν_1 band, which appears now at 668 cm^{-1} . This clearly confirms the

formation of a CoAl_2O_4 phase with well-resolved ν_1 , ν_2' and ν_3' bands characteristic for the IR spectra of a normal spinel (AB_2O_4), containing Co^{2+}O_4 and AlO_6

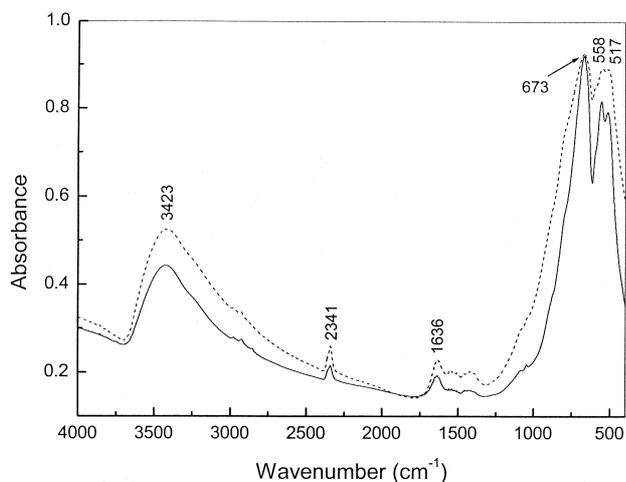


Figure 4: IR absorbance spectra of $\text{Co/Al} = 0.3$ oxide powder (KBr pellets) annealed at 650 $^{\circ}\text{C}$ for 10 min (dashed line) and 90 min (solid line)

Slika 4: IR absorbančna spektra $\text{Co/Al} = 0,3$ oksidnega prahu (v tabletki KBr), žganega na 650 $^{\circ}\text{C}$ 10 min (---) in 90 min (—)

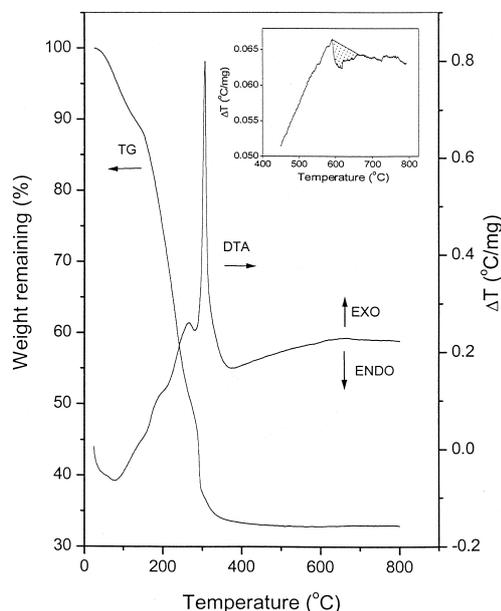


Figure 5: TG and DTA curves of the xerogel powder in a dynamic air atmosphere. Heating rate from 25 to 600 $^{\circ}\text{C}$ was 5 K/min and then decreased to 2 K/min up to 800 $^{\circ}\text{C}$. Sample mass was 13.9 mg for TG and 7.98 mg for DTA measurements. For another DTA measurement (inserted graph) sample mass was 21.4 mg.

Slika 5: Krivulji TG in DTA prahu kserogela v dinamični zračni atmosferi. Od 25 $^{\circ}\text{C}$ do 600 $^{\circ}\text{C}$ je bila hitrost segrevanja 5 K/min, od 600 $^{\circ}\text{C}$ do 800 $^{\circ}\text{C}$ pa 2 K/min. Masa vzorca je bila 13,9 mg za TG- in 7,98 mg za DTA-meritve. Pri DTA-meritvi, ki je prikazana na manjšem grafu (vstavek), je bila masa vzorca 21,4 mg.

groups. As expected, a lower Co/Al molar ratio (0.3) in the precursor solution than in the CoAl_2O_4 spinel (0.5) results in the formation of an additional alumina phase, which we judged from the presence of a broad underlying absorption. The additional shoulder band (ν_2'') at 594 cm^{-1} , also found in some spectra of CoAl_2O_4 published so far⁶, also appeared in our spectra, but its origin remains unclear. Very likely it is due to the combinational band of bending and stretching modes of spinel lattice.

Annealing of the powders at $650\text{ }^\circ\text{C}$ for a longer time (90 min) revealed a sharpening of all the bands attributed to the spinel modes (Fig. 4). In addition, the relative intensity of the ν_2' and ν_3' bands changed so that the ν_2' band became stronger than the ν_3' , and both bands were weaker with respect to the ν_1 band. The spectrum looks identical to that reported by Tarte¹⁷. In the IR spectra analysis, we also focused on collecting evidences about the porosity of the films. Direct evidence that films, even those calcinated for 90 min at $650\text{ }^\circ\text{C}$, are porous was obtained from the presence of the vibrational modes of CO_2 in the range $1300\text{-}1600\text{ cm}^{-1}$, and the band at 2341 cm^{-1} (Figure 4), both of which can undoubtedly be attributed to the CO_2 species adsorbed on the solid matrix.

To sum up, the IR spectroscopic analysis of xerogels and powders (Co/Al = 0.3) obtained at different annealing temperatures revealed that CoO_6 groups are already formed in xerogels. These groups are strongly disturbed by some other CoO_6 or AlO_4 groups which are linked to them via the bridging or bidentate NO_3 groups. The close proximity of Co- and Al-oxide species in xerogel tends to favor the formation of Co-oxide and Al-oxide solid solutions in the annealing temperature interval $450\text{-}550\text{ }^\circ\text{C}$. Above this temperature, the CoAl_2O_4 phase is formed. The presence of adsorbed CO_2 species proves that the films and powders are still not

well crystallised and exhibit a high surface activity to CO_2 adsorption².

3.2 Thermal analysis

The TG and DTA curves of the xerogel powder are presented in Figure 5. From room temperature up to $140\text{ }^\circ\text{C}$, the sample loses approximately 10% of its weight due to dehydration. The mass of the sample decreases continuously up to $350\text{ }^\circ\text{C}$. It is evident from both curves (TG and DTA) that this is a two-step process. In the first step, up to $260\text{ }^\circ\text{C}$, thermal decomposition of the organics takes place. The mass loss in this range ($140\text{-}260\text{ }^\circ\text{C}$), accompanied by a broad exothermic effect, is 38%. In the second step, from $260\text{ }^\circ\text{C}$ to $350\text{ }^\circ\text{C}$, thermal decomposition of nitrates probably occurs (a sharp exotherm on the DTA curve). The mass loss is 17%. From this temperature up to $800\text{ }^\circ\text{C}$, the mass of the sample remains constant. Also, no clear signal was observed in the DTA curve if the sample mass was around 8 mg. Using more sample ($\sim 20\text{ mg}$), a broad and weak endotherm (Figure 5, inserted graph) appears on the DTA trace in the temperature range from $590\text{ }^\circ\text{C}$ to $650\text{ }^\circ\text{C}$. The latter is in accordance with the results of the IR spectroscopy: that the Co/Al-oxide solid solution transforms to the CoAl_2O_4 phase above $550\text{-}600\text{ }^\circ\text{C}$. To determine enthalpy of the phase transformation a single point calibration was performed on DTA instrument using standard aluminum sample with the melting enthalpy of 397.0 J/g . A small piece of aluminum was carefully weighed into the crucible and then heated up to $750\text{ }^\circ\text{C}$. From the integrated peak area of the melting endotherm (onset value $660.4\text{ }^\circ\text{C}$) a calibration coefficient k was determined using the formula $A = k \cdot m \cdot \Delta H$, where A represents peak area, m weight of the

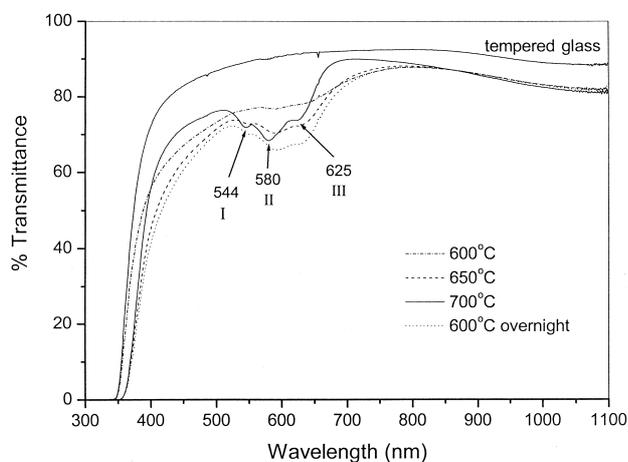


Figure 6: UV-VIS transmittance spectra of Co/Al = 0.3 oxide films on tempered glass substrates annealed at 600, 650 and $700\text{ }^\circ\text{C}$

Slika 6: UV-VIS transmissijski spektri Co/Al = 0,3 oksidnih prevlek na termično obstojnem steklu po žganju na $600\text{ }^\circ\text{C}$, $650\text{ }^\circ\text{C}$ in $700\text{ }^\circ\text{C}$

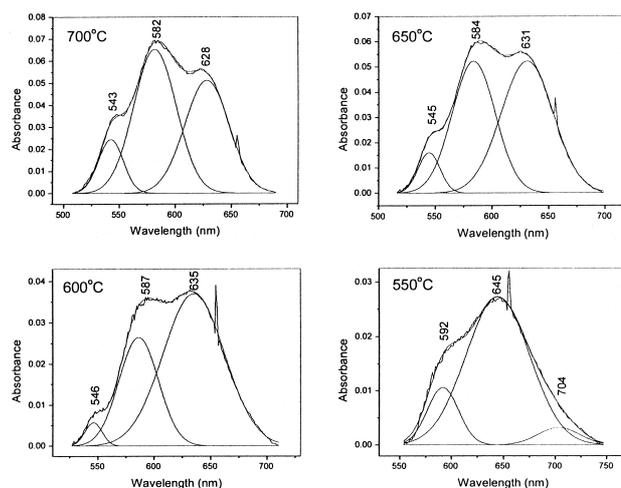


Figure 7: Deconvolution analysis of the bands I, II, III in UV-VIS absorbance spectra of Co/Al = 0.3 oxide films annealed at various temperatures

Slika 7: Dekonvolucija trakov I, II, III v UV-VIS absorbančnih spektrih Co/Al = 0,3 oksidnih prevlek, žganih pri različnih temperaturah

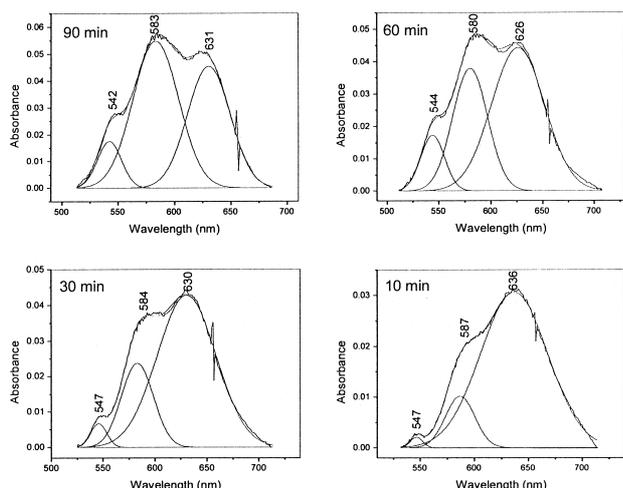


Figure 8: Deconvolution analysis of the bands I, II, III in UV-VIS absorbance spectra of $\text{Co/Al} = 0.3$ oxide films annealed at $650\text{ }^\circ\text{C}$ for 10-90 min

Slika 8: Dekonvolucija trakov I, II, III v UV-VIS absorbančnih spektrih $\text{Co/Al} = 0,3$ oksidnih prevlek, žganih od 10 do 90 min pri $650\text{ }^\circ\text{C}$

sample and ΔH enthalpy of the transformation. The same value of k was then used to estimate ΔH for the phase transformation, which occurs in the sample (see hatched surface in the inserted Graph, **Figure 5**).

3.3 UV-VIS spectra

Zayat and Levy ⁶ showed that the annealing temperature and the stoichiometry of the samples play an important role in their coloration. They found that with increasing Al-content, the temperature of a typical blue color formation decreases, which agrees with the results of the IR spectra analysis of our samples. Too low temperatures of annealing ($< 700\text{ }^\circ\text{C}$) result in greenish colored films. Generally, the temperature at which the color of the samples changes from green to blue depends on the preparation route ^{6,9}.

The UV-VIS spectra of our films (film thickness 150-250 nm) obtained after annealing the xerogel films up to $700\text{ }^\circ\text{C}$ (**Figure 6**) exhibited bands characteristic for spin-allowed transitions of $3d^7$ electrons of Co^{2+} ions in a tetrahedral configuration (${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ and ${}^4\text{A}_2(\text{F}) \rightarrow {}^2\text{T}(\text{G})$) ⁶ at 544, 580 and 625 nm, indicated as I, II and III bands in **Figure 6**. Spin-forbidden transitions found at 408, 447 and 479 nm ⁶ were not observed because this spectral region ($\lambda < 500\text{ nm}$) is characterized by continuous absorption originating from the electrons transition of Co^{3+} ions in an octahedral coordination. This absorption is responsible for the greenish hue of our films annealed at temperatures 600-650 $^\circ\text{C}$.

For the observed range of Co^{3+}O_6 electronic transitions ($\lambda < 550\text{ nm}$) we noted a variation in the film's transmittance with heat treatment. For example, the UV-VIS spectra of the films annealed at $600\text{ }^\circ\text{C}$ and also at $650\text{ }^\circ\text{C}$ exhibit poorly expressed bands I, II and III and a relatively strong decrease of the transmittance at

shorter wavelengths ($\lambda < 520\text{ nm}$). As a result of this, the films exhibit a green color. Heat treatment of the film overnight at $600\text{ }^\circ\text{C}$ turns its color to blue, and bands I, II and III become well pronounced in the corresponding spectrum. However, the continuous absorption stemming from the Co^{3+}O_6 groups ($\lambda < 520\text{ nm}$) is still relatively strong when compared to the absorption that the films heat treated at a higher temperature ($700\text{ }^\circ\text{C}$) exhibit in this spectral range. Lower absorption (i.e. higher transmission of the films at $\lambda < 520\text{ nm}$) clearly indicates a decrease in the number of Co^{3+}O_6 groups, and the simultaneous formation of tetrahedrally coordinated Co^{2+}O_4 groups. This is corroborated by an increase in the intensity of the bands I, II and III.

More detailed information about the appearance of the blue color was obtained from the development of the bands I, II and III observed in the spectra of films annealed at different temperatures ($500\text{--}700\text{ }^\circ\text{C}$) (**Figure 7**) and time of heat treatment (from 10 to 100 min) performed at $650\text{ }^\circ\text{C}$ (**Figure 8**). Such studies have not yet been published mainly because of the experimental difficulties connected with the recording of the UV-VIS transmission spectra of powders ^{6,9}. The smooth baseline recorded in our spectra of films allowed us to make a deconvolution analysis of bands I, II and III (**Figures 7, 8**). **Figure 9** (solid lines) shows the variation of the band frequencies with the annealing temperatures. The band positions shift to shorter wavelengths with higher annealing temperatures. In addition, a new band of unknown origin, not yet reported, was noted at $\sim 710\text{ nm}$. The band disappears in the spectra of films annealed at $600\text{ }^\circ\text{C}$ or higher temperatures. Its extinction coincides with the disappearance of a solid solution composed of Co and Al oxides also established using IR spectra (see IR section) and with the formation of the nanocrystalline

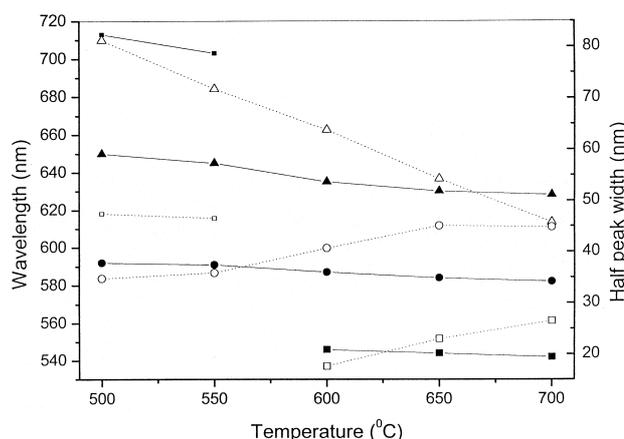


Figure 9: Positions (solid lines) and half-peak widths (dotted lines) of the bands I (squares), II (circles), III (triangles) in UV-VIS absorbance spectra of $\text{Co/Al} = 0.3$ oxide films as a function of annealing temperature

Slika 9: Položaj (—) in širina na polovični višini (...) trakov I (□), II (○), III (▽) iz UV-VIS absorbančnih spektrov $\text{Co/Al} = 0,3$ oksidnih prevlek v odvisnosti od temperature žganja

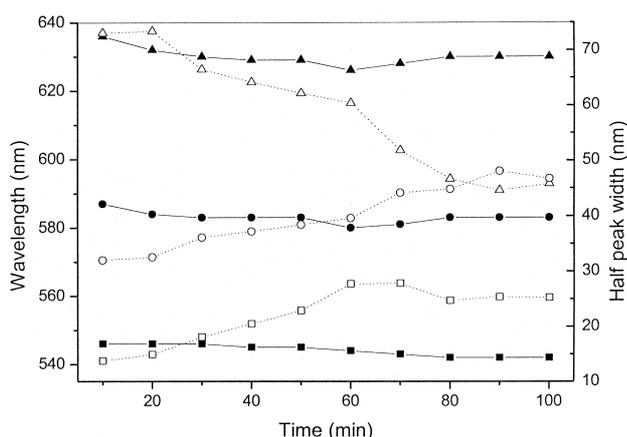


Figure 10: Positions (solid lines) and half-peak widths (dotted lines) of the bands I (squares), II (circles), III (triangles) in UV-VIS absorbance spectra of Co/Al = 0.3 oxide films as a function of heat-treatment time at 650 °C

Slika 10: Položaj (—) in širina na polovični višini (...) trakov I (□), II (○), III (△) iz UV-VIS absorbančnih spektrov Co/Al = 0,3 oksidnih prevlek v odvisnosti od časa žganja pri 650 °C

CoAl_2O_4 phase at temperatures above 600 °C. The shifts of the bands I, II and III with an increasing annealing temperature agree with the results of Meyer et al.⁹, who observed similar systematic blue-wavelength shifts using samples annealed at much higher temperatures (800-1400 °C). Also, the band intensities (**Figure 7**) change in the same manner as those found for samples prepared from bimetallic alkoxide precursors. The band II increases in intensity with respect to band III when the annealing temperature is enhanced. At the same time, band III sharpens, contrasting a small increase of the band II and band I half-peak widths (**Figure 9**, dotted lines).

As we expected, isothermal treatment of the films at 650 °C did not reveal drastic changes of the I, II and III band positions in the UV-VIS spectra (**Figure 10**, solid lines). However, for band I, only a small shift of the peak position to the red part of the UV-VIS spectrum was noted, while the bands II and III were shifted only slightly and not systematically. The corresponding changes of the band intensities (**Figure 8**) are more pronounced. Analogously to the heat treatment performed at different temperatures, longer heat-treatment times result in an increase of the band II intensity with respect to the intensity of the band III, while the band I is less affected. Accordingly, the spectra of annealed samples (650 °C - 90 min) resemble those of the samples annealed at 700 °C. Nevertheless, the intense bands I, II and III in the latter spectra confirmed the fact that annealing films at higher temperatures brings about a more intense blue coloration than a long isothermal heat treatment performed at a lower temperature (650 °C). The half-peak width variation of the bands I, II and III during isothermal treatment (Fig. 10, dotted lines) behaves similarly with regard to the

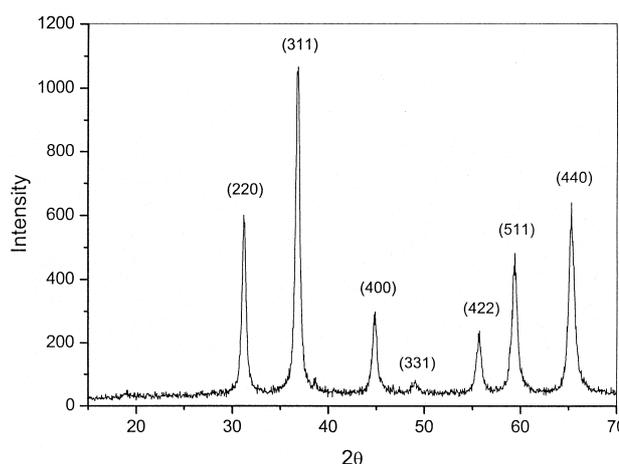


Figure 11: X-ray diffraction pattern of Co/Al = 0.3 oxide powder annealed at 650 °C for 90 min

Slika 11: Rentgenski difraktogram Co/Al = 0,3 oksidnega prahu, žganega 90 min pri 650 °C

heat treatment at different temperatures. It should be noted that isothermal heat treatment did not bring about clear evidence of the time threshold, which is needed to obtain intense blue-colored films. In this respect, UV-VIS spectra measurements performed at increasing temperatures are more illustrative, giving clear evidence about the formation of the crystalline CoAl_2O_4 from the solid solution of Co- and Al-oxide at temperatures 450-600 °C (see IR section).

3.4 X-ray diffraction

The XRD pattern of the powder (Co/Al = 0.3) annealed at 650 °C for 90 minutes (**Figure 11**) exhibits narrow and intense diffraction peaks characteristic for the crystalline CoAl_2O_4 normal spinel phase (space group $Fd3m$, JCPDS 44-0160)⁶. The presence of a spinel phase, which was developed at a relatively low temperature, indicates an advantage of the sol-gel route applied here. It should be stressed that to obtain blue-colored samples at temperatures lower than 750 °C, the Co/Al ratio should not exceed 0.3. As pointed out in ref.⁶, the excess of aluminum in Co/Al = 0.3 samples results in an additional Al_2O_3 phase, but we were not able to confirm the existence of this phase from our XRD spectra.

The presence of a spinel phase is corroborated by the appearance of the weak peak at $2\theta = 49.1^\circ$, which is characteristic for the CoAl_2O_4 phase formed from a mixed-valence Co_3O_4 oxide, stable at lower temperatures⁶. The formation of CoAl_2O_4 is also in accordance with the observation of the intense blue coloration of the corresponding oxide powder. The size of the particles, determined with Scherrer's formula, was found to be in the range of 16-18 nm for the powder samples calcined at 650 °C for 90 minutes. This is in agreement with

previous reports about the particle size of sol-gel-prepared CoAl₂O₄ ^{6,9}.

4 CONCLUSION

Optically selective blue CoAl₂O₄ coatings were produced at an annealing temperature of 700 °C using the sol-gel process. Their good mechanical properties, thermal stability and suitable color coordinates ($x = 0.412$, $y = 0.394$, $z = 0.194$) make them appropriate for use as light filters on automotive halogen lamps. The characteristic blue coloration corresponds to electronic transitions of Co²⁺ in a tetrahedral coordination, which is favored when the heat treatment of the xerogel film is performed at 700 °C.

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