Arabian Journal of Geosciences (2018) 11: 157
https://doi.org/10.1007/s12517-018-3513-7

ICCESEN 2017

Investigation of the photoluminescence properties of Urfa stone powder doped with chromium oxide

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Received: 27 December 2017 / Accepted: 27 March 2018 / Published online: 10 April 2018

Abstract
In this study, the structural properties of Urfa stone (US) doped with chromium oxide (Cr_2O_3) were investigated using X-ray diffraction (XRD) and FT-IR spectroscopy. The photoluminescence properties of US doped with varying amounts of Cr_2O_3 (5, 10, 20, 30, and 40%) were also investigated. US powder was obtained via grinding with an agate mortar, and Cr_2O_3 was then added as a dopant to the US powder. The samples were sintered at 1000 °C for 1 h. The XRD results of the US powder doped with Cr_2O_3 via mechanical alloying showed the presence of some crystalline phases: calcite ($CaCO_3$) and eskolate (Cr_2O_3). Furthermore, it was found that calcium oxide (CaO) and tongbaite (Cr_3C_2) were also present in the sintered samples. The photoluminescence analysis results indicated that the emission and excitation bands of the US-Cr complex shifted to longer and shorter wavelengths in the solid state (non-aqueous media), respectively.

Keywords Urfa stone (US) · Chromium oxide (Cr_2O_3) · Mechanical alloying · Photoluminescence

Introduction

Natural stones, which are sources of information to geologists, are based on the various developments and cultures around the world. The common feature of all stone structures is their impressive and permanent existence. Thus, stone use is always preferred in every culture. Today, natural stones continue to be used. This preference increases the reputation of some natural stones, allows them to be sold, and increases their economic value in the region and in which they are located (Kazancı and Gürbüz 2014). Urfa stone (US), also called "Havara" or "Nahit" stone, is one such natural stone and is used as a building material. It has a porous structure, so is suitable for sound and heat isolation, and is primarily white in color (Gölcük 2015). In recent years, much attention has been given to the preparation and characterization of rare-earth-doped inorganic luminescent materials, mainly focusing on metal oxides because of their high luminosity and chemical stability (Kang et al. 2009).

In this study, US was doped with varying amounts of chromium oxide (Cr_2O_3). The elemental composition of US was determined using the inductive coupling plasma method. These samples were also characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and the photoluminescence method.

Materials and procedure

US powder was obtained via grinding in an agate mortar. Then, Cr_2O_3 was added as a dopant using the mechanical alloying method. The samples were sintered at 1000 °C for 1 h. To identify the crystalline phases formed, XRD (D/max 2000, Rigaku) measurements were performed using CuKα radiation equipped with the "Jade" software between 3° and 60° using a scan speed of 3. FT-IR spectra of the samples were taken by the Perkin Elmer Frontier FT-IR spectrometer between 700 and 100 cm^{-1}. Single-

This article is part of the Topical Collection on *Geo-Resources-Earth-Environmental Sciences*

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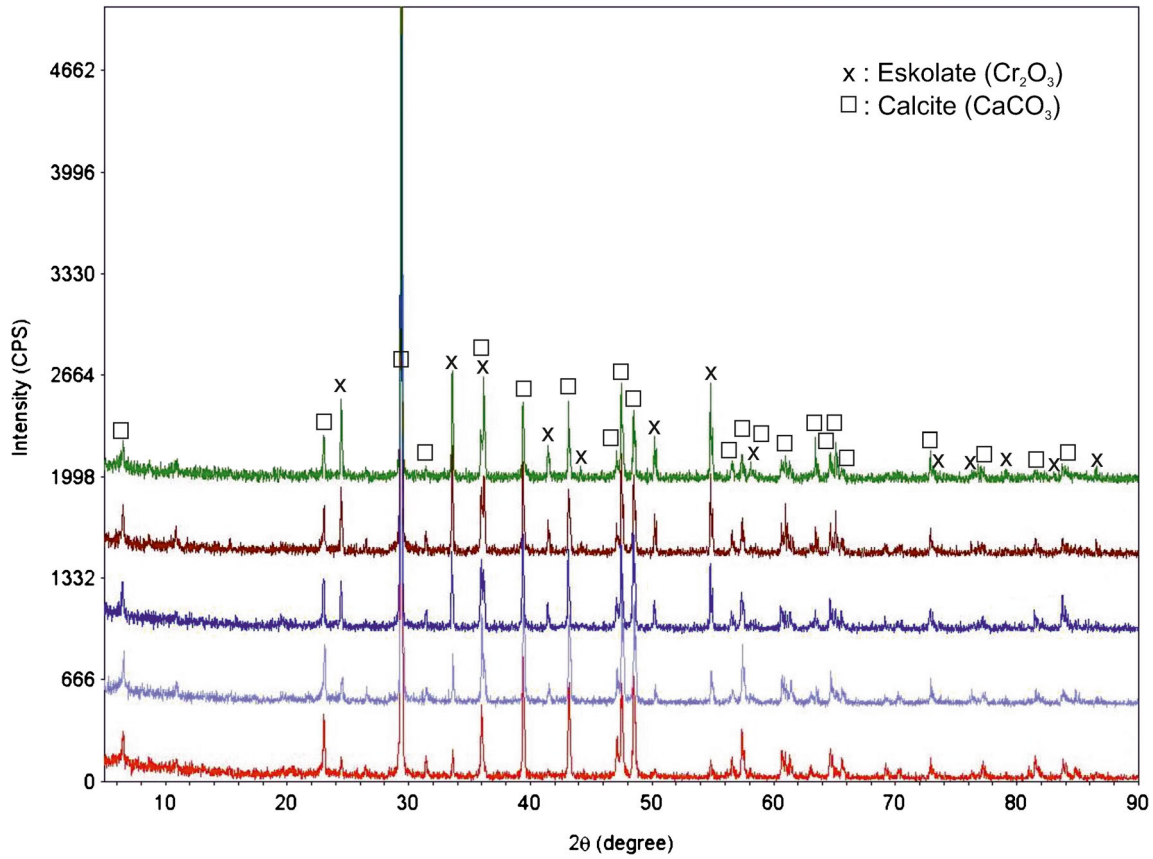

Fig. 1 X-ray diffraction patterns of US doped with Cr_2O_3

photon fluorescence spectra were collected using a Perkin Elmer LS55 luminescence spectrometer. All the samples were prepared in spectrophotometric grade solvents and analyzed in a quartz cuvette with an optical path of 1 cm. A dimethylformamide (DMF) solution with a ligand and complex concentration of 1×10^{-7} mol L^{-1} and a solid state were used to perform different state analyses (Ceyhan et al. 2013).

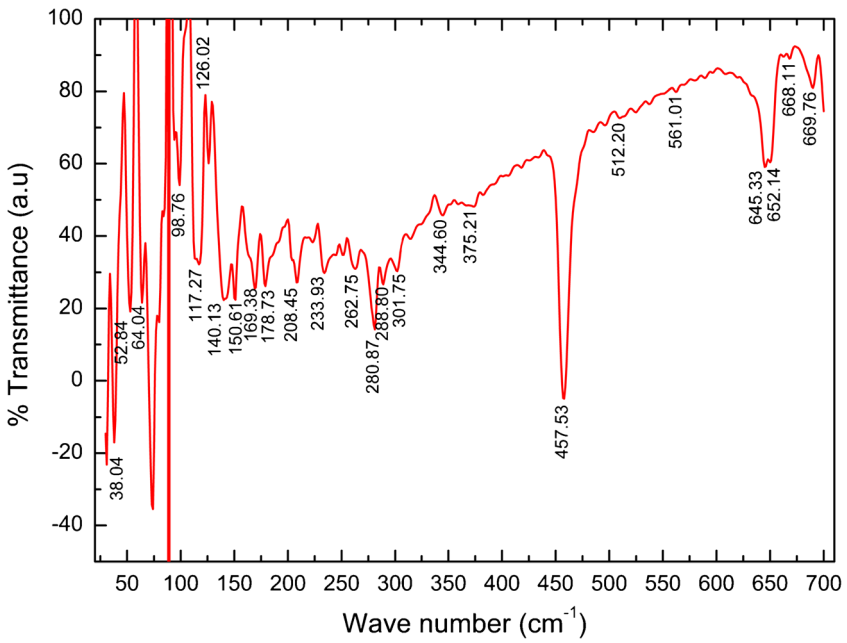

Fig. 2 FT-IR spectrum of US doped with Cr_2O_3

Table 1 Obtained emission and excitation data from the solid state of the US-Cr complexes

Concentration (M)	Excitation		Emission	
	λ (nm)	Intensity (arb.u.)	λ (nm)	Intensity (arb.u.)
US	348	957	701	521
US-Cr10	352	850	732	850
US-Cr20	354	785	738	862
US-Cr30	359	720	742	950
US-Cr40	363	659	756	1000

Results and discussion

The XRD patterns of the ceramic materials composed of US doped with Cr_2O_3 (5, 10, 20, 30, and 40%) are presented in Fig. 1. The presence of various crystalline phases is observed for the powder samples obtained via mechanical alloying: calcite ($CaCO_3$), PDF number 98-000-0022; and eskolate (Cr_2O_3), PDF number 00-038-1479. The characteristic calcite peaks are observed at 23.0, 29.4, 35.9, 39.4, 43.0, 47.0, and 47.5°. The addition of Cr_2O_3 to the US increases the intensity of the peaks at 24.5, 33.6, and 54.9°, which are the chromium peaks. When calcium carbonate ($CaCO_3$) is heated, it decomposes, revealing calcium oxide (CaO) and CO_2 (Barker 1973). The formation of CaO and tongbaite (Cr_3C_2) is observed in the samples after sintering at 1000 °C (Aktas et al. 2017).

The FT-IR spectrum of the ceramic materials is presented in Fig. 2. In the FT-IR spectrum of the US-Cr sample, two sharp peaks are displayed at 650.03 and 461.32 cm^{-1}, attributed to the Cr–O stretching modes, and they are clear evidence for the presence of crystalline Cr_2O_3 (Farzaneh and Najafi 2011).

Single-photon fluorescence spectra of the US and its metal complex (US-Cr) were collected using a Perkin Elmer LS55 luminescence spectrometer. The effect of the solid state on the photoluminescence properties of the US-Cr was investigated using 3 mg of the solid state. All samples were prepared to a spectrophotometric grade and were analyzed a 1-cm optical quartz plate (Ceyhan et al. 2012). The obtained data from the luminescence spectrometer are presented in Table 1. While the US alone exhibits two excitation bands, only one excitation band is observed in the US-Cr metal complexes at different ratios. The US with Cr_2O_3 exhibits similar but intense emission spectra in the UV-vis region.

The emission and excitation spectra of the US-Cr in the DMF are three-dimensionally presented in Fig. 3. When the excitation and emission spectra of Cr_2O_3 added to the US at different rates are examined, the emission intensity increases, while the intensity of excitation decreases with the increasing concentration of dopant. Along with this increased concentration, however, the excitation and emission wavelengths have shifted to higher wave lengths. For this purpose, Cr_2O_3 compounds were prepared with the US at four different concentrations, and powdered, and measured. When we first look at the US-Cr10 compound, it exhibit the same intensity of emission band at 732 nm, indicating a very intense (850) excitation band at 352 nm. As different from US-Cr10, US-Cr20 shows a more intense (862) emission band at 738 nm while exhibiting a very intense excitation band (785) at 354 nm. A more intense excitation band (359 nm) was observed at the third US-Cr30, while a more intense emission band at 742 nm was observed. Finally, it indicated the most intense emission band at 756 nm for a single excitation band at 363 nm in the US-Cr40.

When we look generally, the US with the addition of Cr_2O_3 began to emit stronger emissions against the weaker stimulus

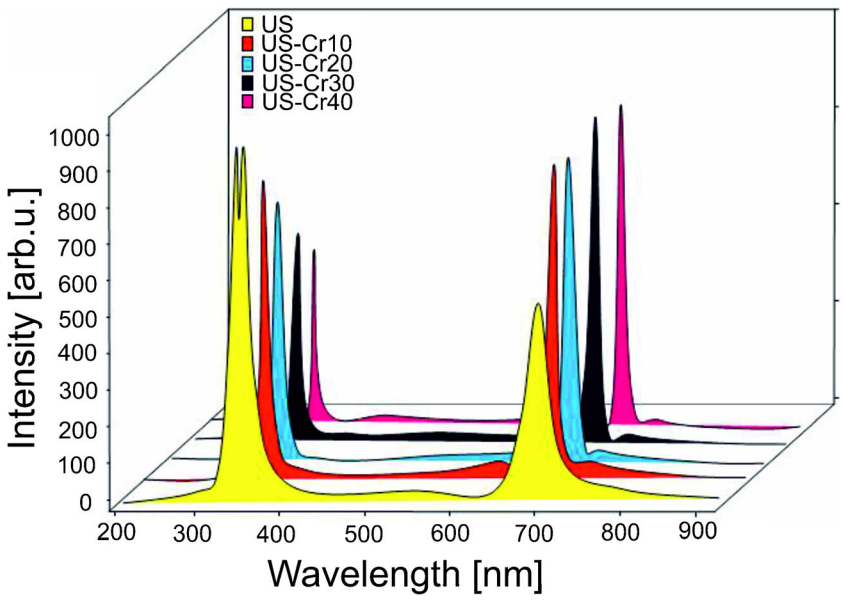

Fig. 3 Fluorescence emission and excitation spectra of the US-Cr in the solid state

band, which is related to the atomic structure of Cr_2O_3. These results show that Cr_2O_3 is absorbing in shorter time than the US, and spreading in longer time. The photoluminescence emission peak of the US-Cr clearly produces red shift with the introduction of the electron-donating groups (Ceyhan et al. 2012).

Conclusions

In this study, the structural properties and elemental composition of US doped with Cr_2O_3 were investigated using XRD and FT-IR spectroscopy. In the FT-IR spectra of the US-Cr sample, two sharp peaks attributed to the Cr–O stretching modes were observed. The US exhibits only one data point in the emission band and two in the excitation band. It has low emission band intensity, while the US has high excitation band intensity at low wavelength. The addition of Cr_2O_3 to the US resulted in a decrease in the intensity of the excitation band, but an increase in the intensity of the emission band. This result shows that the addition of electron-donating groups to the US has led to a red shift in the emission peak.

Acknowledgments The authors thank Harran University Central Laboratory (HUBTAM), Chemistry Department for XRD and FT-IR measurements of the materials, and the Research and Development Center for University-Industry-Public Relations, Kahramanmaras, Sutcu Imam University for photoluminescence measurements of the materials.

Funding This study has been financed by HUBAK under the 14085, 15026, and K17144 project numbers.

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