

# Microprobe and Raman Investigation of the Zoning in Synthetic $\text{Ca}(\text{CO}_3, \text{CrO}_4)$ Crystals

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## INTRODUCTION.

Due to its high mobility and toxic effects even in low concentrations, hexavalent chromium (Cr(VI)) is known as one of the most common environmental contaminants resulting from its widespread use in industrial applications (Katz & Salem, 1994). The chromium (VI) compounds are used mainly because of their acidic and oxidizing properties and their ability to form highly colored and insoluble salts. In this study, experiments to investigate the crystallization of  $\text{CaCO}_3$  in a silica hydrogel medium in the presence of different concentrations of Cr(VI) have been conducted.

## EXPERIMENTAL METHODS.

The crystallization experiments were performed in a double diffusion system (Cruz et al., 2009). Different concentrations of  $\text{Na}_2\text{CrO}_4$  (0.1 M, 0.15 M, and 0.2 M) were added to the sodium silicate solution during the gel preparation. Thus, Cr(VI) was homogeneously distributed within the gel column. Two months after the nucleation, the experiments were stopped.

Crystals comprising a representative range of morphologies and with

different intensities in yellow color were hand-picked and their morphology was studied by scanning electron microscopy (JEOL JSM6400, 40 kV, equipped with a LINK Ex1 energy dispersive spectrometer). The chromium concentration of the crystals and the development of zoning were analyzed by electron microprobe (JEOL JXA 8900).

A confocal Raman microscope (WITec alpha 300 R) was used to identify the  $\text{CaCO}_3$  polymorphs and to investigate the zoning in the crystals.

## RESULTS AND DISCUSSION.

The crystals were analyzed by micro Raman spectroscopy. Figure 1 shows the typical spectra of the crystals obtained from the different Cr concentration. All the spectra reveal the characteristic peak of calcite at  $1085 \text{ cm}^{-1}$  which is caused by the symmetric stretching vibration of the carbonate group. Furthermore, we observed peaks at  $280 \text{ cm}^{-1}$  and  $711 \text{ cm}^{-1}$  corresponding to the translational and rotational lattice mode vibrations (Bischoff et al., 1985) and to the internal translational modes of in-plane bending of the carbonate ions (Urmos et al., 1991), respectively.

In Figure 2, a close up of the  $\nu_2$  region

(peaks between  $700$  and  $1100 \text{ cm}^{-1}$ ) of these samples together with the main vibrational modes for chromatite as a reference is shown. In this region, in addition to the calcite bands mentioned above, some weak Raman bands appear between  $850$  and  $925 \text{ cm}^{-1}$ . The chromatite spectrum was obtained from a natural sample. As mentioned by Urmos et al. (1991), the  $\nu_2$  band at  $875 \text{ cm}^{-1}$  is not allowed in the Raman spectra of crystals with calcite structure. However, this vibrational mode can be clearly correlated with the main band of chromatite. This band at  $875 \text{ cm}^{-1}$  is the most intense in chromatite and could be assigned to the  $\nu_1$  symmetric stretching vibration of  $\text{CrO}_4$ . Some additional weak bands are also present. Frost (2004) studied the Raman spectra of a series of related chromate-bearing minerals and compared the spectra to the structure of the minerals. Wilkins (1971) reported that the Raman spectrum of crocoite gives three bands in the CrO stretching region at  $853$ ,  $838$  and  $825 \text{ cm}^{-1}$ . Frost (2004) shows the Raman spectra of the CrO stretching region of some chromate-bearing minerals. In this region the band position varies from  $825$  to  $972 \text{ cm}^{-1}$  depending on the mineral. We found three main bands at  $855$ ,  $875$  and  $975 \text{ cm}^{-1}$ . The first two values are in agreement with those enunciated by Frost (2004) and subsequently, the new bands can be consequence of the incorporation of Cr(VI) into the calcite structure as chromate groups. Furthermore, Wang et al. (2002) made a Raman spectroscopy study to distinguish the chromate species on Cr-MCM-41 synthesized by a direct hydrothermal synthesis method. The color of the samples was pale green and it changed to pale yellow after the calcinations suggesting the change of the oxidation state of the Cr species from  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ . In this work, the band at  $980 \text{ cm}^{-1}$  was assigned to the Cr-O vibration stretching of the dehydrogenated monochromate species ( $\text{CrO}_4^{2-}$ ). Thus, the third more intense band that we found in our spectra can

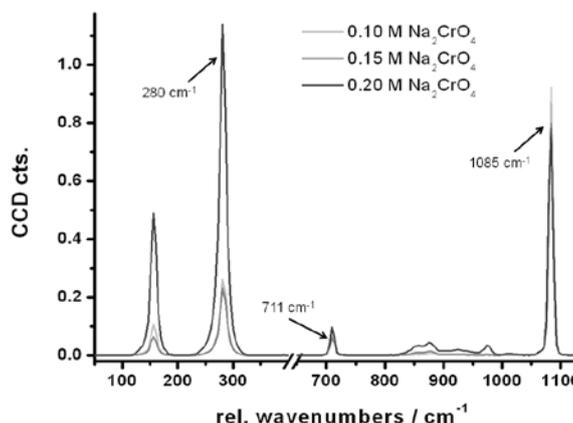


fig 1. Comparison between the Raman spectra corresponding to three calcite crystals showing a strong yellow colour. Bands characteristic of calcite structure are clearly distinguished.

**Palabras clave:** Cromato, Carbonato Cálcico, Microsonda Electrónica, Zonado, Espectroscopía Raman.

**Key words:** Chromate, Calcium Carbonate, Microprobe, Zoning, Raman Spectroscopy.

be also correlated with the presence of Cr (VI) in the structure.

These hypotheses are supported by the fact of the different intensities of the new bands for the crystals growing in the presence of different concentrations of chromate. As can be observed in Figure 2, the intensity of the new peaks is directly proportional to the content of Cr (VI) in the gel medium.

Finally, to investigate the possible zoning of the calcite crystals, a yellow crystal from the experiments with higher Cr concentration was analyzed in detail by Raman and microprobe. The Cr level of the crystals was analyzed. The inner part is chromium-rich, while pure calcite is present in the outer region due to depletion of chromium in the gel (Fig. 3a). Moreover, a Raman profile was obtained from the same crystal. Figure 3c shows a close up of the  $\nu_2$  region of (peaks between 700 and 1100  $\text{cm}^{-1}$ ) with the characteristic peaks of calcite and the bands for chromatite in the inner part of the crystal. Thus, the microprobe analysis correlate perfectly with the Raman analysis showing the zoning of the crystals.

### CONCLUSIONS.

1. Our results confirm the suitability of Raman spectroscopy to characterize the incorporation of impurities in crystalline phases.
2. The incorporation of Cr is evidenced by the appearance of new vibrational bands in the calcite Raman spectrum, which are consistent with the substitution of carbonate groups by chromate groups.
3. Cr incorporation in calcite could be described as resulting from the development of a very restricted anionic solid solution.

### ACKNOWLEDGEMENTS.

This work has been part of the project CGL2007-65523-C02-01 (Spanish Ministry of Science and Innovation). Financial support has also been provided by the DFG cluster of excellence "Nanosystems Initiative Munich" (NIM) and the research group 910148 (UCM-Comunidad de Madrid (Spain)). Nuria Sánchez-Pastor gratefully acknowledges the fellowship from the Humboldt Foundation. We sincerely thank the Microscopy Centre of the Complutense University of Madrid for technical assistance and support.

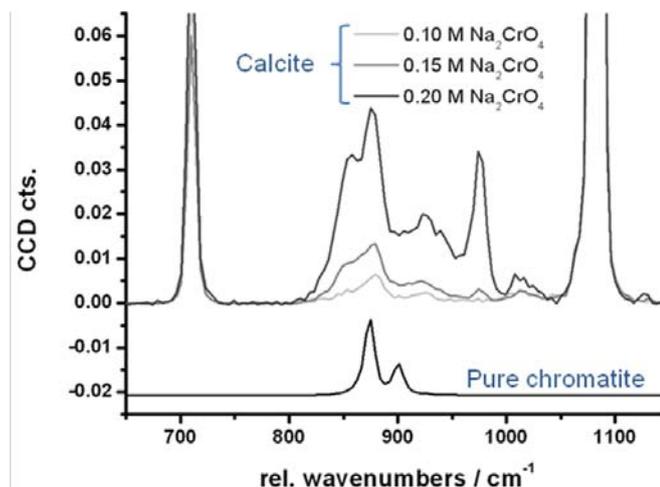


fig 2. Close up of the  $\nu_2$  region of experiments with 0.1 M, 0.15 M, and 0.2 M of  $\text{Na}_2\text{CrO}_4$  in the gel medium with the main vibrational modes for chromatite superimposed.

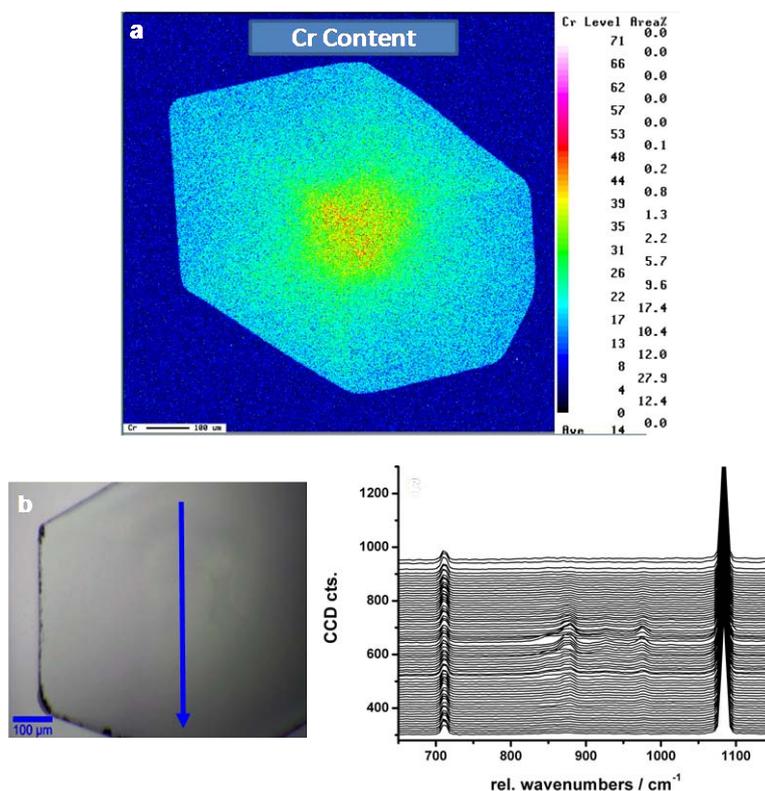


fig 3. (a) Microprobe map showing the Cr concentration; (b) Shows an optical microscope image of the crystal; (c) Raman spectra along the crosssection of the crystal as indicated in (b).

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