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Electrolytic coloration and spectral properties of natural fluorite crystals containing oxygen impurities

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ABSTRACT

Natural fluorite crystals containing oxygen impurities are colored electrolytically by using a pointed cathode and a flat anode at various temperatures and voltages. F and F_2 color centers are produced in colored fluorite crystals. O^{2-}–V_a^+, O^{2-}–V_a^+ aggregate, Yb^{2+}, Ce^{3+} and Sm^{2+} absorption bands are observed in absorption spectra of uncolored fluorite crystals. O^{2-}–V_a^+, O^{2-}–V_a^+ aggregate, Yb^{2+}, Ce^{3+}, Sm^{2+}, F, M (F_2) absorption bands and group of four absorption bands are observed simultaneously in absorption spectra of colored fluorite crystals. Current–time curve for electrolytic coloration of natural fluorite crystal and its relationship with electrolytic coloration process are given. Production and conversion of color centers are explained.

1. Introduction

Pure calcium fluoride crystal is an excellent optical window material. Some of calcium fluoride crystals with appropriate color centers or impurities have very good optical and spectral features. They have been paid a deal of attention to their applications in laser [1], hologram [2–5] and spectral holeburning [6,7] etc. Fluorite is a natural calcium fluoride mineral with general chemical formula CaF_2. Natural pure fluorite is colorless and transparent. In general, natural fluorite exhibits various colors due to different color centers or impurities. It is well known that natural fluorite can also carry some important information on geological structure and radioactivity around fluorite deposit in the earth. Therefore, the natural fluorite can be used for dating or dosimetry [8,9]. Various color centers can be produced in fluorite crystal by additive coloration, high-energy ray irradiation or high-energy particle bombardment [10]. However, the production of the color centers is very sensitive to impurities contained in the fluorite crystal, in particular to oxygen impurities. Early researches have found that only α and β (that is the later F and M (F_2)) absorption bands are observed in absorption spectrum of additively colored natural fluorspar containing oxygen impurities [11]. A group of four absorption bands is observed in absorption spectrum of X-rayed natural or synthetic calcium fluoride crystals [12,13].

The electrolysis is an effective coloration method for producing color centers in some crystals. The quick-speed, visual observation, real-time monitor and control, environmental protection and optional production of the color centers are the substantial advantages of the electrolysis. Moreover, the structure of the apparatus in the electrolysis is much simpler than that in the other coloration methods such as the high-energy ray irradiation and high-energy particle bombardment. In previous research, much attention has been paid to electrolytic coloration of alkali halide crystal, but little to that of alkaline earth halide crystal. In our recent work, lithium-doped strontium fluoride crystals could be colored electrolytically at appropriate temperatures and voltages by using our homemade electrolysis apparatus [14]. In past electrolysis research, it was believed impossible to color directly electrolytically crystals containing anionic impurities because the impurities or their dissociated products, such as oxygen-related impurities, can prevent the formation of the secondary alkali cathode. The formation of the secondary alkali cathode is a very necessary condition to start electrolytic coloration through electron injection by using a pointed cathode and a flat anode. Some electrolysis experiments used sodium fluoride [15], sodium chloride, potassium chloride [16] and calcium fluoride [17] crystals mainly benefit from the substantial elimination of the hydroxyl impurities, the hydroxyl-free or the very high purity of the original material. Therefore, no electrolytic coloration for alkaline earth halide crystal containing anionic impurities has been performed heretofore. In the present work, natural fluorite crystals containing oxygen impurities are colored electrolytically by using the same electrolysis apparatus with a pointed cathode and a graphite anode matrix. F and F_2 color centers are produced in colored fluorite crystals.

2. Research details

Natural fluorite crystals containing oxygen impurities are used and obtained commercially. The actual concentrations of the diva-

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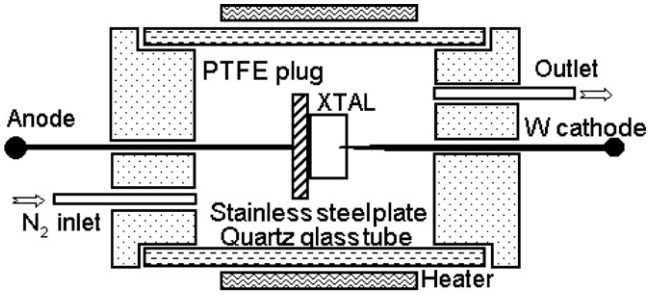

Fig. 1. Structure scheme of electrolysis apparatus.

lent oxygen impurity ions are determined from the parameter of the characteristic absorption bands of the oxygen impurity ions. The fluorite crystals are transparent and light green. Samples with size of several millimeters are cleaved from a large fluorite crystal bulk. The samples are then colored electrolytically in a homemade apparatus at various temperatures (200–600 °C) and DC voltages (300–1500 V) for several hours. The structure scheme of the apparatus used in the electrolytic coloration is shown in Fig. 1. A pointed tungsten cathode and a flat stainless steel anode are used. Some coarse graphite powders damped with alcohol are used between the sample and anode in order to ensure good contact. The coarse graphite grains structure a graphite anode matrix. The sample is held in slowly flowed dry and pure nitrogen during the electrolytic coloration to protect the electrodes against oxidation. The sample is put on a copper bulk for quenching to room temperature (RT) after the electrolytic coloration. Absorption spectra of the samples are measured with a spectrophotometer model UV-240 at RT.

3. Main results

Fig. 2 shows the typical absorption spectrum of a natural fluorite crystal containing oxygen impurities before electrolytic coloration. The thickness of the fluorite crystal is 3.5 mm. In the absorption spectrum, the strong absorption band near 205 nm corresponds to O^{2-}–V_a^+ aggregate color centers [18]. The 259, 274 and 362 nm absorption bands correspond to Yb^{2+} impurity ions [19]. The 304 nm absorption band corresponds to Ce^{3+} impurity ions [20]. The 428 and 609 nm absorption bands correspond to Sm^{2+} impurity ions [21]. The two absorption bands in the blue and red light regions lead the uncolored fluorite crystals to exhibit

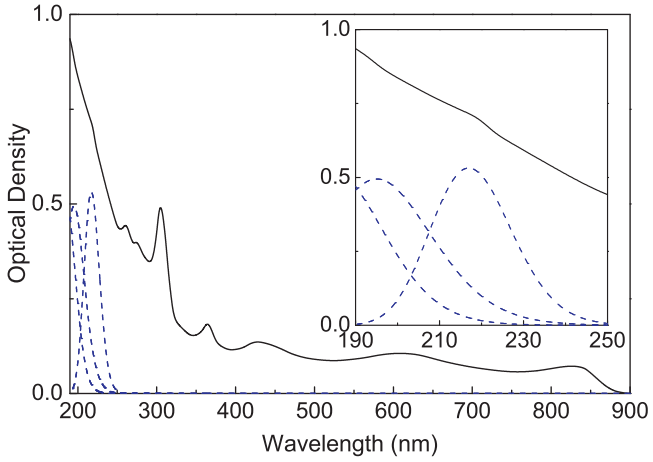

Fig. 2. The absorption spectrum of a natural fluorite crystal containing oxygen impurities before electrolytic coloration. The thickness of the fluorite crystal is 3.5 mm. Dashed curves show resolved absorption peaks. Inset shows local enlarged curves.

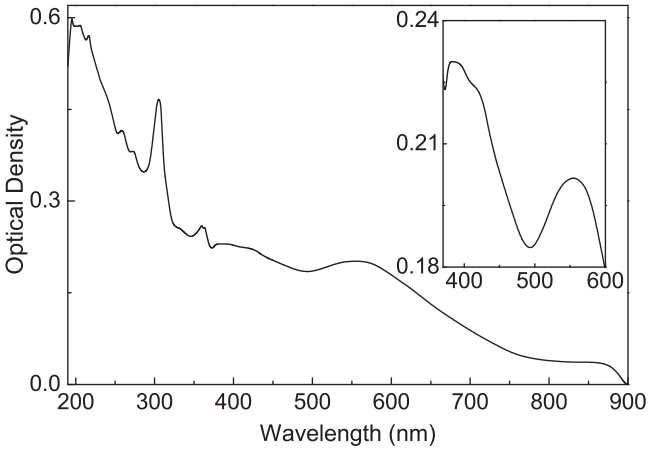

Fig. 3. The absorption spectrum of the same fluorite crystal as used in Fig. 2 after electrolytic coloration at temperature 294 °C and voltage 900 V for 240 min. Inset shows a local enlarged curve.

the light green color. The 828 nm absorption band does not correspond to any known color centers or absorption bands. The high-energy side of the absorption spectrum can be resolved into three Gaussian-type absorption peaks at 185, 195 and 217 nm. The corresponding bandwidths are 0.80, 0.80 and 0.50 eV, respectively. The corresponding maximum absorption coefficients are 2.44, 2.30 and 2.44 cm^{-1}, respectively. The absorption spectrum is plotted against photon energy in the resolution procedure. The absorption spectrum and resolved absorption peaks are replotted against light wavelength after the resolution. The 185 and 195 nm absorption peaks correspond to the O^{2-}–V_a^+ and O^{2-}–V_a^+ aggregate color centers, respectively [19]. The 217 nm absorption peak corresponds to the Sm^{2+} impurity ions [20]. The concentration of the divalent oxygen impurity ions in the fluorite crystal is estimated at 4.70×10^{17} cm^{-3} according to the spectral parameters of the 185 and 195 nm absorption peaks and the Smakula's formula. The calculated results show that the fluorite crystals contain indeed more oxygen impurity ion than other ones.

Fig. 3 depicts the absorption spectrum of the same fluorite crystal as used in Fig. 2 after electrolytic coloration at temperature 294 °C and voltage 900 V for 240 min. In the absorption spectrum, the 195 and 205 absorption bands correspond to the O^{2-}–V_a^+ aggregate color centers. The 216, 258, 273 and 363 nm absorption bands correspond to the Yb^{2+} impurity ions. The 304 nm absorption band corresponds to the Ce^{3+} impurity ions. The 383 and 550 nm absorption bands correspond to F and M (F_2) absorption bands, respectively [10]. The 417 nm absorption band corresponds to the Sm^{2+} impurity ions. The 865 nm absorption band does not correspond to any known color centers or absorption bands.

Fig. 4 shows the typical absorption spectrum of another natural fluorite crystal containing oxygen impurities before electrolytic coloration. The thickness of the fluorite crystal is 1.8 mm. In the absorption spectrum, the 194 nm absorption band corresponds to the O^{2-}–V_a^+ aggregate color centers. The 215 nm absorption band corresponds to the Sm^{2+} impurity ions. The 260, 273 and 363 nm absorption bands correspond to the Yb^{2+} impurity ions. The 304 nm absorption band corresponds to the Ce^{3+} impurity ions. The 428 and 618 nm absorption bands correspond to the Sm^{2+} impurity ions. By comparing the absorption spectra in Figs. 2 and 4, one can see that the distribution of the impurity ions in the large fluorite crystal bulk is inhomogeneous. The 828 nm absorption band does not correspond to any known color centers or absorption bands.

Fig. 5 presents the typical absorption spectrum of the same fluorite crystal as used in Fig. 4 after electrolytic coloration at temperature 552 °C and voltage 1200 V for 75 min. The local absorption