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Application of Cathodoluminescence in Gemstone Identification

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Abstract: According to the different colors, luminous intensity and images presented by gemstones under cathodoluminescence, it can be used to understand the structure of gemstones, including the lattice defects they have, to quickly and nondestructively identify the species of gemstones, to identify the types, valence and quantities of trace elements in them, and to explore the environment of crystal growth and the conditions of formation.

Keywords: Cathodoluminescence; Emerald; Ruby; Diamond; Pearl

1. Introduction

Cathodoluminescence is an electromagnetic wave in the ultraviolet to near infrared range of light or electromagnetic radiation, produced by cathode rays, is a cathodic electron beam bombardment of solid materials to produce electron leaps and luminescence of a physical phenomenon, the electron beam possesses a high energy so that its electrical energy is converted into light radiation energy.

Cathodoluminescence technology is based on mineralogy, spectroscopy, molecular orbital theory, energy band theory, etc., and is usually combined with instruments such as scanning electron microscopes. When the electron beam interacts with the material, the light generated is captured with an optical device or directly captured by a cathodoluminescence detector inside the chamber, and the interaction process can be observed with a scanning electron microscope.

The cathode ray tube sends out a cathodic electron beam to bombard the mineral crystal, the mineral crystal will be distorted, the crystal can be generated inside the electron hole, the local energy level is changed to present the excited state, these excitation centers because in the energy of the sub-stable state will capture electrons to become the luminescent center. [1]

2. Gem Identification Applications

2.1 Emerald

Jadeite is mainly composed of steatite, sodium chromium pyroxene, green pyroxene, may contain a small amount of hornblende, feldspar, chromite, etc., epithermal minerals are hematite, limonite and kaolinite group minerals. Jadeite's color is rich and diverse, the color is often unevenly distributed, generally glassy luster - greasy luster, the head can be from transparent - opaque, its luster and transparency and its structure is related to the non-homogeneous aggregates, the refractive index of 1.666 ~ 1.690 (+0.020, -0.010), the point of measurement is 1.66, the The density is 3.34 (+0.11, -0.09) g/cm^3.

2.1.1 Colorless-White Jadeite

Transparent colorless jadeite, its cathodoluminescence color is often dark blue, there may be bright purple fluorescence, cathodoluminescence spectral characteristics of 370nm luminescence broad peaks, accompanied by weak 554nm luminescence peaks; opaque white jadeite mostly show bright greenish-yellow fluorescence, cathodoluminescence spectral characteristics of the luminescence of 554nm broad peaks, accompanied by weak 370nm luminescence peaks. [2]

2.1.2 Green Jadeite

With the green tone from light to deep, the light-emitting color from yellowish green - green - brownish green - greenish purple - aqua - crimson, cathodic luminescence spectrum from 554nm dominated by a single peak into 554nm and 760nm double peak, the deeper the color of the 760nm peak the stronger, while the 554nm will become weaker until Volume 10 Issue 5-115-disappeared, in the broad peak of the 760nm will be a weak peak of 693nm for the cathodic Cr^{3+} This is the cathodoluminescence characteristic peak of Cr^{3+}, which is very similar to the cathodoluminescence spectrum of emerald. [2]

2.1.3 Purple Jadeite

Pink purple jadeite cathodoluminescence color with a blue tint, bright light purple-orange purple, with the deepening of the pink-purple tone, orange-purple more obvious, cathodoluminescence spectral characteristics from 370nm for the main light-emitting peaks and 680nm for the auxiliary light-emitting peaks gradually transformed into 370nm for the auxiliary light-emitting peaks and 680nm for the main light-emitting peaks. The cathodoluminescence of blue-purple jadeite is blue-green and purple fluorescence, and there are double peaks of 370nm and 508nm peaks. [2]

2.1.4 Yellow Jadeite - Red Jadeite

The tawny and reddish brown color of jadeite is caused by the acicular ferrite and limonite that fill in the microfissures of jadeite, so its color belongs to secondary genesis. Acicular iron ore and limonite do not affect the cathodoluminescence of jadeite, so the cathodoluminescence of yellow Fei and red Fei shows the luminescence characteristics of the primary mineral, jadeite. [2]

2.2 Ruby

Ruby, corundum, chemical formula for Al2O3, due to the complexity of the geological conditions so that it contains a variety of trace elements, such as Fe, Ti, Cr, Ni, Mn, etc., these elements can be qualitatively homogeneous instead of corundum in the Al3+, and make its color. Ruby is mainly colored by Cr3+, and sapphire is mainly colored by Fe3+ and Ti4+. Corundum is a uniaxial crystal negative light, refractive index of 1.762 ~ 1.770 (+0.009, -0.005), birefringent refractive index of 0.008 ~ 0.010. Ruby according to its content of Cr, Fe content of different, UV fluorescence will show different degrees of red fluorescence, sapphire due to the higher content of Fe, generally non-fluorescent. Ruby has 694, 692, 668, 659 nm absorption line, 620 ~ 540 nm absorption band, 476, 475 nm strong absorption line and 468 nm weak absorption line, as well as 450 nm below the full absorption. The darker the color, the stronger the 620~540 nm absorption band.

2.2.1 Natural ruby

Under the excitation of cathode rays, natural ruby luminescence is fast, showing uniform, medium intensity deep red or purple-red light, and the internal features are clearly visible under the cathode rays, such as clefts, tiny bright point-like inclusions, angular growth textures, or hexagonal growth rings. The cathodoluminescence spectrum varies with the Cr concentration in the corundum structure.

2.2.2 Heat-treated ruby (optimized)

Heat-treated ruby, its luminescence speed, luminescence intensity and luminescence characteristics are similar to those of natural ruby, and the degree of luminescence of the vaguely visible core is different from that of the main gemstone.

2.2.3 Filled and dyed rubies (treatment)

Filled, dyed ruby luminous speed and luminous intensity are weaker than the natural ruby, which is caused by glue, glass, dye and other internal filling material, internal filling parts of the luminous intensity is weaker than the main gem, in the microscope is clearly visible in the internal large number of fissures, and along the fissures can be seen in a very small bright spot (bubble luminescence).

2.2.4 Synthetic Ruby

Synthetic ruby cathodoluminescence intensity, luminescence speed is higher than the natural ruby, and synthetic features in the cathodoluminescence is clearly visible, such as hydrothermal synthesized ruby in the microscope can be seen under the characteristics of the wave-like growth texture, flame melting and crystal pulling synthesized ruby in the microscope can be seen under the characteristics of the arc-shaped growth pattern. [3]

2.3 Diamond

Diamond, is in the deep part of the earth about 2000 ℃ high temperature, 50, 000 atmospheric pressure under the conditions of formation of a monolithic crystal composed of carbon elements, often contains a variety of impurities and inclusions, of which nitrogen (N) and boron (B) for the most important impurities, according to the nitrogen and boron in the diamond in the content and the form of the existence of the diamond will be divided into four types --- Ⅰ - a type, Ⅰ - b type, Ⅱ - a type, Ⅱ - b type. - Ⅰ - a type, Ⅰ - b type, Ⅱ - a type, Ⅱ - b type. Diamond for diamond luster, refractive index of 2.417, isometric crystal system, homogeneous body, polarized mirror often abnormal birefringence phenomenon, relative density of 3.52, with a strong fire color, dispersion value of 0.044, Cape series diamonds have 415nm (N3) absorption line.

2.3.1 Natural diamonds

Natural diamonds in the cathodoluminescence can be different strengths of blue, gray, purple, yellow-green or in the form of their combination of colors, and the color is uniform, patchy, parallel stripes or geometric polygonal stripes distribution. Under cathodoluminescence, the characteristics of the growth structure of diamonds are visible. [4]

2.3.2 Irradiation-treated diamonds

Irradiation-treated diamonds are basically the same as natural diamonds under cathodoluminescence, but some have strong orange CL characteristics, and the cathodoluminescence intensity of irradiated diamonds is enhanced.

2.3.3 Synthetic Diamonds

Chemical vapor deposition method (CVD) synthesized diamonds under the cathodoluminescence no phenomenon.

The cathodoluminescence spectrum of chatham synthesized diamonds has UV CL peaks with peak wavelengths of about 234, 268nm and so on. Under the cathodoluminescence, the synthetic colorless diamond is very weak blue-purple fluorescence, can show the growth zoning structural features, the center part of the parallelogram-shaped seed crystals, seed crystals in the cathodoluminescence shows a strong grayish-white; synthetic blue diamond is a very weak blue-gray fluorescence, the growth of the zoning features are obvious, can be seen to have the seed crystals in the form of parallelograms. The obvious difference between seed crystals and synthetic diamonds under cathodoluminescence is that the cathodoluminescence spectra of seed crystals do not have UVCL peaks at 234 and 268 nm, and the fluorescence intensity of seed crystals is much higher than that of synthetic diamonds. [4]

2.4 Pearls

Pearl is composed of inorganic components, organic components and water, inorganic components are mainly aragonite, and contains very little calcite and trace elements, such as Na, K, Mn, Sr, etc., organic components are hydrocarbons - mainly hard proteins, including more than a dozen amino acids, a small amount of porphyrin and so on. The pearl has concentric radio-layered aragonite lamellar structure, its shape is generally round, oval, shaped, color is the result of body color, companion color, halo. The pearls are pearly luster, translucent - opaque, heterogeneous aggregate, refractive index 1.500~1.685, the density of cultured freshwater pearls is 2.74g/cm^3, the density of cultured seawater pearls is 2.72~2.78g/cm^3.

2.4.1 Cultured pearls with pits

Under cathodic luminescence, the nacre of fresh water nucleated pearl showed weak to strong green fluorescence, and the untreated pearl surface and pearl cross section showed strong red fluorescence. The intensity of the green fluorescence showed a certain regularity, while the red fluorescence appeared irregularly, which may appear as a small ball at the junction of the pearl layer and the pearl nucleus, may appear in the pearl material, or may appear as a patch on the pearl surface. The color intensity of the cathode luminescence corresponds to the energy of the crystal, the higher the color intensity, the higher the energy of the crystal, the more unstable the crystal. Under cathodic luminescence, the nacreous layer of nucleated pearls in seawater is usually not luminous, while the nucleated pearls show different degrees of green fluorescence.[5]

2.4.2 Seedless cultured pearls

Under the cathode ray, the fresh water nucle-free pearls of various colors have medium to strong green fluorescence, and the heterogeneous materials have strong green fluorescence. The pearl layer of seawater pearls of different colors showed no extremely weak fluorescence. The luminescence of cultured pearls is mainly related to the content of trace transition elements such as Mn and Sr. Mn2+ is a luminescent activator in inorganic aragonite and calcite, and the radius of Mn2+ is close to Ca2+, which easily replaces Ca2+ and enters the lattice. Mn2+ transitions from the excited state to the ground state due to the action of cathode rays. Emit photons with frequencies in the visible light range, thus producing yellow and green light under cathode ray excitation; Sr2+ has a quenching effect on cathodic luminescence in inorganic aragonite and calcite, and does not emit luminescence under cathodic luminescence. The luminescence of cultured pearls may be related to the ratio of the contents of activator and quencher, and the different contents of trace transition elements lead to different characteristics of cathode luminescence. [6]

2.4.3 Irradiated pearl

Irradiated freshwater cultured pearls of different colors all turn black or gray, because irradiation will oxidize the Mn^{2+} rich in freshwater cultured pearls to Mn^{3+} or Mn^{4+}, resulting in color change. Microscopic observation under cathodoluminescence showed that the nacre was cracked and lamellar peeling after irradiated freshwater cultured pearls, while the mariculture pearls were Mn poor, and the nacre color did not change after irradiation, nor did they emit light under cathode rays.[6]

3. Conclusion

According to the different colors, luminous intensity and images presented by gemstones under cathodoluminescence, it can be used to understand the structure of gemstones, including their lattice defects, to quickly and non-destructively identify the species of gemstones, to determine the types, valence and quantities of trace elements, and to explore the environment of crystal growth and the conditions of formation, etc.

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