1. Introduction

Chatoyancy, known as the cat’s eye effect, is a special optical effect referring to a bright band on the surface of gemstones caused by the reflection of light. Its characteristics depend on the type, size and concentration of the inclusions. Chatoyancy is often observed in gemstones such as chrysoberyl, tourmaline and moonstone; however, it is rarely observed in sapphires.1,2 The research on the chatoyancy of sapphires is relatively rare; thus, it is necessary to investigate it innovatively.

Sapphire is categorised in the corundum (Al₂O₃) group, which belongs to the trigonal system.3 As a gemstone, sapphire is one of the most valuable gemstones and is produced in many countries worldwide, for example, Myanmar, Thailand, Sri Lanka, Australia, etc.4-7 The sapphire ores in the Shandong province are the largest reserves and have the best quality in China; it is located in the western part of the Tan-Lu fault zone, southeast of the North China Craton.8 To the best of our knowledge, the gemological properties, mineralogical properties, chromogenic mechanism, color modification and inclusion study of Shandong sapphires have been investigated systematically and thoroughly.9-11 Based on the analysis of the relationship between basalt and corundum formation,12,13 scholars believe that the sapphires of the Shandong province crystallize in the early alkaline basalt magma rich in Al and poor in Si at a great depth under high pressure.14 One of the most prominent features of the sapphires obtained from Shandong is the coexistence of primary and secondary ores; this area mainly contains magmatic-type sapphires, which are mainly distributed in the central part of Shandong.15,16 Besides, Shandong sapphires are rich in solid inclusions and fluid inclusions. The solid inclusions include zircon, corundum, feldspar, spinel, and rutile;17 the fluid inclusions are mainly CO₂, H₂S and N₂, which can indicate the composition of the corundum magma system.18

In addition, the analyses of Shandong sapphires show Fe as the main chromophore, with minor Ti, which is one of the important reasons for the deep color of the Shandong sapphire.19 Another important feature of the Shandong sapphire is the well-developed color zones, showing hexagonal, angular and flat color belts in the direction vertical to the C axis.19 The direct formation of a color belt in sapphires is related to the fluctuation of Fe²⁺ concentration.20 Because the Shandong sapphire is darker in color, according to the Mössbauer spectrum data, the color can be improved by increasing the Fe³⁺/Fe²⁺ ratio with oxidation or reduction.

Shandong sapphires commonly show special optical effects such as asterism;21 however, they rarely show chatoyancy. Asterism of the Shandong sapphire is caused by directional acicular rutile inclusions,8 but to the best of our knowledge, the formation mechanism of chatoyancy in sapphires remains unclear. To clarify this issue, the mechanism of chatoyancy of the sapphires of Shandong has been...
analyzed typically. Sapphires have long received attention as technologically sensitive materials because of their mechanical and optical properties; thus, sapphires are widely valued in the material industry.\textsuperscript{22–25} Considering the importance of sapphires, it is necessary to study them in all aspects, including their special optical effects. The aim of this study was to help determine the classification, systematic study, and quality evaluation of sapphires and provide research ideas for the cause analysis of cat’s eye phenomena of other gemstones.

2. Materials and methods

Seven Shandong sapphire samples, showing slightly different chatoyancy, were collected (Fig. 1), and the descriptions of the samples are shown in Table 1. The samples were polished to a cabochon cut and divided into two groups according to their color and chatoyancy effects: greenish-blue series A and yellowish-green series B.

All sapphire samples were investigated using gemological methods, spectroscopic analysis and chemical analysis. Conventional experiments were conducted in the Gem Testing Laboratory of the Gemological Institute, China University of Geosciences, Beijing. Ultraviolet-visible spectrophotometry was carried out with a Shimadzu UV-3600 UV-Vis spectrophotometer (200–900 nm, high speed, 0.5). An EDX-7000 Energy Dispersive X-ray fluorescence spectrometer was used (50 kV, 113 μA, 30% DT). The microstructure was observed using geological microscopy, polarizing microscopy, and SEM (Zeiss Ultra Plus, acceleration voltage from 10 to 15 kV, 1 atm, 5–15 mm). An HR-Evolution Laser Microscopic Raman Spectrometer of HORIBA (200–4000 cm\(^{-1}\), excitation wavelength of 532 nm, laser energy of 100 mW, resolution of 1 cm\(^{-1}\)) was used to measure the samples’ chemical composition. Samples were tested by infrared spectroscopy with a Tensor 27 Fourier Infrared Spectrometer (4000–100 cm\(^{-1}\), 210–230 V, 50–60 Hz, reflection method).

3. Results

3.1 Gemological properties

The samples in series A exhibited poor transparency and showed a large number of inclusions when observed with the naked eyes. The light band of A1 and A2 was bright and thick, whereas that of A3 and A4 was slightly thinner. The physical and chemical properties of sapphire in the Changle area are similar.\textsuperscript{19} The color distribution of series A was uneven with color zones. All samples exhibited refractive index of 1.76 and similar.

3.2 Microscopic observation

Microscopy images show many fracture surfaces in almost all the samples of series A and B. The fractures have approximately parallel orientations (Fig. 2a) with a mass of fluid inclusions above (Fig. 2b), and the light band is perpendicular to them. Large amounts of multiphase inclusions lead to a misty, translucent, and uneven appearance (Fig. 2b).

The light band of sample A1 was oriented parallel to the straight color belt and from previous studies, it is clear that the color belt of a sapphire is compatible with its crystal structure. Series B showed large numbers of veil-like and fingerprint-like microinclusions. Fluid inclusions tend to be clustered and distributed on the fracture surface; these are mostly colorless, transparent, and irregular in shape. Under a spotlight, series A showed a thick light band (Fig. 2c). Sample B2 showed a thin light band and under 40× magnification, dense twin striae perpendicular to the light band and arranged in a regular straight orientation were seen (Fig. 2d). The corundum with more developed cracks means obvious late melt infiltration metasomatism.\textsuperscript{26} In a previous report, a systematic study was performed to investigate the effect of crystallographic orientation on the
deformation and cracking of sapphires by means of nano-indentation using spherical indenters.\textsuperscript{27} The study of the composition and properties of deep fluids has become one of the hotspots in recent years. Besides, the fluid components in inclusions or crystal gaps are the real records of the fluids in the earth.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Color</th>
<th>Weight</th>
<th>Relative density</th>
<th>Morphology</th>
<th>Description of light band</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Blue-green</td>
<td>7.90 ct</td>
<td>4.000</td>
<td>Oval cambered</td>
<td>Thin, inflexible</td>
</tr>
<tr>
<td>A2</td>
<td>Greenish-blue</td>
<td>6.80 ct</td>
<td>4.018</td>
<td>Water drop profile</td>
<td>Thick, inflexible</td>
</tr>
<tr>
<td>A3</td>
<td>Blue-green</td>
<td>4.47 ct</td>
<td>3.994</td>
<td>Oval cambered</td>
<td>Thin, inflexible</td>
</tr>
<tr>
<td>A4</td>
<td>Blue-green</td>
<td>4.74 ct</td>
<td>3.986</td>
<td>Oval cambered</td>
<td>Thin, inflexible</td>
</tr>
<tr>
<td>B1</td>
<td>Yellowish-green</td>
<td>1.48 ct</td>
<td>4.012</td>
<td>Oval cambered</td>
<td>Thin, bright, and flexible</td>
</tr>
<tr>
<td>B2</td>
<td>Greenish-blue</td>
<td>2.31 ct</td>
<td>4.029</td>
<td>Water drop profile</td>
<td>Thin, bright, and flexible</td>
</tr>
<tr>
<td>B3</td>
<td>Yellowish-green</td>
<td>1.97 ct</td>
<td>4.025</td>
<td>Water drop profile</td>
<td>Thin, bright, and flexible</td>
</tr>
</tbody>
</table>

Fig. 2 Microscopy images of samples: (a) fractures of sample A3, (b) fluid inclusions of sample A2, (c) fracture surfaces of sample A2, (d) dense twin striae of sample B2, and (e and f) microfractures in polarizing microscopy with single polarization.
3.3 Polarizing microscopy

Because some samples are gemstone grade and cannot be treated destructively, a representative sample A1 was selected to be cut into two 0.03 mm form chips along two directions: parallel and perpendicular to the light band. Sample A1 showed straight light band parallel to the angular color belt. The bottom plane of the sample was vertical to the c axis, and the direction of the chips is the direction of 1210 and 1010. Sample A1 showed directional microfractures under a polarizing microscope (Fig. 2e) and no obvious solid inclusions above the fractures.

When observed with a higher magnification, the microfractures showed abundant directional fluid inclusions that were irregular, elliptic, or beaded in shape (Fig. 2f). They were interconnected and formed a crisscross network. The elongated forms of the fluid inclusions indicate fluid flow along the fissure during crystal growth and the instability of the crystalline environment. This envelope is oriented along the closed intra-crystal fissure and is a false secondary cause. Such symmetrical cracks are believed to be caused by defects and dislocations during growth and not by dendrite growth.

3.4 Scanning electron microscopy

SEM was used to observe the micromorphology of the sample surface; a representative sample A1 was selected for SEM tests. The sample structure was tight with a smooth fracture surface; a representative sample A1 was selected for SEM tests. SEM was used to observe the micromorphology of the sample. A1 showed directional microfractures under a polarizing microscope (Fig. 2e) and no obvious solid inclusions above the fractures.

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3.5 XRF

XRF detection was carried out on the samples, and the data of element composition and the spectra of each sample were obtained. The 10 elements with higher content in the samples were summarized and arranged in the form of oxides (Table 2).

Sapphire is an allochromatic mineral whose trace element concentration depends on the origin and has influence on the color. The results of XRF showed that the highest content of Al2O3 is about 97%–99%, which is the main component of the sample. Impurity elements exist in ionic lattices as isomorphic or mechanical mixtures, while Fe2O3 and SiO2 contents are higher, accounting for around 2% in total. The content of Fe oxides is slightly higher than that of SiO2, which is about 0.9–1.2%. Because of the close coordination radius and the same valence state as that of Al3+, Fe mainly exists in the form of Fe3+.

In addition, there are small amounts of transition metal ions such as Ti and Cr. Because of the relatively high content of Fe in the Shandong sapphire, the fluorescence of the sapphire will be inhibited, which is similar to previous gemological studies. The valence information of iron ions can be obtained from the difference in the total iron and titanium contents mentioned above. According to the principle of isomorphism, in order to replace Al3+ in sapphires, Ti4+ must replace two Al3+ ions at the same amount of Fe2+ to maintain charge balance. The proportion of Ti4+ and Fe2+ should be close to 1 : 1; thus, the most dominant element in total iron should be Fe3+.

3.6 UV-Vis spectra

The characteristics of the absorption spectra of different color varieties were investigated by ultraviolet-visible (UV-Vis) absorption spectroscopy. The absorption peaks of all samples were mainly concentrated in the following four regions: 200–400 nm, 430–470 nm, 520–600 nm and 710–800 nm (Fig. 4). Except for the clear absorption peaks in the second region, the other three regions showed wide absorption bands and a few absorption peaks. The intensities at 377 and 452 nm in the UV-Vis spectrum of A1 were stronger than that of A3 and A4.

Fig. 3  Straight growth lines (left) and hexagonal growth texture (right) of sample A1.
Pure $\alpha$-Al$_2$O$_3$ should be colorless because of no selective absorption of light but precisely because of the complexity of geological conditions, corundum generally contains trace impurity elements such as Fe, Ti, Cr, Ni, and Mn. These impurity elements can exist in the form of isomorphism in the crystal lattice of sapphire, and light waves can be selectively absorbed in the crystal structure, finally showing the corresponding color.

According to the XRF data, the main chromogenic element in sapphires is Fe, which can exist in the bivalent or trivalent state. The essence of Shandong sapphire color formation is the result of the interaction of absorption mechanisms such as Fe$^{3+}$, Fe$^{2+}$–Ti$^{4+}$, Ti$^{3+}$, Fe$^{2+}$–Fe$^{3+}$, and Fe$^{2+}$–O$^{2-}$–Ti$^{4+}$. The green tone in sapphires is the result of the superposition of yellow tone and blue tone. The former is generally considered to be due to the interaction of Fe$^{3+}$–Fe$^{3+}$ coupled ion pairs, while the latter is related to the electron transfer of Fe$^{2+}$–Ti$^{4+}$. The absorption peaks at 375, 387 and 450 nm can be attributed to the transition of 6A$_1$–4A$_1$ 4E (G) of Fe$^{3+}$ and the broadband absorption around 500–700 nm is caused by the charge transfer between Fe$^{2+}$ and Ti$^{4+}$. The spectrum is smooth. The absorption peaks of the samples are observed around 472 cm$^{-1}$, 622 cm$^{-1}$, 665 cm$^{-1}$, 700 cm$^{-1}$, 811 cm$^{-1}$ and 870 cm$^{-1}$ (Fig. 5), while the peak at 472 cm$^{-1}$ is sharper. Actually, the stretching and bending vibrations of Al–O result in these special peaks.

Since the infrared spectra mainly reflect the vibrational information of a mineral skeleton structure, for the samples in this experiment, the chemical composition and crystal structures of gemstones were almost unchanged, which could explain why the infrared spectra of gemstones were very similar. According to previous analysis, transition metal ions such as Fe, Ti and Cr will replace few Al ions and occupy their positions, causing a change in vibration because of the difference in radius, atomic spacing and bonding force between these transition metal ions and Al ions, which is reflected in the shift in the characteristic absorption peaks in the spectra.

### 3.8 Raman spectra

All samples were tested by Raman spectroscopy, and samples of different colors had similar Raman spectra but slightly different locations. The color differences indicate differences in the concentrations of chromogenic ions in the samples. The Raman shift is a characteristic feature because of the difference in the bond energies and bond lengths of the impurity ions, such as Fe$^{3+}$, Fe$^{2+}$, and Ti$^{3+}$, which replace Al$^{3+}$ in the isomorphic mode. However, such ionic substitution did not cause significant changes in the main vibration modes of the samples, thus the distribution and strength of the wave crest of the Raman spectra remained regular.

### Table 2  X-ray fluorescence spectrum data of samples

| Content (%) | Al$_2$O$_3$ | Fe$_2$O$_3$ | SiO$_2$ | SO$_3$ | TiO$_2$ | Ga$_2$O$_3$ | K$_2$O | CaO | CuO | Cr$_2$O$_3$
<table>
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</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>97.601</td>
<td>0.940</td>
<td>1.125</td>
<td>0.287</td>
<td>0.023</td>
<td>0.024</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A3</td>
<td>98.716</td>
<td>0.926</td>
<td>—</td>
<td>0.311</td>
<td>0.023</td>
<td>—</td>
<td>0.008</td>
<td>0.012</td>
<td>0.004</td>
<td>—</td>
</tr>
<tr>
<td>B1</td>
<td>97.484</td>
<td>1.219</td>
<td>0.920</td>
<td>0.323</td>
<td>—</td>
<td>0.026</td>
<td>0.016</td>
<td>0.010</td>
<td>0.002</td>
<td>—</td>
</tr>
<tr>
<td>B2</td>
<td>97.470</td>
<td>1.063</td>
<td>0.940</td>
<td>0.400</td>
<td>0.038</td>
<td>0.020</td>
<td>0.059</td>
<td>0.006</td>
<td>—</td>
<td>0.003</td>
</tr>
<tr>
<td>B3</td>
<td>97.659</td>
<td>1.077</td>
<td>0.960</td>
<td>0.263</td>
<td>—</td>
<td>0.033</td>
<td>—</td>
<td>0.008</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Fig. 4  Data of UV-Vis spectra of samples (a) for series A, (b) for series B.
For example, samples A3 and B3 exhibit typical Raman displacement of a sapphire mainly concentrated at 300–800 cm\(^{-1}\). The samples showed similar spectra with characteristic peaks caused by seven Raman-active vibrations of Al\(_2\)O\(_3\) located at 748, 645, 575, 450, 416, 432, and 378 cm\(^{-1}\) (Fig. 6).\(^{28,32,33}\) The peak caused by the A\(_{1g}\) vibration of Al\(^{3+}\) displacement at 416 cm\(^{-1}\) was the strongest and sharpest peak.

The intensity of a Raman peak is positively correlated with the ion concentration to some extent. The content of Fe was the highest except that of Al according to XRF, which was also reflected in the spectra. The peak at 245 cm\(^{-1}\) is caused by the E\(_g\) vibration of Fe\(^{3+}\) displacement, while the Raman displacement of Fe\(^{2+}\) observed mainly at 426 cm\(^{-1}\) is not found in the spectogram, which shows that Fe mainly exists in the form of Fe\(^{3+}\) in the sample.

In addition, characteristic absorption peaks of the solid inclusions were not detected in the microscopic Raman test. Thus, we concluded that the Shandong sapphire's chatoyancy was not caused by solid inclusions as thought previously.

4. Discussion

The effects of structure and composition on the genesis of the cat's eye effect of sapphire were comprehensively analyzed. Unlike the chatoyancy effect of other gemstones, which is typically caused by parallel needle-like or tubular inclusions, one of the formation mechanisms of the cat's eyes effect in sapphire involves a large number of internal parallel fracture surfaces. Microscopic observations revealed abundant irregularly shaped multiphase inclusions gathered together, forming a complex fingerprint network, and chatoyancy appears because of the existence of such directional fluid inclusions. We can orientate the chatoyancy effect through some samples' color belt. The light band of the sample is parallel to the straight color belt, while the direction of the color belt is consistent with the hexagonal cylinder, that is, the direction of the healing crack is perpendicular to the color belt. Therefore, the distribution of the healing fissure tends to be vertical to the hexagonal cylinder of a crystal. The SEM results showed only finely laminated growth lines and no solid inclusions. In contrast, if the light band was caused by directional solid inclusions as assumed, SEM observations should show the existence of solid inclusions, but they were not observed. Raman spectroscopy also revealed no solid inclusions, verifying the observations from SEM.

The results of the XRF test showed that the main component of the sample was Al\(_2\)O\(_3\) and its content was the highest: about 97–99%. The contents of Fe and Si were higher than those of other impurity elements. On the basis of the XRF data, the ultraviolet spectra analyzed the coloration mechanism of the samples. It was found that there were clear single absorption peaks at 452 and 377 nm produced by the crystal field spectra of Fe\(^{3+}\) related to the d-electron transition. The wide absorption band at 710–800 nm was related to the charge transfer of Fe\(^{2+}\)–Fe\(^{3+}\), indicating that the origin of the samples is basalt. In summary, we can conclude that Fe is mainly present in the form of Fe\(^{3+}\) in the sapphires obtained from Shandong. Infrared spectroscopy shows the vibration information of the mineral skeleton structure of a sample. For the samples studied in this paper, the mineral structures were basically unchanged.

Chatoyancy results because of the light reflection on the parallel fracture surface. Different cutting orientations may result in differences in the thickness and direction of the light band. However, the light band is not sharp because the
inclusions are not dense enough. Overall, the study results indicate that chatoyancy is caused by fluid inclusions as well as fracture surfaces.

5. Conclusion

A sapphire’s chatoyancy is a special optical effect among corundum materials. Chatoyancy appears because of the abundant gas–liquid inclusions in fracture surfaces. The chemical and physical characteristics and inner structures of sapphire samples were analyzed using microscopic observations, polarizing microscopy, SEM, and Raman spectroscopy. The results showed that one of the causes of chatoyancy in the Shandong sapphire is the large number of internal parallel fracture surfaces and the existence of such directional fluid inclusions. When the cambered gemstone was illuminated by a point light, the light reflected off the surface of the parallel cracks intensively, thus forming a bright light band on the top of the convex gemstone.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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