

基于分光透射比模型提高镉等离子体特征光谱识别能力的研究

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摘要 为了降低或消除激光诱导击穿光谱(LIBS)检测过程中激光能量、背景辐射、噪声信号对特征光谱信息的影响,以镉靶材为对象,构建偏振分辨激光诱导击穿光谱(PRLIBS)系统,探索提高重金属污染物 LIBS 分析能力的方法。结合光波在多层媒介传播过程中的菲涅耳方程,分析入射光波长对光强透射比的作用机理,构建正入射方向上的等离子体辐射强度分光透射比模型。利用该模型获得了相同条件下的 LIBS、PRLIBS 光谱数据,比较了镉元素特征谱线强度的相对标准偏差(RSD),并分析了不同延迟时间下特征谱线强度的变化趋势。结果表明:在低能量密度情况下,PRLIBS 具有明显的测量优势,可以采集到更多的特征峰信号,并且 PRLIBS 光谱特征谱线强度的 RSD 值小于相同检测参数下 LIBS 光谱特征谱线强度的 RSD 值,说明分光透射比模型能够有效提高等离子体光谱的稳定性;LIBS 与 PRLIBS 的谱线强度随延迟时间的变化趋势一致,说明 PRLIBS 并不影响原有 LIBS 的延迟时间;随着脉冲能量增大,分光透射比模型可以有效降低基线漂移和背景辐射,增强光谱的分辨能力;分光透射比模型不仅保留了连续谱中的有效信息,还提高了谱线识别的稳定性,对于提高低激光能量诱导条件下 LIBS 特征谱线识别能力具有重要的参考意义。

关键词 光谱学; 偏振分辨激光诱导击穿光谱; 分光透射比; Glan-Thompson 棱镜; 镉; 识别能力

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1 引言

重金属污染给生态环境、经济发展和人体健康带来了威胁^[1-2]。镉作为重金属污染元素之一,难以被微生物分解,摄入过量会导致肾脏等器官发生病变^[3-4],镉及其化合物已被世界卫生组织国际癌症研究机构列入 1 类致癌物清单。因此,对镉离子的准确高效识别将有助于减少重金属污染物的危害。目前,镉元素的常规检测方法主要包括电感耦合等离子体质谱法(ICP-MS)、电感耦合等离子体发射光谱法(ICP-OES)、原子吸收光谱法(AAS)等抽样实验室化学分析方法。这些方法具有灵敏度高和检测限低等优势,但需要使用化学试剂消解样品,而且检测过程繁琐,对环境不友好^[5-6]。从现代社会绿色可持续发展的趋势来看,亟待发展一种快速、原位、实时的重金属污染物分析方法。

激光诱导击穿光谱(LIBS)技术是一种典型的元素分析方法,其分析速度快,可多元素同时测量,并具有原位、实时检测等优点,已在环境检测、工业生产过

程控制和航空航天等领域被广泛应用^[7-10]。但是,基于纳秒脉冲对样品进行激发的 LIBS 技术,在高功率密度激光脉冲与物质相互作用产生等离子体过程中,由于样品存在基体效应,采集到的光谱数据基底高、背景噪声大,而且自吸收现象十分严重,分析结果的稳定性、精度以及灵敏度都有待提高^[11-12]。为此,国内外在传统 LIBS 系统优化方面进行了诸多有价值的研究,并提出了双脉冲法^[13]、气体辅助法^[14]、火花放电法^[15]、等离子体约束法^[16-17]等多种光谱信号增强方法。这些改进方法都取得了不错的效果,但大部分改进方法增大了系统的复杂性,造成了误差叠加,在一定程度上牺牲了 LIBS 原有的便捷性。基于前人的研究,寻找一种简单可行的方法来提高 LIBS 的分析性能是研究人员追求的目标。

偏振分辨激光诱导击穿光谱(PRLIBS)技术是近年来提升目标成分分析性能的热点方法,在地质、农产品等成分探测方面极具研发潜力^[18-21]。PRLIBS 对土壤中重金属元素铅、镉的分析能力较传统 LIBS 具有明显优势^[22-23]。镉属于过渡金属元素,相比钠、钾等碱

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金属元素难以用激光激发。目前虽然也有研究人员探讨了 PRLIBS 用特定脉冲激光激发重金属原子的光激发和光电离过程^[24-25],但缺乏 PRLIBS 在镉重金属污染物方面系统、深入、细致的研究。LIBS 检测的理想状态是能够感知目标成分变化,且目标元素特征谱线信息清晰显示。对于镉元素限量在 1 mg/kg 以下的农产品,镉元素的 LIBS 特征谱线极易被背景辐射掩盖。此外,复杂的基体效应也会导致镉的分析性能降低。基于此,笔者结合 LIBS 过程连续谱与分立谱的偏振特征,构建分光透射比模型,利用多层媒介的双折射特性获取包含目标成分较多的等离子体光谱特征谱线信息的分立谱信号,探索基线漂移和背景辐射的抑制效应,提高 LIBS 对镉元素特征谱线的识别能力。本研究为复杂基体样品中镉元素检测的可行性提供了参考。

2 实验装置

偏振分辨激光诱导击穿光谱(PRLIBS)系统装置示意图如图 1 所示。脉冲激光发射源为 Nd:YAG 激光器(Vlite-200),波长为 1064 nm,脉宽为 6~8 ns,频率在 1~10 Hz 范围内可调,激光能量在 0~300 mJ 范围内可调。激光器发出的脉冲光束被反射镜(与水平方向呈 45°角)反射后垂直向下,经平凸透镜($f=100$ mm)聚焦后击打在样品表面产生等离子体。等离子体光谱信号先由检偏系统收集,检偏系统由焦距为 30 mm 的平凸透镜、焦距为 50 mm 的聚焦透镜和 Glan-Thompson 偏振棱镜(GTH10M-A,波长范围为 350~2300 nm)组成,旋转棱镜可以改变检偏角。光谱信号经由检偏系统聚焦耦合入光纤分光,然后由八通道光谱仪(AvaSpec-2048-USB2-RM,波长范围为 198~1058 nm)探测采集,光电转换后传输至计算机进行储存和分析。光谱仪与激光器之间的延时由数字脉冲发

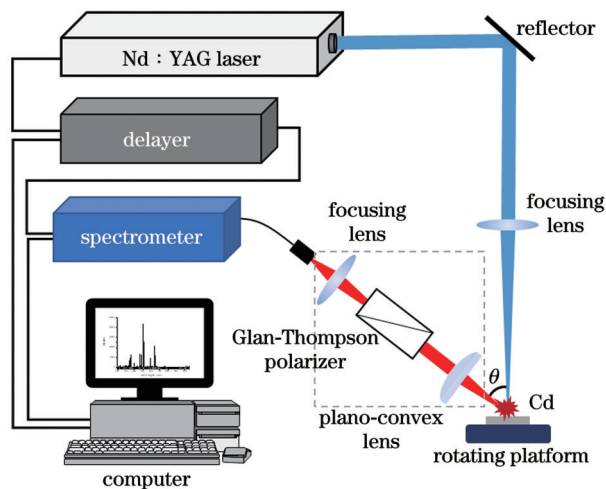


图 1 PRLIBS 系统装置示意图

Fig. 1 Schematic of polarization-resolved laser induced breakdown spectroscopy (PRLIBS) system setup

生器(DG535)控制。将样品(镉靶材,纯度不低于 99.99%)放置于顺时针匀速旋转的二维旋转平台(SC300 控制器)上,以消除激光烧蚀坑带来的影响。

PRLIBS 系统装置中的检偏系统如图 1 中虚线框所示,该系统由平凸透镜、Glan-Thompson 偏振棱镜和聚焦透镜组成。激光脉冲烧蚀样品形成等离子体,等离子体产生的样品信号首先经过平凸透镜变为平行光光谱信号,之后进入 Glan-Thompson 偏振棱镜,在棱镜双折射的作用下,连续辐射和背景信号被过滤,分立谱信号透射出棱镜并经聚焦透镜聚焦后进入光纤,最终由光谱仪分光和计算机分析后形成 PRLIBS 光谱。

3 分光透射比理论分析

当一束平行光正入射棱镜时,光在棱镜中的光路如图 2 所示。 S 为棱镜的结构角,1、4 分别为棱镜的入射端面和出射端面,2、3 为棱镜胶合层的界面,晶体光轴垂直于纸面, i_0 为 e 光从第一块直角棱镜(L1)入射到胶合层的入射角, i_1 为 e 光在胶合层内的折射角, i_2 为 e 光在第二块直角棱镜(L2)中的折射角, n_e 、 n_1 分别为 e 光在方解石和胶合层的折射率。单色非偏振光进入 Glan-Thompson 棱镜后分为 o 光和 e 光,到达晶体-胶合层界面时,o 光被全反射,e 光透过。

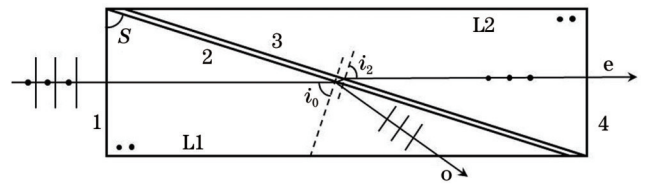


图 2 正入射时 Glan-Thompson 棱镜中的光路

Fig. 2 Optical path in Glan-Thompson polarizer at normal incidence

需要说明的是,当胶合层厚度为 10 μm 时,可将其近似看作一层薄膜。根据菲涅耳公式,可以推导出光在膜层的反射率^[26]为

$$R = \frac{(\eta_0 - \eta_2)^2 \cos^2 \delta + \left(\frac{\eta_0 \eta_2}{\eta_1} - \eta_2\right)^2 \sin^2 \delta}{(\eta_0 + \eta_2)^2 \cos^2 \delta + \left(\frac{\eta_0 \eta_2}{\eta_1} + \eta_2\right)^2 \sin^2 \delta}, \quad (1)$$

式中: δ 为相邻两透射光之间的相位差; η_0 、 η_2 和 η_1 分别为直角棱镜 L1、L2 和薄膜对 e 光的光学导纳,并且,

$$\begin{cases} \eta_0 = n_e \cos i_0 \\ \eta_1 = n_1 \cos i_1 \\ \eta_2 = n_e \cos i_2 \end{cases} \quad (2)$$

结合多光束干涉理论和菲涅耳公式可以得到从厚度为 h 的胶合层出射的每相邻两透射光之间的相位差 δ 为

$$\delta = \frac{2\pi}{\lambda} n_1 h \cos i_1, \quad (3)$$

并且,

$$n_1 \sin i_1 = n_e \sin i_0, \quad (4) \quad \text{将式(2)~(5)代入式(1)可得 e 光在胶合层的反射率为} \quad i_0 = i_2 = S, \quad (5)$$

$$R(\lambda) = \frac{\left(\frac{n_e^2 \cos^2 i_0}{n_1 \cos i_1} - n_1 \cos i_1 \right)^2 \sin^2 \frac{2\pi h n_1 \cos i_1}{\lambda}}{4n_e^2 \cos^2 i_0 \cos^2 \frac{2\pi h n_1 \cos i_1}{\lambda} + \left(\frac{n_e^2 \cos^2 i_0}{n_1 \cos i_1} + n_1 \cos i_1 \right)^2 \sin^2 \frac{2\pi h n_1 \cos i_1}{\lambda}}. \quad (6)$$

Glan-Thompson 棱镜由方解石晶体制成,其折射率用寻常光(o光)折射率 n_o 和非常光(e光)折射率 n_e 来表示。在可见光区,方解石晶体的色散性质 (n_o 和 n_e) 均表现为正常色散,而正常色散区的色散曲线通常由修正的 Sellmeier 方程^[27]描述。由于通过偏光棱镜透射出的是 e 光, e 光折射率 n_e 的 Sellmeier 方程可表示为

$$n_e^2 = A_e + \frac{B_e}{\lambda^2 - C_e} - D_e \lambda^2, \quad (7)$$

式中: λ 为入射光在真空中的波长,单位为 nm; A_e 、 B_e 、 C_e 、 D_e 均为待定参数。

Glan-Thompson 棱镜的波长范围为 350~2300 nm, 光谱仪的波长范围为 198~1058 nm, 根据光学手册^[28], 获得了 4 组不同波长对应的方解石 e 光的折射率: $\lambda=330 \text{ nm}, n_e=1.50746$; $\lambda=508 \text{ nm}, n_e=1.48956$;

$\lambda=706 \text{ nm}, n_e=1.48353$; $\lambda=905 \text{ nm}, n_e=1.48098$ 。将其分别代入式(7)中,联立求解可得到方解石晶体 e 光折射率 n_e 的 Sellmeier 方程为

$$n_e^2(\lambda) = 2.1829 + \frac{9033.2}{\lambda^2 - 8156.1} - 8.5810 \times 10^{-10} \lambda^2. \quad (8)$$

辐射光强可以分解为两个方向垂直、振幅相等、无相关性的线偏振光分量。正入射的平行光通过棱镜后透射出的 e 光为线偏振光,而正入射时水平分量和垂直分量的透射比公式是一样的,入射端面和出射端面的光强透射比均可用菲涅耳公式表示为

$$T_d = \frac{4n_e(\lambda)}{[1 + n_e(\lambda)]^2}. \quad (9)$$

根据上述分析, e 光经过 Glan-Thompson 棱镜后的透射比为

$$T(\lambda) = \frac{\left\{ \frac{4n_e(\lambda)}{[1 + n_e(\lambda)]^2} \right\}^2 [1 - R(\lambda)]}{4n_e^2(\lambda) \cos^2 i_0} = \frac{\left\{ \frac{4n_e(\lambda)}{[1 + n_e(\lambda)]^2} \right\}^2 \cdot 4n_e^2(\lambda) \cos^2 i_0}{4n_e^2(\lambda) \cos^2 i_0 \cos^2 \frac{2\pi h n_1 \cos i_1}{\lambda} + \left[\frac{n_e^2(\lambda) \cos^2 i_0}{n_1 \cos i_1} + n_1 \cos i_1 \right]^2 \sin^2 \frac{2\pi h n_1 \cos i_1}{\lambda}}. \quad (10)$$

值得说明的是,分立谱来自原子在束缚能级之间的跃迁,综合光谱接收效率和探头接收角度,实际测得的 LIBS 信号强度为 I_0 。LIBS 信号经过 Glan-Thompson 棱镜后获得 PRLIBS 信号,其信号强度的表达式为

$$I_{pr} = I_0 \times T(\lambda) = I_0 T(\lambda) \cos \varphi, \quad (11)$$

式中: \times 表示叉乘,表示向量空间中向量的二值运算; φ 表示入射光垂直方向与入射面垂直方向之间的夹角; $T(\lambda)$ 表示波长为 λ 的光在棱镜中的透射比。式(11)描述了激光诱导介质等离子体后由偏振棱镜得到的垂直于入射表面的光强信息。通过该模型能够在较低入射光强条件下提取等离子体的有效信息,大大降低了对样品表面的损伤。

4 分光透射比模型验证

4.1 理论模拟

Glan-Thompson 棱镜中胶合材料的折射率为 1.52, 结构角 $S=71.5^\circ$, 入射光的波长范围为 300~1100 nm。采用 MATLAB 软件,根据式(8)得到了方解石晶体 e 光折射率 n_e 的 Sellmeier 方程曲线,如图 3 所

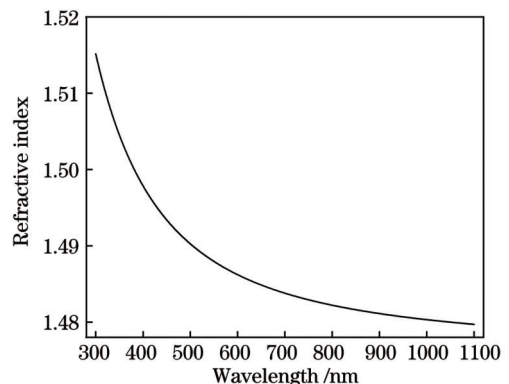


图 3 方解石晶体中 e 光折射率 n_e 的 Sellmeier 方程曲线
Fig. 3 Sellmeier equation curve for e-light refractive index n_e in calcite crystals

示。根据式(11)得到了正入射时 e 光透射比随入射光波长变化的理论关系曲线,如图 4 所示。

可以看出,透射比 $T(\lambda)$ 为振荡函数, e 光折射率 n_e 和透射比 $T(\lambda)$ 随着波长增加呈现出下降趋势,并且 $T(\lambda)$ 具有明显的波动特征。当入射进棱镜的光波长

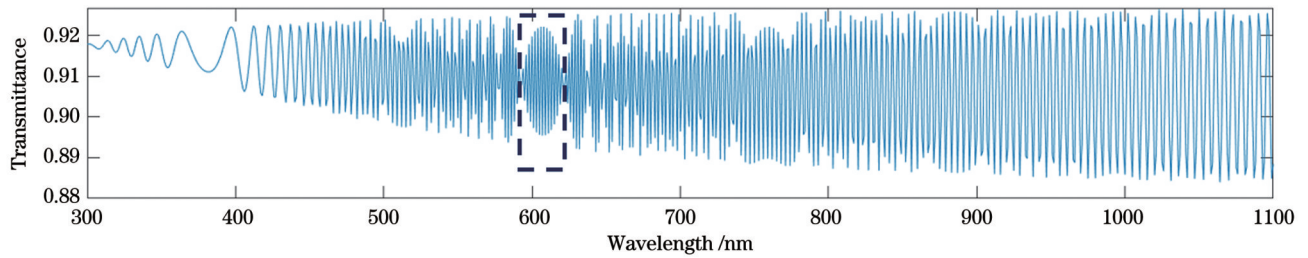


图4 正入射时e光透射比与入射光波长的理论关系曲线

Fig. 4 Theoretical relationship curve between e-light transmittance and incident light wavelength at normal incidence

变大时, $T(\lambda)$ 的振幅增大而频率显著减小。经计算, 在 300~1100 nm 波长范围内正入射时, 棱镜的透射比介于 0.88~0.93 之间, 其平均值为 0.9088。

在图 4 所示虚线框中, 可见光 590~630 nm 波长范围内的透射比出现了异常情况, 下面对其进行分析。结合图 5 和图 6 可以看出相位差 δ 为非线性曲线, 波长的变化对相位差幅值的影响很大, 导致其余弦值与正弦值均呈现波动较大的非周期振荡变化趋势, 将 δ 代入式 (11) 后就会出现图 4 虚线框所示情况。除此之外, 胶合层厚度和胶合层材料的折射率对棱镜的透射比也有重要影响。为此, 选择膜层厚度更小和折射率更接近 e 光折射率的光学胶制作的棱镜能够获得比较稳定的透射比^[29-31]。

从式 (11) 和图 4 可以看出, 由于透射比小于 1, 样品信号经过 Glan-Thompson 棱镜后, 光谱特征峰的特征信号经过检偏系统后, 强度值会降低, 但不同波长的透射比存在差异, 因而出现了部分强度值高的特征峰的特征峰强度降低幅度更

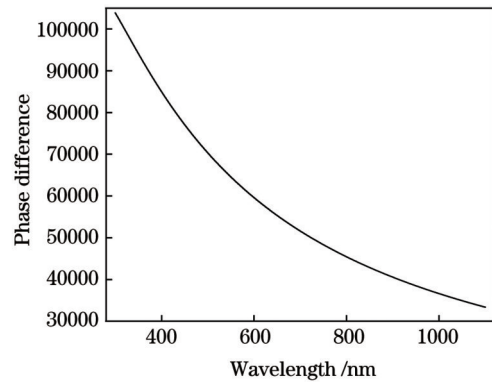
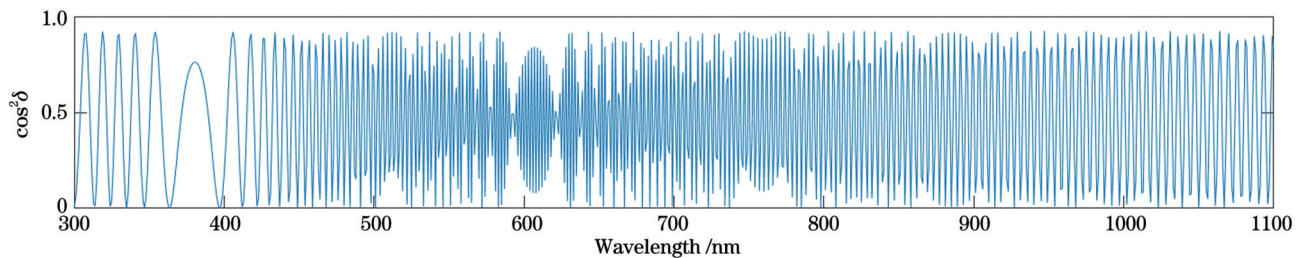


图5 相位差与波长之间的理论关系曲线

Fig. 5 Theoretical relationship curve between phase difference and wavelength

大, 而强度值低的特征峰的特征峰强度降低幅度反而更小的现象, 从而使得最高的特征峰与最小的特征峰的特征峰强度之差相比于未经过检偏系统时的差值更小。这一特点有利于光谱信号强度值偏低的谱峰的认识, 从而获得更多的有效信号。

图6 $\cos^2 \delta$ 与波长的理论关系曲线Fig. 6 Theoretical relationship curve between $\cos^2 \delta$ and wavelength

4.2 镉等离子体实验验证

根据图 1 所示实验装置分别采集镉靶材样品的 LIBS 信号与 PRLIBS 信号。不同脉冲激光能量对样品表面烧蚀的宏观结果如图 7 所示。可以看出, 随着激光能量增加, 烧蚀坑明显增大。为减小激光对样品表面的损伤, 实验所用脉冲能量为 23.68 mJ, 延迟时间为 1.28 μs 。采集样品表面激光烧蚀的 20 个不同位置处的光谱数据, 取其平均值得到了镉靶材样品的 LIBS 光谱图与 PRLIBS 的光谱图, 如图 8 所示。

可以看出, 在同样较低的激光脉冲能量下,

PRLIBS 系统比 LIBS 系统检测出了更多的特征峰信号, 谱线 422.7、441.5、538.1、766.2、769.6 nm 等均在 PRLIBS 光谱中清晰显示。此外, 由于棱镜的双折射作用, PRLIBS 光谱中的特征峰强度呈现出小于对应的 LIBS 光谱特征峰强度的趋势, 但是在图 8 中, 低能量情况下 PRLIBS 系统采集的部分镉特征峰的强度值高于 LIBS 系统采集的镉特征峰的强度值。出现这一情况主要是由于采用低能量激光激发时, PRLIBS 检偏系统前端的平凸透镜与等离子体羽之间的距离相比 LIBS 收光装置中的聚焦透镜与等离子体羽之间的距离更近, 更多透镜边缘的光被耦合进入光纤, 对

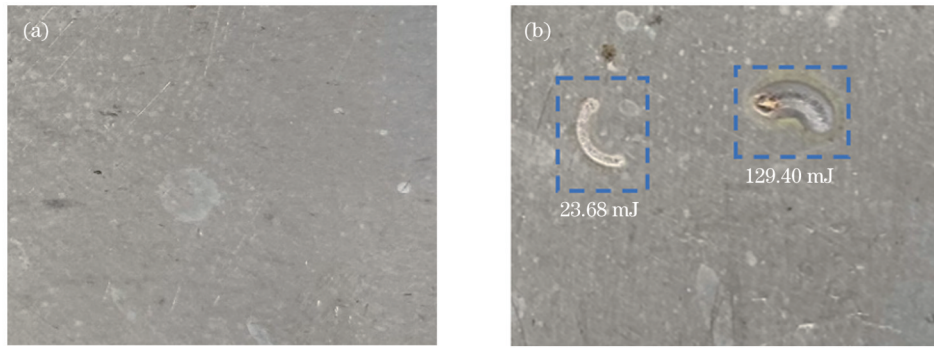


图 7 镉靶材表面。(a)原始表面;(b)烧蚀的表面

Fig. 7 Surfaces of Cd targets. (a) Original sample; (b) ablative surface

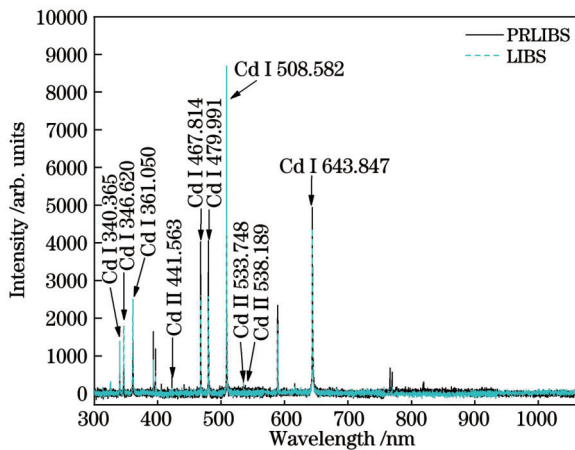


图 8 23.68 mJ 脉冲激光能量下镉靶材的等离子体光谱

Fig. 8 Spectra of Cd targets plasma at pulsed laser energy of 23.68 mJ

收光装置进行补偿,但等离子体羽到光纤探头之间的距离是相等的。这也导致部分波段的背景信号相对较高,但与特征信号相比,基波可以忽略不计,这并不影响对特征信号的识别。此外,PRLIBS 光谱特征信号强度的最大值与最小值之差小于对应的 LIBS 光谱特征信号强度差值,与式(11)所示变化趋势一致,该差值越小越有利于对特征信号强度值低的谱线的识别。

4.3 不同脉冲激光能量下镉特征光谱的采集

为了比较分析 PRLIBS 的优势,分别在 42.52、70.95、98.85、129.40、177.30、198.10 mJ 脉冲激光能量下采集 PRLIBS 与 LIBS 的镉靶材等离子体光谱,结果如图 9 所示。可以看出,随着激光能量增强,等离子体温度升高,更多的粒子被激发,连续谱与分立谱的强度随之增大,总体光谱特征信号呈增大趋势。这一现象表明等离子体的诱导率与激光强度有关,在一定范围内会随着激光强度的增加而增大。

此外,LIBS 光谱中产生的基线漂移现象较为明显,并随着脉冲能量的增大而愈发严重。相比之下,PRLIBS 光谱中几乎没有出现基线漂移问题,而且背景信号明显降低。产生上述差异的主要原因是光谱由连续谱(背景辐射和噪声信号)和分立谱(有效信号)组

成,而连续谱和分立谱的偏振特性不同,连续谱的偏振特性比离散谱的偏振特性强得多^[32]。等离子体光谱信号经过偏振器后,背景辐射和噪声信号被明显过滤掉,离散信号被保留。因而,虽然采集到的 PRLIBS 光谱谱线的强度弱于 LIBS 光谱,但 PRLIBS 能够在保留有效信号的情况下有效减少背景辐射和噪声信号,降低基线漂移,获得更高质量的原始数据,从而有利于开展后续的定性或定量分析工作。随着激光能量增大,光谱中连续谱的强度有明显的增强趋势,检偏器的作用逐渐减弱^[33],即:在低激光能量情况下,PRLIBS 光谱的分辨能力更强。这一特点有利于 PRLIBS 系统在低能量情况下对样品进行检测,减小了对样品表面的损伤,同时可以采集更多的光谱特征信号,提高 LIBS 特征谱线的识别率。

由于 LIBS 中的大部分镉特征谱线在 70.95 mJ 激光能量时达到饱和,因而选择 23.68 mJ 和 42.52 mJ 脉冲能量下的特征谱线强度的相对标准偏差(RSD)对检测稳定性进行分析,分析结果如表 1 所示。在 LIBS 检测中,RSD 通常在 0~1 之间变化,RSD 越接近 0,光谱越稳定。在 23.68 mJ 激光能量下,LIBS 未采集到 Cd II 441.563 nm 和 Cd II 538.189 nm 特征谱线信号,仅显示为背景、噪声信号,导致 RSD 为异常值。分析表 1 可以看出,PRLIBS 光谱中特征谱线强度的 RSD 值呈现出小于 LIBS 光谱中对应特征谱线 RSD 值的趋势,且 23.68 mJ 激光能量下 PRLIBS 特征谱线的 RSD 明显优于 LIBS,大部分都在 10% 以下。这一结果说明等离子体经过检偏系统后获得的 PRLIBS 光谱的稳定性有一定程度的提高,有利于提高 LIBS 对等离子体特征光谱识别的稳定性。

4.4 不同延迟时间下各特征光谱的采集

光谱仪采集到的等离子体数目与其设置的延迟时间有关。为了验证 PRLIBS 不影响原有 LIBS 的延迟时间,在激光能量为 62 mJ,延迟时间分别为 1.28、1.38、1.48、1.58、1.68、1.78、1.88 μs 时,分别采集 LIBS 与 PRLIBS 的镉靶材等离子体光谱,对样品击打 20 次后取光谱的平均值。特征峰 Cd I 340.365 nm 和 Cd II 441.563 nm 的强度随延迟时间的

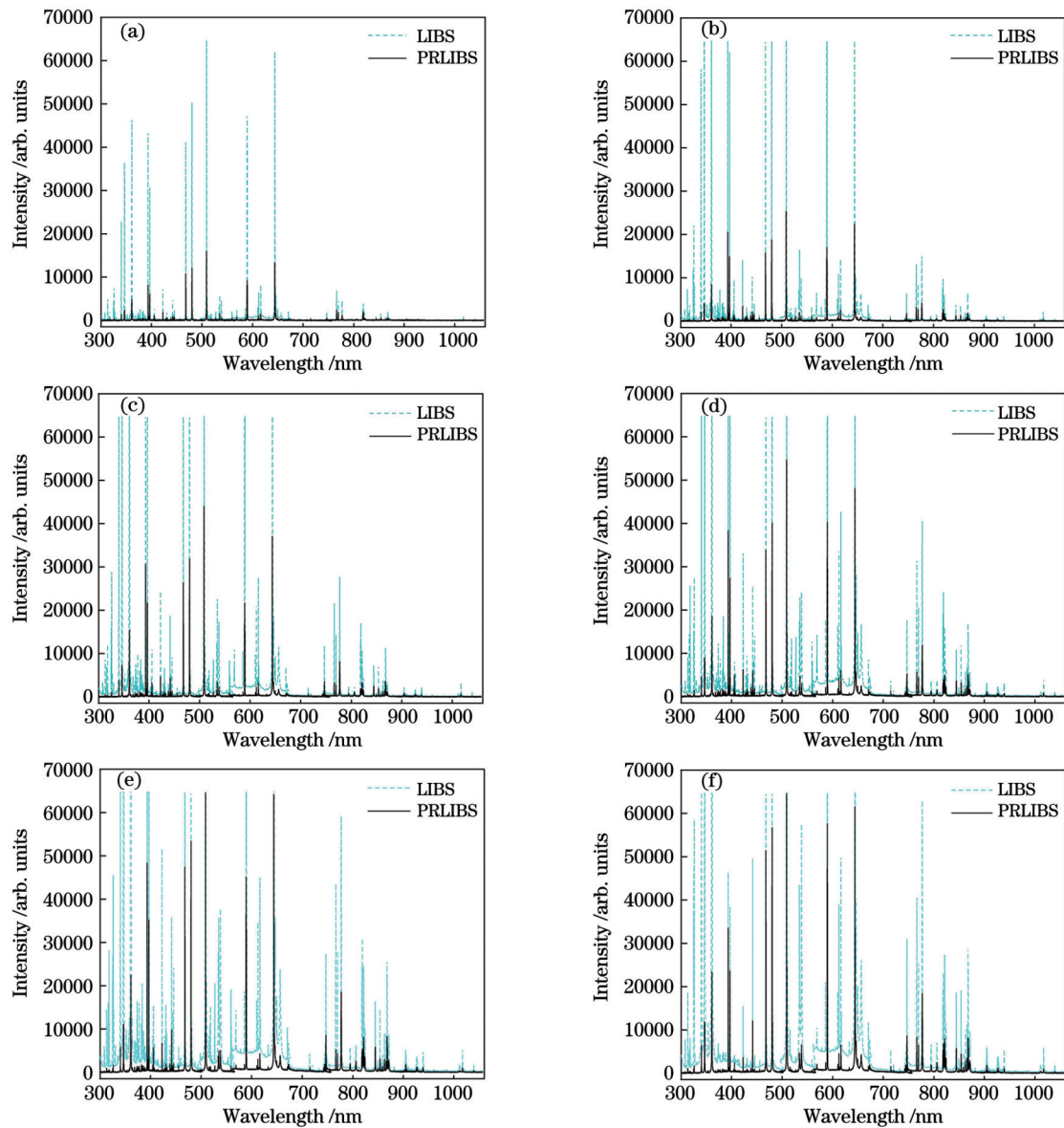


图9 不同脉冲激光能量下PRLIBS与LIBS的镉靶材等离子体光谱。(a) 42.52 mJ; (b) 70.95 mJ; (c) 98.85 mJ; (d) 129.40 mJ; (e) 177.30 mJ; (f) 198.10 mJ

Fig. 9 Plasma spectra of Cd targets for PRLIBS and LIBS at different pulsed laser energies. (a) 42.52 mJ; (b) 70.95 mJ; (c) 98.85 mJ; (d) 129.40 mJ; (e) 177.30 mJ; (f) 198.10 mJ

表1 23.68 mJ和42.52 mJ脉冲激光能量下部分特征谱线的RSD
Table 1 RSD of partial characteristic spectral lines at 23.68 and 42.52 mJ pulsed laser energy units: %

Characteristic spectral line	RSD at 23.68 mJ		RSD at 42.52 mJ	
	LIBS	PRLIBS	LIBS	PRLIBS
Cd I 340.365 nm	18.75	11.68	8.62	9.14
Cd I 346.620 nm	20.58	7.80	8.97	7.22
Cd I 361.050 nm	14.39	10.75	8.30	6.28
Cd II 441.563 nm	133.28	23.48	4.65	5.35
Cd I 467.814 nm	13.79	6.71	5.88	4.16
Cd I 479.991 nm	14.98	8.70	5.78	4.91
Cd I 508.582 nm	13.18	8.79	0.04	5.35
Cd II 538.189 nm	380.64	23.46	6.83	11.34
Cd I 643.847 nm	10.49	7.79	3.45	6.53

变化如图10所示。

从图10中可以看出,在相同条件下采集的LIBS与PRLIBS光谱特征峰的强度随延迟时间的变化趋势一致。这说明PRLIBS系统中的检偏系统起的是滤过背景辐射的作用,并不会改变原有LIBS的延迟时间。随着延迟时间延长,等离子体数目的衰减增加,特征峰强度降低,当延迟时间为1.28 μs 时,特征峰强度最大。

5 结 论

在已有LIBS检测模型研究的基础上,笔者推导了不同波长光正入射进Glan-Thompson棱镜时的透射比理论公式,建立了等离子体辐射强度的PRLIBS检测模型,采集了不同激光能量密度条件下镉元素的

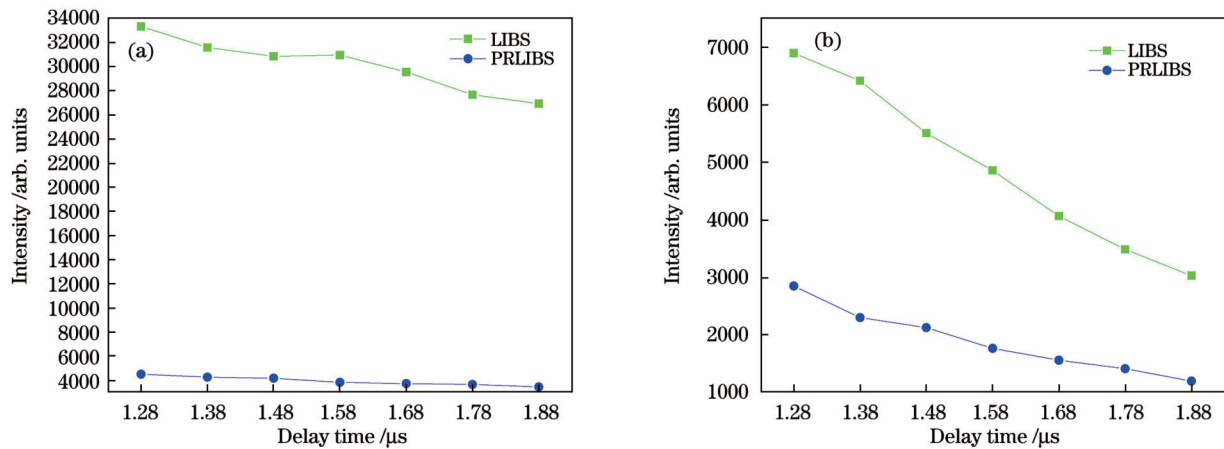


图 10 不同延迟时间下 LIBS 与 PRLIBS 的镉特征谱线强度变化曲线。(a) Cd I 340.365 nm; (b) Cd II 441.563 nm

Fig. 10 Intensity variation curves of Cd characteristic spectral lines of LIBS and PRLIBS at different delay time.

(a) Cd I 340.365 nm; (b) Cd II 441.563 nm

LIBS 与 PRLIBS 光谱。与 LIBS 系统相比, PRLIBS 系统能够测量到更多的特征信号, 明确了分光透射比模型在低能量条件下能够降低基线漂移和背景辐射。PRLIBS 光谱特征信号强度的最大值与最小值之差小于 LIBS 对应的差值, 展现出了 PRLIBS 方法识别特征谱线的优势。比较了 23.68 mJ 和 42.52 mJ 激光脉冲能量下 LIBS 与 PRLIBS 特征谱线的 RSD 值, PRLIBS 方法 RSD 值的平均值在 10% 以下, 且整体 RSD 值小于 LIBS 方法的 RSD 值。这表明 PRLIBS 能有效提高对特征谱线识别的稳定性。通过实测实验验证了分光透射比模型能够提高镉元素等离子体光谱特征谱线的识别能力。此外, 还采集了 7 个不同延迟时间下 LIBS 与 PRLIBS 光谱的镉特征峰信号, 两种特征峰强度随延迟时间的变化趋势一致, 说明 PRLIBS 并不会改变原有 LIBS 的延迟时间。

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Improvement of Recognition Ability of Cadmium Plasma Characteristic Spectrum Based on Light-Splitting Transmittance Model

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Abstract

Objective Heavy metal pollution poses a threat to the ecological environment, economic development, and human health. As a heavy metal pollutant, cadmium (Cd) is difficult to be decomposed by microorganisms, and its excessive intake can lead to cancerous lesions in the kidneys and other organs. Presently, the routine detection methods of Cd element, such as ICP-MS, ICP-OES, and AAS, require the use of chemical reagents to digest the samples, and the detection process is environmentally unfriendly and tedious. Laser-induced breakdown spectroscopy (LIBS) is a typical elemental analysis method with the advantages of a high analysis speed, multi-element measurement, and real-time detection. This has been widely studied in many fields. However, owing to the existence of the matrix effects in the samples, the collected spectral data have high bases and large background noise, and the self-absorption phenomenon is highly severe. Therefore, the stability, accuracy, and sensitivity of the analysis results must be improved. To reduce

or eliminate these problems during the LIBS detection process, we constructed a polarization-resolved LIBS (PRLIBS) system to explore methods to improve the analytical ability of LIBS. Stability is promoted, and the baseline drift and background radiation are reduced using PRLIBS. We hope that our study provides a reference for the improvement of the analytical ability of LIBS.

Methods A Cd target was selected as the object in the present study. Combined with the Fresnel equation of light wave propagation in multilayer media, the mechanism of the effect of the incident light wavelength on the light intensity transmittance is analyzed. A light-splitting transmittance model of the plasma radiation intensity in the normal incident direction was established. MATLAB software was used to simulate the model and analyze the changes in the transmitted light intensity. A Cd target was used for the actual measurement verification. The spectral data of the LIBS and PRLIBS with different laser energies and delay time were obtained, and their effects on the spectral signals were analyzed. The relative standard deviation (RSD) of the characteristic spectral line intensity of Cd was calculated to compare the stabilities of LIBS and PRLIBS.

Results and Discussions PRLIBS has obvious measurement advantages in terms of the low energy density of the laser, and more characteristic peak signals can be collected by PRLIBS (Fig. 8). The plasma temperature increase with an increase in the laser energy, and the overall spectral characteristic signal tends to increase (Fig. 9). The phenomenon of the baseline drift in the LIBS spectrum is evident, whereas the PRLIBS spectrum has almost no baseline drift problem, and the background signal is significantly reduced. This phenomenon shows that the continuous radiation and background signal are filtered out after the plasma spectral signal passes through the polarizing system, while the discrete signal is retained. The polarization characteristics of the continuous spectrum are much stronger than those of the discrete spectrum. Additionally, the RSD values of the characteristic spectral line intensity were calculated (Table 1), which in PRLIBS are less than those obtained by the LIBS method at the same detection parameters. This indicates that the light-splitting transmittance model effectively improves the stability of the plasma spectrum. With the increase in pulse energy, the light-splitting transmittance model can effectively reduce the baseline drift and background radiation and enhance the spectral resolution. This model not only retains effective information in the continuous spectrum but also improves the stability of spectral line identification. Moreover, the characteristic Cd peak signals of LIBS and PRLIBS with seven different delay time were collected to analyze their effect on the spectral signal (Fig. 10). The variation trends of the characteristic peak intensity with the delay time under the two methods are consistent.

Conclusions Based on the existing LIBS detection model, the theoretical formula of the transmission ratio for different wavelengths of light directly incident onto the Glan-Thompson prism is deduced, and the PRLIBS detection model of the plasma radiation intensity is established. By collecting and comparing the LIBS and PRLIBS spectra of Cd element under different laser energy densities, it was deduced that PRLIBS can measure more characteristic signals, whereas the spectral transmittance model can reduce the baseline drift and background radiation under low-energy conditions. Moreover, the difference between the maximum and minimum values of the spectral characteristic signal intensity of PRLIBS is smaller than that of LIBS, reflecting the advantages of the PRLIBS method for characteristic spectral line recognition. The RSD values of the LIBS and PRLIBS characteristic spectral lines at laser pulse energies of 23.68 mJ and 42.52 mJ were compared. The average RSD value of the PRLIBS method was less than 10%, and the overall RSD value was smaller than that of the LIBS method, indicating that PRLIBS can effectively improve the stability of the identification of the characteristic spectral lines. The experimental results show that the model can improve the ability to identify the characteristic spectral lines of Cd plasma spectra. Additionally, the characteristic Cd peak signals of LIBS and PRLIBS with seven different delay time were collected. The variation trends of the characteristic peak intensity with the delay time under the two methods were consistent, indicating that PRLIBS does not change the delay time of LIBS.

Key words spectroscopy; polarization-resolved laser-induced breakdown spectroscopy; light-splitting transmittance; Glan-Thompson polarizer; cadmium; recognition ability