Electrolytic coloration and spectral properties of natural calcite crystals

HONGEN GU,* RUI ZHU, WEIWEI CHEN, DONGLIANG MA, YANG LI, AND YUTONG LI

Department of Physics, Tianjin University, Tianjin 300072, P.R. China

ABSTRACT

Natural colorless calcite crystals are colored electrolytically by using a pointed cathode and a flat anode at various temperatures and voltages. Ca\(^+\) and CO\(_3\)\(^-\) color centers, Ca\(^{2+}\) vacancies, and CO\(_3\)\(^2-\) units are produced in colored crystals. Absorption spectral bands of the Ca\(^+\) and CO\(_3\)\(^-\) color centers, Ca\(^{2+}\) vacancies, and CO\(_3\)\(^2-\) units are reported for the colored crystals at room temperature. Pb\(^{2+}\) spectral bands are observed in absorption and fluorescence spectra of uncolored and colored crystals. The current-time curve for electrolytic coloration of natural calcite crystal and its interpretation with respect to the electrolytic coloration process are given. Creation and conversion of color centers are explained.

Keywords: Calcite crystal, electrolytic coloration, color center

INTRODUCTION

Calcite is a calcium carbonate mineral with ideal chemical formula CaCO\(_3\). Natural pure calcite crystal is colorless and transparent. Colorless and transparent calcite is a good optical material. Natural calcite can carry information with respect to geological structure such as deformation and radioactive radiation in its surrounding (Debenham 1983; Sunta 1984). Therefore, natural calcite can be used in dating or dosimetry. The information carriers are generally impurities of varying valence state and trapped-electron, trapped-hole color centers in the crystal. These impurities and color centers can also be produced artificially. Calcite crystals can be colored by ionizing radiation, where some trapped-electron and trapped-hole color centers such as Ca\(^+\) and CO\(_3\)\(^-\) color centers are produced (Kolbe and Smakula 1961). All the investigated crystals in this study are colored at room temperature (RT) or low temperature. Spectroscopic measurements were performed at low temperature due to thermal instability of the Ca\(^+\) and CO\(_3\)\(^-\) color centers at RT. However, our present research shows that natural colorless calcite crystals can be colored electrolytically at high temperature and spectroscopically characterized at RT. Electrolysis is an efficient coloration method for inducing color centers in alkali halide crystal (Hauckaylo and Groetzinger 1952). Among the advantages of electrolysis is its speed, the possibility for visual observation and thus real-time monitoring and control, as well as selectivity with respect to color centers. Moreover, the experimental setup for electrolysis is much simpler than in other coloration methods such as high-energy electromagnetic irradiation or high-energy particle bombardment. However, no electrolytic coloration for calcite crystal is performed hitherto according to the literature. Our present results show that electrolysis may also be a more practical method for coloring natural calcite crystals and other minerals.

EXPERIMENTAL DETAILS

Natural calcite crystals from Ma Mountain in Guizhou province in China used for this study were obtained commercially. The calcite crystals are colorless and transparent. Samples with sizes of several millimeters were cleaved off a large crystal along \{10\(\overline{1}\)0\} faces. The samples are colored electrolytically in a homemade apparatus at various temperatures (200–600 °C) and dc voltages (300–1500 V) for several hours. The accuracy of the temperature is estimated to be ±5 °C, the voltage was regulated within ±1 V. A schematic of the experimental setup is shown in Figure 1. A pointed tungsten cathode and a flat stainless steel anode are used. Some graphite powder damped with alcohol is used between the sample and anode to ensure good contact. The coarse graphite grains in the graphite powder form a graphite anode matrix, which is equal to multiple pointed anodes. The sample is held in slowly streaming dry nitrogen during the electrolytic coloration to protect the electrodes against oxidation. The use of the pure nitrogen is necessary to avoid oxygen contamination. The sample is put on a copper bulk for quenching to RT after the electrolytic coloration. The annealing of the colored samples is carried out in the same apparatus with no voltage applied. Unpolarized absorption spectra of the samples are measured with a spectrophotometer model UV-240 at RT. Spectral resolution is 0.3 nm. Unpolarized fluorescence spectra of the samples are measured with a fluorescence spectrophotometer model WFY-28 at RT. Spectral resolution is 0.1 nm.

RESULTS

Typical absorption spectra of a natural calcite crystal before (dash-dot curve) and after (solid curve) electrolytic coloration (276 min at 500 °C and 1200 V) are shown in Figure 2. The crystal thickness is 3.0 mm. There is one intense absorption band

\[
\begin{align*}
\text{Anode} & \quad \text{PTFE plug} \\
\text{Outlet} & \quad \text{XTAL} \\
\text{W cathode} & \quad \text{Stainless steel plate} \\
\text{N\(_2\) inlet} & \quad \text{Quartz glass tube} \\
\text{Heater} &
\end{align*}
\]

**FIGURE 1.** Schematic sketch of the experimental setup for the electrolysis experiment.