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Chameleon 钻石与其相似黄色钻石光谱学特征的对比分析及颜色成因

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摘要：Chameleon 钻石(俗称“变色龙钻石”)是一种具有光致变色和热致变色现象的彩色钻石，在受热后或长时间在暗室中会由黄绿色变为黄色，在实际工作中发现与 Chameleon 钻石颜色相似的黄色钻石并不具有此类“变色”现象。为了研究 Chameleon 钻石与相似黄色钻石的差异，并进一步探究产生光致变色和热致变色现象的原因，本文选取 Chameleon 钻石和与其颜色相似的黄色钻石作为研究对象，进行加热实验，观察加热前后钻石颜色、紫外可见光吸收光谱的变化情况，探寻导致热致变色的原因，并对样品的红外吸收光谱及光致发光光谱特征进行详细分析与比较。结果表明：Chameleon 钻石受热后由黄绿色变为黄色，在超短波紫外线下显示绿色荧光和磷光，相似黄色钻石样品无磷光及变色现象；所有样品均有从紫外光至 510nm 逐渐减弱的连续吸收和 480nm 吸收宽带，Chameleon 钻石具 650~800nm 吸收宽带，相似黄色钻石无该吸收带，加热后吸收带消失是其产生热致变色的主要原因；进一步对样品的缺陷类型进行对比分析，Chameleon 钻石红外光谱可见孤氮特征及与片晶无关的 1430cm^{-1} 宽吸收带，该峰未在相似黄色钻石中出现，但产生该吸收的原因未知，仍需进一步研究，此外与 Chameleon 钻石相比，相似黄色钻石中氮杂质的聚合程度更高；Chameleon 钻石及相似黄色钻石表现出以 700nm 为中心的特征发光带，此外 Chameleon 钻石还可检测到 H3 等与 N-V 相关缺陷及 489、883、884nm 等与 Ni-N 相关缺陷产生的发光峰。综合以上光谱学特征对比分析可知，Chameleon 钻石存在与 A 型氮、孤氮、镍杂质及氢杂质有关的某种缺陷结构，与相似黄色钻石的光谱特征具有明显差异。本次研究对探明 Chameleon 钻石具热致变色现象的根本原因具有参考意义。

关键词：Chameleon 钻石；黄色钻石；480nm 中心；紫外可见光吸收光谱；红外吸收光谱；光致发光光谱；镍杂质

要点：

(1)Chameleon(变色龙)钻石具有特征的 650~800nm 吸收带及与片晶无关的 1430cm^{-1} 吸收峰，与相似黄色钻石的光谱特征具有明显差异。

(2) 480nm 及 650~800nm 吸收宽带较差的热稳定性，是 Chameleon 钻石具有热致变色现象的主要原因。

(3)Chameleon 钻石中存在与孤氮、A 型氮、氢杂质和镍杂质相关的某种缺陷，为进一步研究该类钻石热致变色现象的根本原因提供了基础。

中图分类号：P585；P575.4　　**文献标识码：**A

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钻石中含有大量的杂质元素，如氮、氢、镍、硅等，不同杂质元素及其相互组合形成钻石中各类缺陷色心，缺陷色心吸收不同波段的可见光，从而导致钻石产生不同颜色[1]，除了丰富多彩的颜色，极少部分钻石还具有光致变色和热致变色现象，即 Chameleon 钻石（俗称“变色龙钻石”）。Chameleon 钻石的光致变色和热致变色现象（以下简称“变色现象”）与其他宝石（如变石等）具有的，在不同光源下表现出不同颜色的现象不同，将 Chameleon 钻石长时间放置在暗室中或加热钻石，可由黄绿色变为黄色，当钻石冷却后恢复原来颜色。除了本文研究的 Chameleon 钻石之外，含高浓度 Si 杂质的 CVD 合成钻石[2]、部分粉色钻石[3] 等也具有光致变色现象，这是由于钻石受光照后缺陷色心发生改变，从而导致颜色发生变化。

前人对于 Chameleon 钻石的研究主要集中在光谱特征，通过大量样品的测试，总结出 Chameleon 钻石的宝石学及光谱学特征，并对其变色现象的原因进行探索。Hainschwang 等[4] 将 Chameleon 钻石进一步划分为“Classic Chameleon”钻石和“Reverse Chameleon”钻石，其共同特征为在短波紫外线下具有弱到中等的黄色磷光，钻石类型为 IaAB 型，即钻石中氮杂质以 A 型氮和 B 型氮为主，具有较强的与氢相关缺陷，两种 Chameleon 钻石中 A 型氮和 B 型氮的相对含量明显不同，紫外可见光吸收特征亦不相同，绿色“Classic Chameleon”具有 415nm 吸收峰（N3 心）及 480nm 和 775~825nm 宽吸收带，“Reverse Chameleon”则具有 415、478nm 吸收峰（N3、N2 心）及 750~800nm 宽吸收带，两种 Chameleon 钻石均具有镍杂质相关缺陷及与 480nm 缺陷相关的特征发光峰。蒙宇飞等[5] 对 Chameleon 钻石进行扫描电镜能谱、X 射线荧光光谱等谱学研究，发现钻石晶格中含有镍、钴杂质，产生变色的原因主要为浅色心的产生与湮灭；Fritsch 等[6-7] 总结了 Chameleon 钻石的特征，包括持久的黄色磷光，具有 480nm 吸收带，氮杂质以 A 型氮为主等，并首次提出一个模型试图解释 Chameleon 钻石的热致变色和光致变色现象，推测变色现象很可能与钻石中的氮-氢杂质缺陷有关；Ardon 等[8] 发现了一粒绿色 Chameleon钻石具有与镍杂质相关的吸收峰，再次证明了 Chameleon 钻石中含有镍杂质。前人研究发现的 Chameleon 钻石特征在少数黄色钻石中也同样具备，Breeding 等[9] 在研究 480nm 缺陷致色的天然黄色钻石发现，其在短波紫外线下具黄色荧光和磷光，氮含量较低，具有较强的氢、镍杂质相关缺陷等特征，但其并无明显的变色现象。

为了研究 Chameleon 钻石与相似黄色钻石的异同点，进一步探索 Chameleon 钻石具有变色现象的原因，本文收集了 2 粒 Chameleon 钻石及与其相似的 4 粒黄色钻石样品，通过宝石显微镜观察加热前后样品颜色的变化，通过 DiamondView^{TM} 观察样品在超短波紫外线下的荧光、磷光特征及生长结构，通过对比加热前后样品紫外可见光吸收光谱的变化情况，分析 Chameleon 钻石与相似黄色钻石吸收光谱的差异，探究产生变色现象的原因，同时通过红外光谱及光致发光光谱分析 Chameleon 钻石与相似黄色钻石中的杂质元素及缺陷类型的差异，旨在对产生变色现象的缺陷结构有更深一步的认识。

1　实验部分

1.1　实验样品

本次研究样品为 6 粒天然黄色钻石，包括：Chameleon 钻石样品 2 粒，编号为 ChaD1、ChaD2；相似黄色钻石样品 4 粒，编号为 YD1~YD4。6 粒样品均为水滴形刻面，质量为 0.13~0.18ct，由珠宝公司借用，产地来源未知，本次研究样品数量有限，测试数据结果不能涵盖所有 Chameleon 钻石及其他黄色钻石。为了观察热致变色现象，分别对 6 粒样品进行加热，加热温度约 400℃，加热时间约 1min。

1.2　测试仪器及工作条件

本次研究主要采用宝石显微镜、荧光灯、DiamondView^{TM}、紫外可见光吸收光谱仪、红外光谱仪、激光拉曼光谱仪对样品进行测试，测试内容、条件及仪器型号如下。

1.2.1　宝石显微镜观察样品内部特征

分别采用顶部照明和散射照明的方法对样品内部特征及颜色分布状态进行观察，放大倍数为 10~40 倍。

1.2.2　荧光灯观察样品荧光及磷光特征

使用普通荧光灯，观察样品在长波（365nm）和短波（254nm）下的荧光及磷光特征。

1.2.3　DiamondView^{TM}（钻石观测仪）分析

超短波紫外光源下（<220nm）观察钻石样品的荧光、磷光特征及生长结构，该仪器由 Diamond Trading Company（DTC）公司生产。测试条件为室温，能量 50%，光圈大小 90%。

1.2.4　紫外可见光吸收光谱分析

采集钻石样品在紫外光可见光范围内的吸收特

征，分析钻石样品的致色原因。采用广州标旗公司生产的 Gem 3000 紫外可见光光纤光谱仪，在加热前后采集样品光谱，采集范围为 300~1000nm。

1.2.5　红外光谱分析

测试钻石样品的红外光谱，分析钻石类型及杂质元素。采用美国 ThermoFisher 公司制造的 Nicolet iZ10 傅里叶变换红外光谱仪和 6×Beamcondensor 红外漫反射附件对样品进行透射扫描，光谱采集范围为 400~4000cm^{-1}，分辨率为 2cm^{-1}，扫描次数为 256 次。

1.2.6　光致发光光谱分析

采集样品的光致发光光谱(PL 光谱)，分析样品中微量杂质元素及缺陷类型。采用英国 Renishaw 公司制造的 InVia 型激光拉曼光谱仪，分别用 473nm、532nm、830nm 激光器在液氮温度下对样品进行测试，得到 PL 光谱。

2　结果与讨论

2.1　宝石学特征

通过宝石显微镜观察，样品 ChaD1、ChaD2、YD3、YD4 内可见暗色包体，YD1、YD2 内部洁净。6 粒钻石样品颜色分布均匀，未见沿八面体滑移面分布，由塑性变形导致的褐色色带[10]。加热后 ChaD1、ChaD2 由黄绿色变为黄色，YD1、YD2 由浅黄色变为褐黄色，而 YD3、YD4 颜色没有发生明显改变，YD1、YD2 虽然出现了一定程度颜色深浅改变，但是根据前人对于 Chameleon 钻石的颜色表述[7]，不能将样品 YD1、YD2 划分为 Chameleon 钻石。

在长波紫外光源(365nm)照射下，6 粒样品均表现出强黄色荧光，无磷光；在短波紫外光源(254nm)照射下，6 粒样品为弱黄色荧光，无磷光。本次研究样品在长短波紫外光下表现一致，但与前人研究认为 Chameleon 钻石有持久的黄色磷光[5]不同，根据对本次研究样品的荧光观察可以得知，Chameleon 钻石的变色现象与磷光现象并无直接联系。

钻石日常检测中，DiamondView$^{\mathrm{TM}}$ 常用于钻石生长结构的观察[11]，从而帮助判断钻石天然性及钻石类型[12]。在超短波紫外光源(＜220nm)激发下(图 1)，6 粒样品整体为绿色荧光，局部可见蓝色生长环带、亮绿色滑移线及荧光惰性区域，该特征与由 480nm 缺陷致色的黄色钻石[9]及镍杂质导致绿色钻石的发光图像相似[13]，蓝色荧光由 N3 缺陷发光产生[14]，而 H3 及镍杂质相关缺陷都可以产生绿色荧光[9,13]，因此仍需进一步进行光谱学测试。关闭光源后样品 ChaD1、ChaD2 为中等强度的绿色磷光，YD1、YD2 为弱绿色磷光，YD3、YD4 无磷光现象。

2.2　紫外可见光吸收光谱变化特征

选取样品 ChaD1、YD1 和 YD 3 分别代表 Chameleon 钻石、具轻微变色黄色钻石及不具变色现象黄色钻石，进行后续光谱学测试。紫外可见吸收光谱可以解释钻石的致色原因，天然黄色钻石主要致色原因有：孤氮中心致色，钻石中少量的取代单氮在 270nm 处产生极强吸收，该吸收可以延伸到可见光范围内，形成从紫外光至 510nm 逐渐减弱的连续吸收[15]，产生鲜艳的黄色；N3、N2 缺陷致色，被称为“Cape”型钻石，N3 由 3 个氮原子和 1 个空穴组成，零声子线位于 415nm，N2 常伴随 N3 出现，产生 478nm 处的吸收峰，其组合使钻石吸收蓝紫区可见光，使钻石呈现黄色[16]；H3 缺陷致色，H3 缺陷由 2 个氮原子和一个空穴组成，H3 的存在说明钻石经历过高温，常见于辐照退火处理和高温高压处理黄绿色钻石[17]，天然黄色钻石中亦可见 H3 缺陷，但其强度比处理钻石弱得多，且常伴随 550nm 宽带，使钻石常呈褐黄色[9]；480nm 宽带吸收常见于天然 Ib-Ia 型褐黄色钻石中，其缺陷结构未知，前人推断与晶格中氧原子有关[18]，处理钻石中未见。为了探究 Chameleon 钻石和相似黄色钻石的致色机理及颜色变化的原因，将 3 个样品及每个样品加热前后的紫外可见光吸收光谱进行对比分析。

样品 ChaD1、YD1 和 YD3 加热前紫外可见光吸收光谱(图 2a)表明，3 个样品均具 550~400nm 连续吸收增强的孤氮特征吸收，并叠加 480nm 吸收带。ChaD1 还可见明显 650~800nm 宽吸收带，结合孤氮特征吸收及 480nm 宽带，在 520~600nm 附近产生透过窗，使 ChaD1 呈现黄绿色。YD3 除 480nm 宽带，还可见延伸到 650nm 附近连续吸收，使 YD3 呈现褐黄色，由钻石晶格塑性变形导致的从近红外到紫外光逐渐增加的连续吸收是钻石产生褐色的主要原因之一[19]。YD1 则为黄色，不带有其他色调。根据加热前样品紫外可见光吸收光谱可知，所有样品均无与处理有关的 503.2、595、741、986nm 等吸收峰，且 480nm 吸收带从未出现在处理钻石中，可以确定本次样品颜色为天然成因。

样品 ChaD1 加热前后紫外可见光吸收变化较大(图 2b)，加热后 480nm 吸收带和 650~800nm 吸收

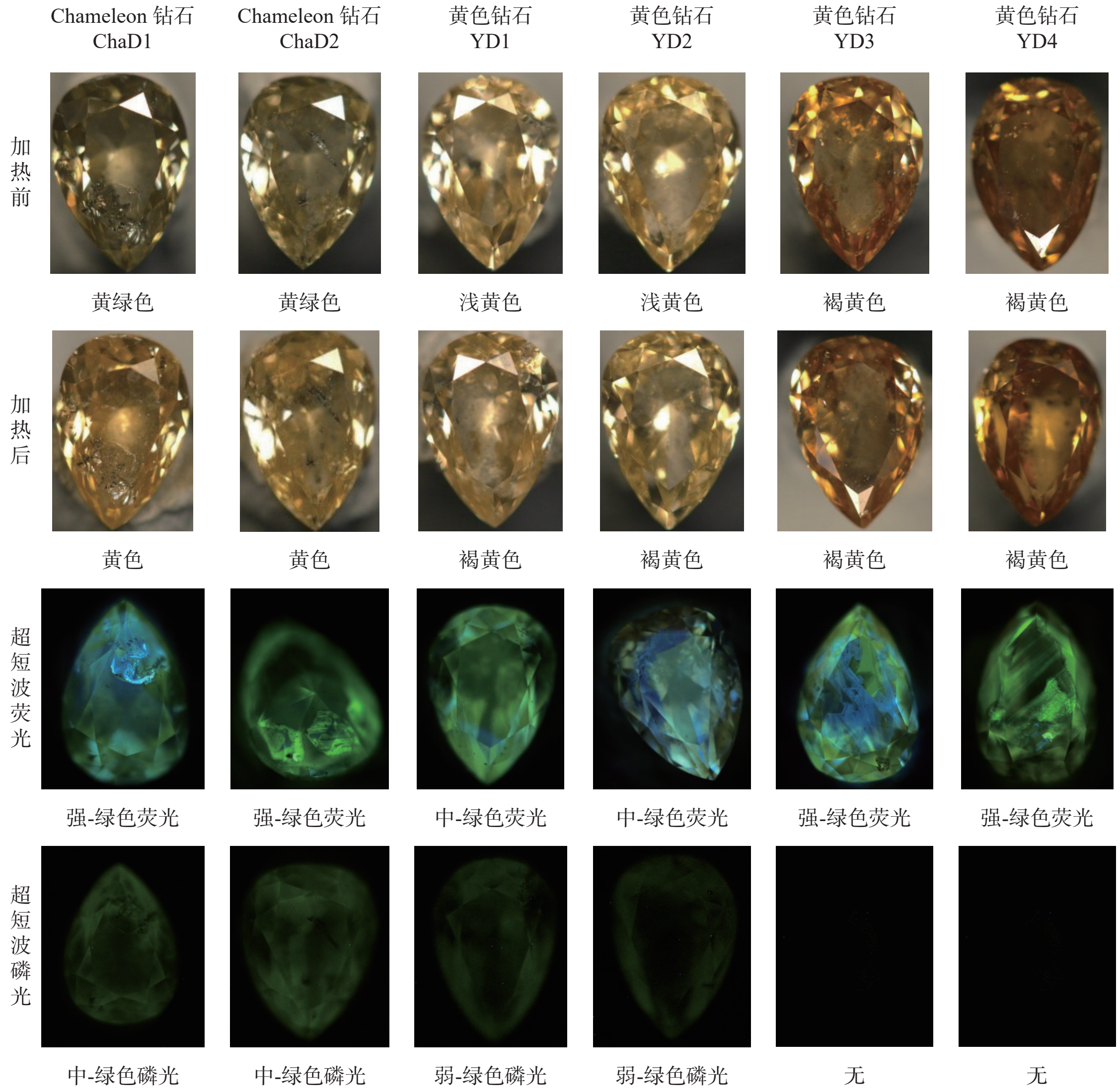
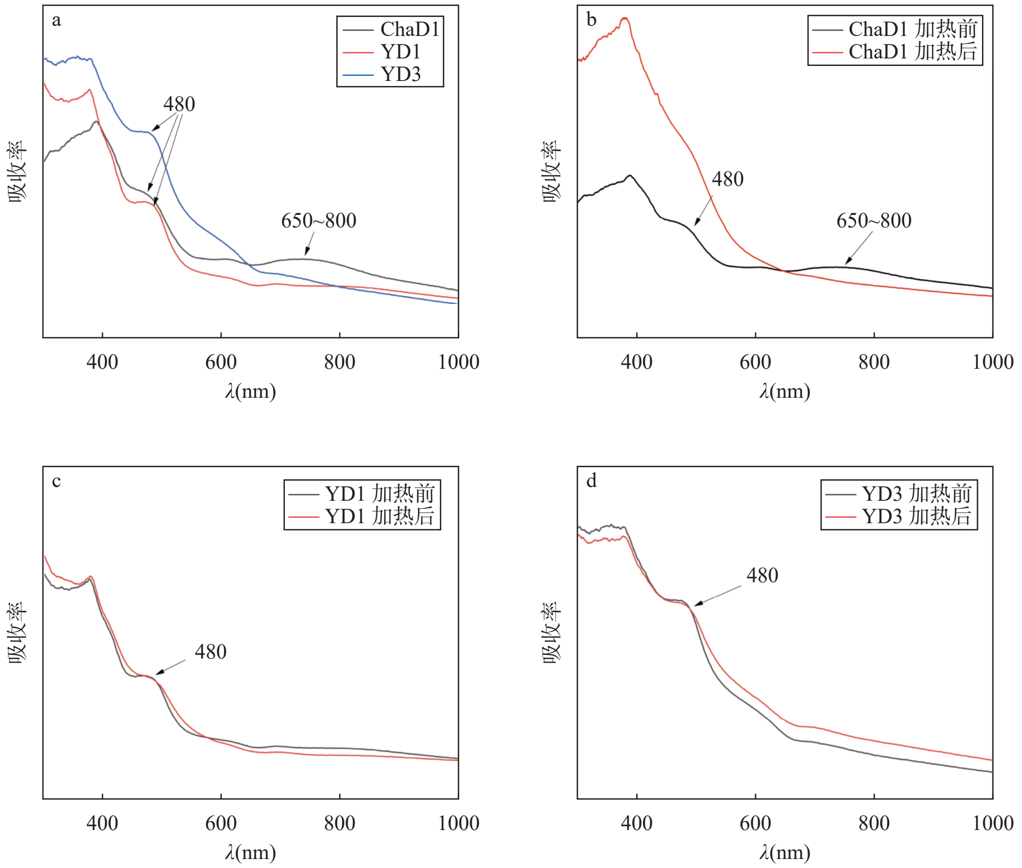


图1 Chameleon **钻石及相似黄色钻石样品加热前后颜色变化及在** DiamondView^{TM} **下的发光图像**

Fig. 1 Color change of chameleon diamond and similar yellow diamond samples before and after heating and luminescence images by ultra-violet light of DiamondView^{TM}. After heating, the chameleon diamonds showed obvious change, while the similar yellow diamond did not. Under ultra-violet light of DiamondView^{TM}, all samples showed green fluorescence, the chameleon diamond showed green phosphorescence, while sectional yellow diamond samples were phosphorescent inertia.

带几乎完全消失，400~550nm 连续吸收明显增强，钻石颜色也因此改变，加热后由黄绿色变为黄色。样品 YD1 加热前后紫外可见光吸收有轻微改变（图 2c），480nm 吸收带减弱，原本 400~550nm 连续吸收延伸到 600nm 附近，因此黄色减弱，褐色调增加，由原来的浅黄色变为褐黄色。样品 YD3 加热前后紫外可见光吸收无明显改变（图 2d），钻石颜色无变化。

根据 3 个样品加热前后紫外可见光吸收光谱对比后可知，虽然样品均存在 480nm 缺陷，但其 480nm 缺陷的热稳定性明显不同，在样品 ChaD1 加热后 480nm 完全消失，YD1 加热后有轻微减弱，而在 YD3 加热后 480nm 无变化，导致 480nm 缺陷热稳定性不同的原因仍需进一步研究。Fritsch 等[6]为解释 Chameleon 钻石的变色现象，提出了一种可能的电子跃迁模型，当钻石在暗室中缺陷中心能量最低（即基态），此时钻石为黄色，黄色为稳定态的颜色，当钻石曝露在可见光下，电子受到激发吸收能量，跃迁至激发态（Ea），随后电子很快落入势阱并被捕获（Eb），此时钻石为亚稳态的绿色。当势阱深度（Eb-Ea）远大于热活化能（kBT）时，电子跳出势阱的概率极低，在室温下，电子保持在亚稳定状态，此时钻石呈



a—样品 ChaD1、YD1 和 YD3 加热前后紫外可见光吸收特征对比； b—样品 ChaD1 加热前后紫外可见光吸收特征对比； c—样品 YD1 加热前后紫外可见光吸收特征对比； d—样品 YD3 加热前后紫外可见光吸收特征对比。

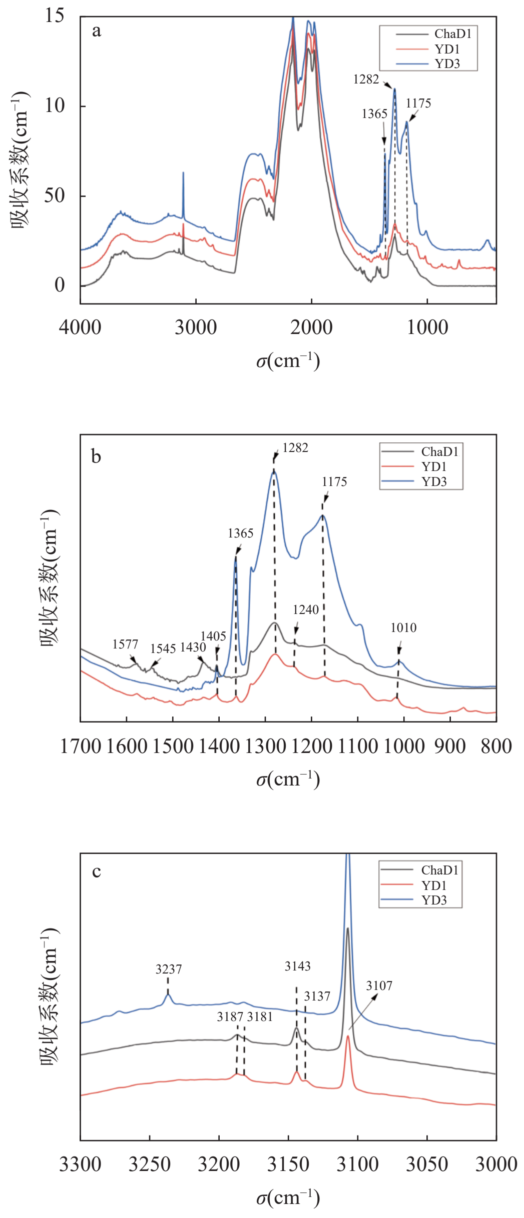
图2　样品 ChaD1、YD1 和 YD3 紫外可见光吸收特征

Fig. 2　UV-Vis absorption characteristics of ChaD1, YD1 and YD3 samples. a: Prior to heating, the samples have C defect absorption continuum and 480nm absorption band. In addition, the chameleon diamond has 650-800nm band. b: After heating the chameleon diamond ChaD1, the 650-800nm band disappeared, and the 480nm band significantly weakened. c and d: The change of similar yellow diamond sample was not obvious before and after heating.

绿色。当加热钻石，电子热活化能升高，从势阱中逃逸落回基态，钻石则恢复成黄色，利用该模型结合本次研究样品，样品 ChaD1 在常温下呈黄绿色，为其亚稳态，出现 650~800nm 吸收带。当受热后，电子热活化能升高，从势阱中逃逸落回基态，其 650~800nm 吸收带消失，钻石呈现黄色。

2.3　红外吸收光谱特征

红外光谱不仅可以用来区分钻石类型，还可以对其内部杂质元素(如氮、氢等)的存在形态及含量有明确的指示[20]。对光谱进行归一化后对比可以发现(图 3a)，样品 ChaD1、YD1 和 YD3 在一声子区(400~1500cm^{-1})范围内具 A 型氮吸收峰(1282cm^{-1})、B 型氮吸收峰(1175cm^{-1}、1010cm^{-1})，表明 3 个样品均为 IaA/B 型钻石[21]，并且 A 型氮强于 B 型氮，ChaD1 中 B 型氮的吸收峰最弱，1010cm^{-1} 吸收峰几乎不可见。ChaD1、YD1 总氮含量较低，YD3 总氮含量要明显高于 ChaD1、YD1。此外 YD3 还具有明显片晶峰(1365cm^{-1})，YD1 中片晶峰较弱，而 ChaD1 则未见片晶峰，ChaD1 中可见明显 1430cm^{-1} 吸收峰(图 3b)，其半峰宽较大，峰形不对称，不同于 Cape 型钻石中与片晶峰(吸收峰位于 1358~1378cm^{-1} 之间)有关的 1430cm^{-1} 吸收峰[22-23]，后者吸收较强且半峰宽较小，ChaD1 中无片晶峰吸收，则进一步证明此处 1430cm^{-1} 吸收峰与片晶峰无关。ChaD1 和 YD1 中还具 1240、1545、1577cm^{-1} 吸收峰，常见于 480nm 缺陷致色的褐黄色钻石中[24]，1240cm^{-1} 吸收峰的结构未知，是 Ib 型钻石特征指示[25]，与其紫外可见光吸收特征一致。



a—样品 ChaD1、YD1、YD3 红外光谱特征；b—样品 ChaD1、YD1、YD3 一声子区红外吸收特征；c—样品 ChaD1、YD1、YD3 中与氢杂质相关缺陷吸收特征。

图3　样品 ChaD1、YD1 和 YD3 红外光谱吸收特征

Fig. 3　The FTIR spectra of tested samples ChaD1, YD1 and YD3. a: ChaD1, YD1 and YD3 are all type Ia diamonds, the nitrogen concentration of similar yellow diamonds is significantly higher than that of chameleon diamonds. b: Chameleon diamond has the 1430cm^{-1} absorption, which has a different origin from the platelet-related 1430cm^{-1} feature. In addition, the similar yellow diamond has obvious aggregates of nitrogen absorption, while chameleon diamond shows a weak type Ib character. c: The hydrogen-related absorptions indicates chameleon diamond has a type Ib character.

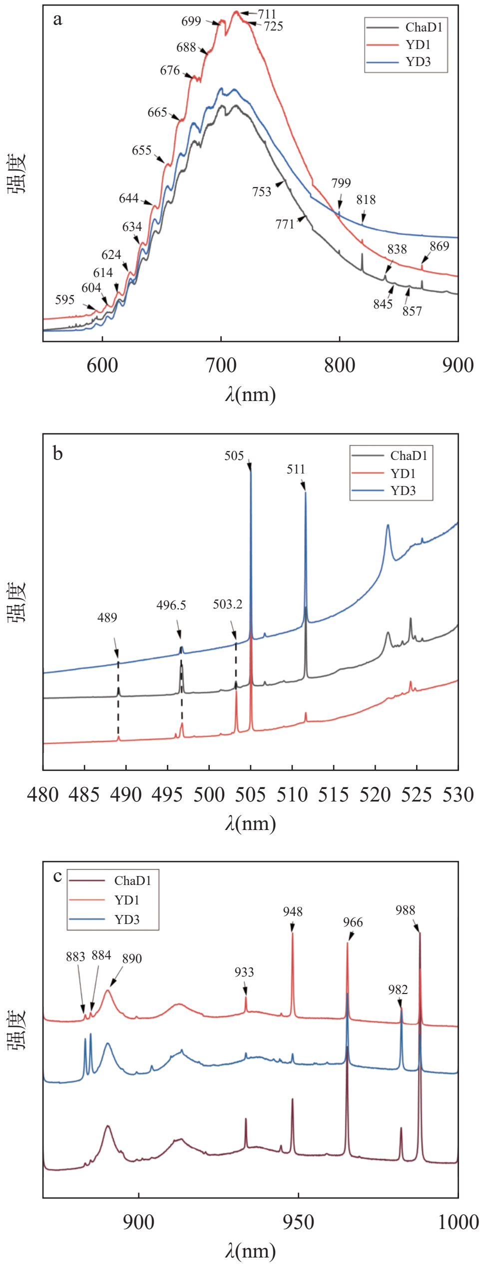
3 个样品中均可见 1405、3107cm^{-1} 等与氢杂质相关的缺陷，YD3 中 3107cm^{-1} 明显强于其他两者。3107cm^{-1} 缺陷结构为 VN$_3$H，天然、合成钻石及处理钻石中均可出现，天然钻石中 3107cm^{-1} 由 N3 中心捕获一个氢原子形成，说明该钻石中氮杂质聚合程度较高[26]，1405cm^{-1} 与 3107cm^{-1} 结构相同，振动模式不同，其强度与 3107cm^{-1} 呈线性关系[27]。除 3107cm^{-1} 外，3000~3500cm^{-1} 范围内还可见多个与氢杂质相关的吸收峰(图 3c)，但 ChaD1、YD1 与 YD3 明显不同，ChaD1、YD1 具有 3137、3143、3181、3187cm^{-1} 等吸收峰，常见于含氢杂质的 Ib 型钻石，与孤氮和氢杂质有关。

本次研究样品 ChaD1 红外光谱吸收特征与前人研究 Chameleon 钻石结论大体相同[4,6-7]，主要表现为氮杂质聚合程度较低，以 A 型氮为主，可见孤氮特征和氢杂质相关吸收，以及特征的 1430cm^{-1} 宽吸收峰，根据上文分析其与片晶无关。但由于本次 Chameleon 钻石样品数量有限，未见 Hainschwang 等[4] 研究中发现部分 Chameleon 钻石氮杂质在一声子区吸收溢出的情况。颜色及紫外可见光吸收光谱相似的黄色钻石则具有较高的氮含量，并且氮杂质的聚集程度更高，不具 Ib 型钻石特征。

2.4　光致发光光谱特征

光致发光光谱(PL)可以更加有效地检测出钻石中一些含量极少的缺陷，甚至是 ppb 级含量缺陷也可轻易检测出来[28]。为了进一步研究 Chameleon 钻石及其相似黄色钻石中缺陷类型差异，探究 Chameleon 钻石具有热致变色现象的原因。在液氮温度下，使用 473、532、830nm 激光器分别对样品 ChaD1、YD1 和 YD3 进行 PL 光谱采集，结果见图 4。

532nm 激光器对样品进行 PL 光谱采集，3 个样品均表现为以 700nm 为中心的发光带(图 4a)，在 595~725nm 范围内，出现 595、604、614、624、634、644、655、665、676、688、699、711、725nm，即每 10nm 一个发光带，并伴随 753、771、799、818、838、845nm 等尖锐发光峰，在 ChaD1 中更明显。Breeding 等[9] 在研究由 480nm 缺陷致色的黄色钻石发现其具有与本次研究样品相同的发光特征。含 CO$_2$ 的天然褐色钻石[29] 也具有相同的发光峰，前人认为其与 480nm 缺陷中心有关。本次 3 个样品紫外可见光吸收光谱也均具有明显的 480nm 宽带，PL 光谱特征与紫外可见光吸收光谱互相印证，进一步证明 480nm



a—532nm 激光源下样品的 PL 光谱特征; b—473nm 激光源下样品的 PL 光谱特征; c—830nm 激光源下样品的 PL 光谱特征。

图4　样品 ChaD1、YD1 和 YD3 的 PL 光谱特征

Fig. 4　PL spectra of ChaD1, YD1 and YD3 samples. a. PL spectral characteristics of samples with 532nm excitation. The main feature is a broad emission band centered at about 700nm, this band consists of a dozen of peaks from 595nm to 725nm in steps of about 10nm. Additionally sharp peaks at 753, 771, 799, 818, 838, 845nm present in the chameleon diamond. b, c: PL spectral characteristics of samples with 473nm, 830nm excitation, respectively. The peaks at 503.2, 489, 883, 884nm are detected in the samples, indicating the presence of N-V and Ni-N related defects.

缺陷是 Chameleon 钻石具有热致变色现象的要素之一。

使用 473nm 激光器激发样品, 钻石的发光峰位于 505nm 处, 利用钻石发光峰对 3 个光谱进行归一化(图 4b), 3 个样品均可见由 A 型氮与空穴组成的 H3 中心(503.2nm), 强度较弱, 与天然 H3 缺陷致色的黄色钻石和经辐照退火处理黄色钻石极强的 H3 中心明显不同[30-31], 3 个样品 H3 缺陷含量较低, 只有 YD1 中 H3 较明显, YD3 几乎不可见, 说明样品未经过长时间自然受热过程。此外, 3 个样品具不同强度的 489、496.5、511、799、883、884、933、948nm 发光峰(图 4c), 为 Ni-N 相关缺陷产生的发光峰[32-34]。而产生 890、966、982、988nm 发光峰的缺陷结构未知, 仍需进一步研究。根据 PL 光谱可知, Chameleon 钻石及相似黄色钻石都含有 N-V 和 Ni-N 相关缺陷, 但含量有所差异, 仅根据钻石的 PL 光谱特征不能有效地区分 Chameleon 钻石。此外镍杂质为样品在超短波紫外线下发绿色荧光的主要原因。

3　结论

本次研究着重对 Chameleon 钻石及其相似黄色钻石的宝石学特征、紫外可见光吸收特征、红外吸收特征、光致发光特征进行对比分析。结果显示, Chameleon 钻石为 Ia 型钻石, 氮杂质聚合程度不高, 具有部分 Ib 型钻石特征; 具有 480nm 及 650~800nm 吸收带, 且热稳定性较差; 含有镍、氢杂质相关缺陷。而本次 Chameleon 钻石特征与前人研究大致相同, 根据 Fritsch[7] 研究认为短波下持久黄色磷光是 Chameleon 钻石的特征之一, 但本次样品未见, 由此可知磷光与变色现象无直接关系。

通过对比分析可知, 650~800nm 吸收带及 1430cm^{-1} 吸收峰(与片晶无关)是本次 Chameleon 钻石样品与其相似黄色钻石的主要差异, 据此推测 650~800nm 吸收带及 1430cm^{-1} 吸收峰与产生变色现象的原因有关。通过对比样品加热前后紫外吸收特征, 可以表明 480nm 缺陷吸收及 650~800nm 吸收带是导致 Chameleon 钻石黄绿色体色和热致变色现象的主要原因。虽然相似黄色钻石样品也具 480nm 缺陷, 但其与 Chameleon 钻石中 480nm 缺陷的热稳定性不同, 导致这一现象的原因未知, 仍需进行后续开展研究。

Comparative Analysis of Spectral Characteristics and Color Origin of Chameleon Diamond and Similar Yellow Diamond

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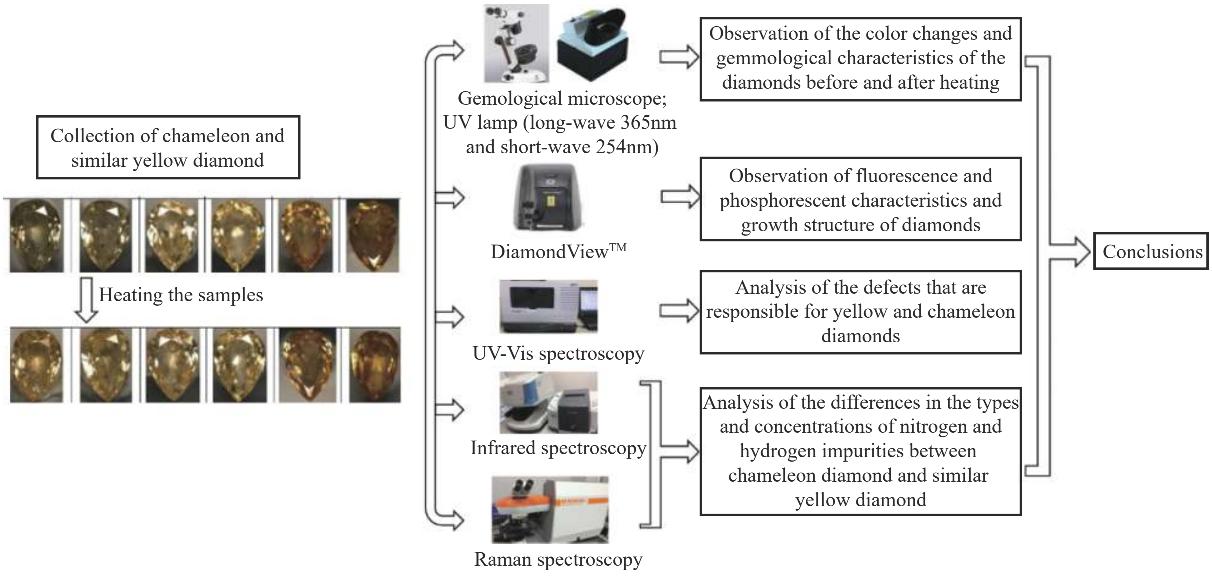
HIGHLIGHTS

(1) Chameleon diamond has a characteristic absorption band of 650-800nm and an absorption peak of 1430cm^{-1} independent of the crystal, which is significantly different from that of similar yellow diamonds.

(2) Poor thermal stability of 480nm and 650-800nm absorption band is the main reason for the thermochromic phenomenon of chameleon diamond.

(3) The existence of some defects in chameleon diamonds, which are related to C defects, A defects, hydrogen and nickel impurities, provides a basis for further research on the root cause of the thermochromic phenomenon of chameleon diamonds.



ABSTRACT

BACKGROUND: Chameleon diamond is a type of color diamond with photochromic and thermochromic phenomenon. If the chameleon diamond is placed in a dark room or heated for a long time, it can change from greenish yellow to fancy yellow, and return to its original color when it cools. Previous studies on chameleon diamond focus mainly on spectral characteristics. Through testing a large number of samples, the gemological and spectral characteristics of chameleon diamond are summarized. The characteristics of chameleon diamond, include a persistent yellow phosphorescence, a 480nm absorption band, and mainly the A-aggregate of nitrogen. A model to explain the thermochromic and photochromic phenomenon of chameleon diamond was proposed.

The characteristics of chameleon diamond discovered by previous studies are also found in a few yellow diamonds. Diamonds colored by the 480nm band show yellow fluorescence and phosphorescence under short wave ultraviolet light, low nitrogen content, high concentrations of defects related to hydrogen and nickel, but no obvious thermochromic and photochromic phenomena. Previous studies of the chameleon diamond and similar yellow diamonds were conducted independently and did not compare the two similar diamonds.

OBJECTIVES: To ascertain the difference of spectral characteristics and defect types between chameleon diamonds and similar yellow diamonds, and then analyze the causes of thermochromic phenomenon of chameleon diamond to gain a deeper understanding of the possible structure of the center responsible for the chameleon effect.

METHODS: Firstly, two chameleon diamond samples and four similar yellow diamond samples were collected to observe the color changes of the diamonds before and after heating. Top illumination and scattering illumination were used to observe the internal characteristics and color distribution of the samples. The fluorescence and phosphorescence characteristics of diamonds at long wave (365nm) and short wave (254nm) were observed by ordinary fluorescent lamp. The fluorescence and phosphorescent characteristics and growth structure of the samples under ultra-violet light were observed by DiamondView$^{\mathrm{TM}}$. Secondly, in order to investigate the causes of thermochromism in chameleon diamond, the absorption characteristics of diamond samples in the range of ultraviolet visible light were collected before and after heating and compared with those of similar yellow diamonds. The differences in absorption spectra between chameleon diamond and similar yellow diamond were analyzed, and the causes of thermochromic phenomena were explored. Finally, an infrared spectrometer was used to collect the infrared spectrum of diamond samples and analysis of the types and impurity elements of diamond samples was conducted. Through the comparative analysis of the infrared spectrum of samples, the differences in the types and contents of nitrogen and hydrogen impurities between chameleon diamond and similar yellow diamond were obtained. The laser Raman spectrometer was used to collect PL spectra of the samples at liquid nitrogen temperature by using 473nm, 532nm and 830nm lasers. By comparing the PL characteristics of chameleon diamond and similar yellow diamond, the differences between the two defects were obtained.

RESULTS: The color distribution of the 6 diamond samples is uniform. After heating, the chameleon diamond samples change color from yellow-green to yellow, while similar yellow diamonds have no obvious color change. Under long and short wavelength UV light, the samples are yellow fluorescence without phosphorescence. The performance of the samples in this study is consistent under long and short wavelength ultraviolet light, but it is different from the previous study results that the chameleon diamond has persistent yellow phosphorescence, which further indicates that the chameleon effect is not directly related to the phosphorescence. Under ultra-violet light, the samples have green fluorescence with irregular patterns which are markedly similar to diamonds colored by the 480nm band. Chameleon diamonds show moderate green phosphorescence.

All the samples have C defect absorption continuum combined with 480nm absorption band. The specific wide absorption band of 650-800nm is obvious in chameleon diamond. After being heated, the 480nm and 650-800nm absorption band of chameleon diamond completely disappears. However, the 480nm absorption band of similar yellow diamonds is weakened or has no obvious change. Therefore, the poor thermal stability of 480nm and 650-800nm absorption band is responsible for the thermochromic phenomenon of chameleon diamonds.

The infrared absorption characteristics of chameleon diamond mainly show A-defect absorption. Isolated nitrogen and hydrogen-related features can be seen, in addition to the characteristic 1430cm^{-1} wide absorption, which has a different origin than the platelet-related 1430cm^{-1} feature in Cape diamond. The similar yellow diamond has higher nitrogen content, and the degree of nitrogen aggregation is higher, and does not show any type Ib character. The broadband emission of all samples occurs mainly as one band centered at 700nm, this band consists of a dozen of peaks from 595nm to 725nm in steps of about 10nm. Additionally sharp peaks at 753, 771, 799, 818, 838, 845nm are present in the chameleon diamond samples. This spectrum is virtually identical to that reported previously for diamonds containing the 480nm absorption band. Chameleon diamonds and similar yellow diamonds all contain nitrogen-vacancy, nickel-nitrogen related defects, but the amount of defects is different. Chameleon diamonds cannot be effectively distinguished based on the PL spectral. The PL spectrum analysis shows that the nickel impurity is responsible for the green fluorescence of the samples under ultra-violet light.

CONCLUSIONS: This study focuses on the comparative analysis of gemology, UV-visible absorption, infrared absorption and photoluminescence characteristics of chameleon diamond and its similar yellow diamond. Chameleon diamond is type Ia diamond with low concentration of A defect, and shows some type Ib character, such as 1240cm^{-1} absorption. Chameleon diamond has 480nm and 650-800nm absorption bands, that are responsible for the chameleon effect. The characteristics of chameleon diamond in this study are consistent with those in previous studies. Absorption bands of 650-800nm and absorption peaks of 1430cm^{-1} (unrelated to platelet) are the main differences between the chameleon diamond and similar yellow diamond sample. It is inferred that the absorption band of 650-800nm and the absorption peak of 1430cm^{-1} are related to the center causing the thermochromic phenomenon. Although similar yellow diamond samples also have a 480nm center, their thermal stability is different from that of chameleon diamonds. The reason for this phenomenon is unknown, therefore further studies are needed.

KEY WORDS: chameleon diamond; yellow diamond; 480nm center; UV-Vis absorption spectrometry; infrared absorption spectrometry; photoluminescence spectrometry; nickel impurity

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