Li₂BaSiSe₄: 一种具有显著二次倍频效应的新型复合金属硒化物

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摘要 红外激光变频技术急需新型的具有优良性能的非线性光学晶体, 但获得能够实现大倍频和高激光损伤阈值平衡的新型红外非线性光学晶体依然是巨大的挑战, 进一步的工作仍是科研工作者的研究热点. 本文通过高温溶液法将高正电性的碱金属锂, 碱土金属钡以及无机半导体硅与硒熔合高温反应得到了一种新型红外非线性光学晶体 Li₂BaSiSe₄, 并获得了其光学性质的实验数据. 经过漫反射数据转化得到的光学带隙实验值为2.47 eV, 2.09 μm光源下的倍频效应与商业化使用的AgGaS₂相当, 约为KH₂PO₄(KDP)的30倍. 第一性原理计算还分析了它的能带结构、态密度分布等.

关键词 红外, 非线性, 倍频效应, 晶体

非线性光学晶体材料由于能够实现激光频率转换, 从而扩展激光器的可调谐范围, 在激光技术领域具有重要应用价值^[1~11]. 随着人们对非线性光学晶体材料的探索研究, 在紫外和可见光范围, 非线性晶体研究已取得重大进展, 发现了如β-BaB₂O₄(β-BBO)^[7], LiB₃O₅(LBO)^[12]和KBe₂BO₃F₂(KBBF)^[13]等性能优异的晶体, 新材料的研究朝向更短紫外波长发展. 在红外及远红外波段(2~20 μm), 目前商业化使用的非线性光学晶体材料为AgGaS₂(AGS)^[14,15], AgGaSe₂(AGSe)^[14,16], ZnGeP₂^[17~19]等, 它们在军事和民用方面有重大应用, 如在光学器件、能源探测、远距离激光通讯、激光制导、激光红外对抗、环境监测等领域^[20~28]. 非线性光学晶体, 可通过倍频效应, 光参量放大和差频等技术对目前已有光源的激光进行频率转化获得可调谐红外激光, 是固态激光器中最重要的光学器件. 但是, 随着各行业科学技术的发展, 对红外非线性光学晶体性能的需求越来越高. 目前商

业使用的晶体存在一定的缺陷: 带隙不够大、双光子吸收和低激光损伤阈值等. 因此, 探索新型红外非线性光学晶体受到了越来越多的关注, 获得具有高激光损伤阈值与大倍频效应综合性能平衡的新材料也成了主要发展方向^[29~31].

在新型材料的探索中, 首先是要设计合成非中心对称的结构, 一般的方法包括: (1) 在结构中加入含有π共轭的平面结构基元(如BO₃, BS₃), 因为它们能产生大的电子极化率, 如紫外非线性光学晶体KBe₂BO₃F₂和β-BBO; (2) 将具有立构活性孤对电子的阳离子(Se⁴⁺, Sb³⁺, Te⁴⁺, I⁵⁺等)引入到结构体系中可以形成大畸变阴离子基团^[32~34], 可更易形成非中心对称结构; (3) 引入具有二阶姜泰勒效应的d⁰阳离子如Ti⁴⁺, V⁵⁺, Nb⁵⁺, Mo⁶⁺, W⁶⁺等形成非极性配位环境^[35]; (4) 将易形成大畸变的基元如第四主族元素SiS₄, GeS₄, SnS₄和具有d¹⁰电子的ZnS₄和CdS₄引入结构, 同时可以使获得的化合物具有大的倍频效

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应^[24,36-42]. 此外, 为了调节化合物的性能, 设计合成带隙大的化合物, 在体系选择时将碱金属和碱土金属选择入内, 可以避免形成d-d, f-f电子跃迁, 从而获得大带隙. 在最近报道的一系列性能优良的化合物中, 碱金属和碱土金属经常被引入体系中, 如Cs₂HgI₂Cl₂^[43], Li₂In₂GeS₆^[44], BaGa₄S₇^[45], BaGa₄Se₇^[25], Na₂ZnGe₂S₆^[29], Na₂BaSiS₄^[23]等. 基于以上设计思路, 本工作选择了Li/Ba/Si/Se体系作为新材料的研究体系, 并获得新化合物Li₂BaSiSe₄. 单晶X射线衍射仪收取了其晶体结构数据, 通过Shelxtl结构解析软件解析了其结构, 结果表明其结晶于四方晶系的 $I-42m$ 空间群(其晶体结构解析数据及晶胞数据见表1), 性能测试显示该化合物倍频效应与AgGaS₂相当, 具有大的光学带隙(2.47 eV, AGSe带隙为1.87 eV)和宽的红外透光范围. 粉末X射线衍射图表征了其样品的单相, 理论值与实验值匹配较好. 拉曼光谱分析了结构

中化学键的种类, 表明该结构的正确与合理. 此外, 基于第一性原理的理论计算分析了该化合物结构与性能之间的关系, 计算了其能带结构(band structure, BS)和态密度(density of states, DOS).

1 实验

(i) 合成. 实验所用药品(纯度 $\geq 99.99\%$)购自上海阿拉丁生化科技有限公司. 所有药品储存在无水无氧的充满氩气的手套箱中. Li₂BaSiSe₄固相合成法的步骤如下: (1) 在氩气环境下将Li, Ba, Si, Se的单质按照化学计量比2:1:1:4称量并放置于内径为7 mm的石墨坩埚中; (2) 在氩气环境下将坩埚放入内径为10 mm的石英玻璃管中; (3) 将石英玻璃管内抽真空至 10^{-3} Pa并用烷氧焰将玻璃管封口; (4) 封口的玻璃管放在程序控温的炉子中, 50 h内加热到800℃, 保温100 h后以5℃/h的速率降温到200℃, 然后关闭炉子直到常温. 在以上过程结束后, 可以获得Li₂BaSiSe₄的多晶粉末, 在高倍偏光显微镜下将粉末多晶分散于硅油中, 挑选出质地均匀、形状规则的单晶颗粒用于单晶结构测试, 多晶样品用于粉末X射线衍射(XRD)测试.

(ii) 粉末X射线衍射. 实验制得的反应产物用氮氮二甲基酰胺(DMF)洗过之后干燥, 然后研磨成粉末用于粉末XRD测试. 衍射仪为配有铜靶的Bruker D2 X射线衍射仪, 测试温度是298 K, 2θ 设定范围为 $10^\circ\sim 70^\circ$, 扫描步长为 0.02° , 扫描速度为1 s/步. 实验XRD图与由Mercury通过Cif文件导出的理论数据图匹配良好, 证明本文得到的是Li₂BaSiSe₄的纯样.

(iii) X射线单晶衍射. 在显微镜下挑选出一颗均匀透明的晶体, 将晶体用黏合剂粘在玻璃棒的顶端, 用装有钼靶的Bruker SMART ARES II 4K CCD衍射仪在296 K的温度下收集了晶体数据, 其中测试电压为50 kV, 电流为40 mA. 数据收集完毕之后, 我们用直接法确定晶体结构, 用全矩阵最小二乘法对结构进行精修, 用XPREP进行面吸收校正, 用PLATON对结构进行检索, 结果确认没有更高对称性的结构发现^[46,47]. 表1列出了数据收集, 结构精修和晶体参数的具体数据. 各向同性位移参数与原子计算键价罗列在表S1中, 键长和键角数据罗列在附件中的表S2中.

(iv) 紫外-可见-近红外漫反射光谱. 漫反射光

表1 Li₂BaSiSe₄的晶体数据和结构精修数据

Table 1 Crystal and structural refinement data of Li₂BaSiSe₄

实验式	Li ₂ BaSiSe ₄
分子量	495.15
温度(K)	296(2)
波长(Å)	0.71073
晶系, 空间群	四方晶系, $I-42m$
单胞尺寸	$a=6.921(3)$ Å, $\alpha=90^\circ$ $b=6.921(3)$ Å, $\beta=90^\circ$ $c=8.253(8)$ Å, $\gamma=90^\circ$
体积(Å ³)	395.3(5)
Z值, 计算密度	2, 4.160 mg/m ³
吸收系数(mm ⁻¹)	23.477
晶体尺寸(mm ³)	0.159×0.113×0.105
θ 范围	$3.842^\circ\sim 27.525^\circ$
限定范围	$-7\leq h\leq 8$, $-8\leq k\leq 7$, $-10\leq l\leq 9$
全部衍射点数/独立衍射 点数unique	1201/257($R_{int}=0.0218$)
$\theta=27.525^\circ$ 时完整度	100.00%
吸收校正	半经验
精修方法	F^2 的全矩阵最小二乘法
F^2 的适合度	1.065
最终R值($I>2\sigma(I)$)	$R_1=0.0179$, $wR_2=0.0458$
R值(全数据)	$R_1=0.0180$, $wR_2=0.0458$
绝对结构参数	0.09(5)
消光系数	n/a
最大的衍射峰、谷	0.481, -0.904(e Å ⁻³)

谱的测试由Shimadzu SolidSpec-3700DUV光谱仪完成, 光谱扫描范围是190~2600 nm, 能够显示出所测样品的紫外截止边. 漫反射数据通过Kubelka-Munk公式^[48]转换成吸收光谱, 用以估测样品带隙.

(v) 拉曼光谱. 拉曼光谱数据由装有CCD探测计的LABRAM HR转换光谱仪测试并收集. 测试的晶体挑选出之后放在玻璃片上, 用放大50倍的物镜选择晶体透光区域, 激光束半径为35 μm , 最高能量60 mW, 数据收集在15 s内完成(图S1).

(vi) 二次倍频效应. 二次倍频效应的测试使用了Kurtz-Perry方法^[49], 通过一个发射2.09 μm 光源的Q-开关激光器完成. 晶体研磨后用筛子筛出颗粒度为55~88, 88~105, 105~150, 150~200, 200~250 μm 的5组样品, 用相同颗粒度的AgGaS₂晶体作为对比项. 不同颗粒度的晶体被放置在圆形载玻片上, 用一个内径为8 mm, 厚度为1 mm的硅胶垫片包围, 然后用另外一个载玻片将样品密实地填充在中间的空隙, 之后将样品放入小样品池中, 拧紧固定之后进行测试. 光源为具有Q-开关的Ho:Tm:Cr:YAG激光器发射的2.09 μm 的红外光, 倍频信号由探测器接收之后在示波器上显示并记录.

(vii) 理论计算. 晶体结构的第一性原理^[50]计算是通过CASTEP软件包运用密度泛函理论进行的. 通过广义梯度近似, 运用Perdew-Burke-Ernzerhof公式计算了交换关联能, 能量截止边设定为900 eV. 通过四面体优化法^[51]将布里渊区设定为4 $\times$ 4 $\times$ 2. 倍频系数的计算是在零频限制下, 通过带波函数计算得到的, 其中静电二阶非线性极化率 $\chi_{\alpha\beta\gamma}^{(2)}$ 用下式表示^[6]:

$$\chi_{\alpha\beta\gamma}^{(2)} = \chi_{\alpha\beta\gamma}^{(2)}(\text{VE}) + \chi_{\alpha\beta\gamma}^{(2)}(\text{VH}) + \chi_{\alpha\beta\gamma}^{(2)}(\text{TB}).$$

该求和公式中, 总倍频极化率由虚拟空穴(VH)、虚拟电子(VE)和双波段(TB)三部分组成. 根据上式计算了Li₂BaSiSe₄的倍频来源.

2 结果与讨论

2.1 结构描述

Li₂BaSiSe₄结晶于四方晶系的 $I-42m$ 空间群, 晶胞参数为 $a=b=6.921(3)\text{\AA}$, $c=8.253(8)\text{\AA}$, $Z=2$, 在其最小不对称单元中Li, Ba, Si, Se各有一种结晶学位置. 在其结构中, 每个Li和Si均与4个Se原子配位形成四面体; 其中[LiSe₄]四面体通过共边连结形成了平行

于 ab 平面的层. 如图1(b), (c)所示, 相邻的两个层中[LiSe₄]四面体发生了一定的角度扭转, 因此LiSe₄层定义为A层和B层, 并且如图1(a)按照ABAB...沿着 a 方向排列, 但A层和B层中[LiSe₄]四面体的连接方式及两种层的形状均相同. 每个Si与4个Se原子形成[SiSe₄]四面体, 这些四面体作为桥梁将相邻的LiSe₄层连结在一起形成带有孔洞的三维框架, Ba原子填充在孔道中, 如图1(a)所示. 图1(a)和(d)是Li₂BaSiSe₄的整体结构分别在 bc 和 ab 平面的视图, 从图中可以看出相邻的LiSe₄层中Li原子的位置在 ab 平面是重合的, 但相应的四面体之间有一定的角度旋转; 此外, 相邻两层中Si与Ba原子的排列是交替排列, 每个Si或Ba最邻近的均为4个Ba或者Si原子.

2.2 合成

Li₂BaSiSe₄必须在无水无氧的环境下合成, 其原料包括金属Li单质、金属Ba单质、Si单质和Se单质粉末. 按照化学计量比2:1:1:4将反应物称好, 先放入石墨坩埚中, 盖好盖子; 之后, 将石墨坩埚放入玻璃管中进行抽真空封管; 将封好的玻璃管放入程序控温马弗炉中, 缓慢升温至800 $^{\circ}\text{C}$, 期间在450 $^{\circ}\text{C}$ 下保温10 h; 在800 $^{\circ}\text{C}$ 下保温100 h, 以5 $^{\circ}\text{C}/\text{h}$ 的速率缓慢降温至300 $^{\circ}\text{C}$, 关闭炉子降温至室温. 在以上过程结束后, 可以获得Li₂BaSiSe₄的多晶粉末, 在高倍偏光显微镜下将粉末多晶分散于硅油中, 挑选出质地均匀、形状规则的单晶颗粒用于单晶结构测试, 多晶样品用于粉末XRD测试. 其单晶结构参数以及结构精修参数在表1中显示, 其粉末XRD图的理论值和实验值在图2中显示. 如图2, 实验值与理论值匹配完好.

2.3 光学性质

紫外-可见-红外光漫反射图谱由Shimadzu SolidSpec-3700DUV光谱仪完成, 光谱扫描范围190~2600 nm. 通过Kubelka-Munk公式将漫反射数据转化, 可以得到Li₂BaSiSe₄的光学带隙, 如图3(a)所示. 在商业化使用的红外非线性光学晶体中, 著名的硒化物为AgGaSe₂, 其光学带隙为1.83 eV. Li₂BaSiSe₄的光学带隙为2.47 eV, 相比于AgGaSe₂, 其光学带隙增大了35%. 光学带隙的增大意味着材料将可能获得更高的激光损伤阈值和未来应用的更大可能性. Li₂BaSiSe₄结晶于非中心对称空间群, 具有明显的非线性效应, 通过Kurtz-Perry方法我们测试了其在不同

图1 (网络版彩色) $\text{Li}_2\text{BaSiSe}_4$ 的结构图. (a) 沿 a 方向 $\text{Li}_2\text{BaSiSe}_4$ 的整体结构以及 LiSe_4 层; LiSe_4 形成的层A(b)和层B(c)的单层结构; (d) 沿 c 方向 $\text{Li}_2\text{BaSiSe}_4$ 的整体结构

Figure 1 (Color online) Structures of $\text{Li}_2\text{BaSiSe}_4$. (a) Structure of $\text{Li}_2\text{BaSiSe}_4$ along a axis and LiSe_4 layers. Monolayer A (b) and monolayer B (c) formed by LiSe_4 . (d) Whole structure of $\text{Li}_2\text{BaSiSe}_4$ along c axis

图2 (网络版彩色) $\text{Li}_2\text{BaSiSe}_4$ 的粉末XRD图的理论值和实验值对比图

Figure 2 (Color online) Theoretical and experimental powder XRD patterns

颗粒度下的倍频效应. 作为对比, 商业化使用的 AgGaS_2 晶体磨成粉之后过筛分离出6种颗粒度的粉末, 在相同条件下同时进行了测试, 结果如图3(b)所示.

从图3(b)可以看出, $\text{Li}_2\text{BaSiSe}_4$ 的倍频效应随着颗

粒度的增大而增大, 表明其具有一类相位匹配的性能, 在最大颗粒度下其倍频效应相当于1倍 AgGaS_2 . 在探索新材料的过程中, 获得1倍 AgGaS_2 的倍频效应是令人满意的.

此外, 为了能够深入分析结构与性能的关系, 以第一性原理计算为工具, 我们获得了 $\text{Li}_2\text{BaSiSe}_4$ 的一些光学性质的理论值. 其中非线性系数的理论值为 $d_{14}=17.31 \text{ pm/V}$, 该数值与AGS的非线性系数的理论值(13 pm/V)相当; $\text{Li}_2\text{BaSiSe}_4$ 的双折射率计算值为 0.02; 能带结构和态密度计算结果分别如图4(a)和(b)所示.

综合图4(a)和(b)可以看出, $\text{Li}_2\text{BaSiSe}_4$ 为直接带隙化合物, 带隙理论值为 2.07 eV , 具有半导体特性, 可能被应用为锂电池材料. 材料的光学性质主要受费米面附近电子影响, 因此, 分析费米面附近电子能带可以深入了解结构与性能的关系. 在费米面附近的价带顶和导带底, 占据的均是Se的 $4s \ 4p$ 轨道和Si

图3 (网络版彩色)光学性质. (a) $\text{Li}_2\text{BaSiSe}_4$ 的光学带隙图; (b) $\text{Li}_2\text{BaSiSe}_4$ (圆形)和 AgGaS_2 (方形)的粉末倍频效应

Figure 3 (Color online) Optical properties. (a) Band gap of $\text{Li}_2\text{BaSiSe}_4$. (b) Powder SHG responses of $\text{Li}_2\text{BaSiSe}_4$ (round) and AgGaS_2 (square)

图4 (网络版彩色) $\text{Li}_2\text{BaSiSe}_4$ 的理论能带结构图谱(a)和态密度图谱(b)

Figure 4 (Color online) Calculated band structure (a) and density of states (b) of $\text{Li}_2\text{BaSiSe}_4$

的3s3p轨道,表明 $\text{Li}_2\text{BaSiSe}_4$ 的带隙主要由 $[\text{SiSe}_4]$ 四面体决定.

3 总结

本文主要报道了一种新型碱金属碱土金属复合

硒化物 $\text{Li}_2\text{BaSiSe}_4$, 利用粉末XRD, 单晶XRD, 紫外-可见光-近红外漫反射光谱, 粉末倍频测试以及第一性原理计算进行了表征. 结果表明其具有较大的倍频效应, 为1倍的AGS, 作为红外非线性光学晶体材料, 具有一定的应用前景.

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补充材料

表 S1 $\text{Li}_2\text{BaSiSe}_4$ 的原子键价及各向同性参数

表 S2 $\text{Li}_2\text{BaSiSe}_4$ 的键长和键角

图 S1 $\text{Li}_2\text{BaSiSe}_4$ 的拉曼光谱

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Summary for “ $\text{Li}_2\text{BaSiSe}_4$: 一种具有显著二次倍频效应的新型复合金属硒化物”

$\text{Li}_2\text{BaSiSe}_4$: A new metal-mixed selenide with outstanding second-harmonic generation

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Nonlinear optical (NLO) materials as important frequency-conversion devices in solid state lasers, have attracted unprecedented attentions in laser science and technology. In infrared (IR) region, NLO materials display more important roles in view of critical application prospect including laser guidance, resource exploration and long-distance laser communication etc. AgGaS_2 , AgGaSe_2 and ZnGeP_2 are selected as the commercial IR NLO materials, but they exhibit low laser damage thresholds (LDT) induced by their small bandgaps, which limit their further applications in high energy laser systems. Therefore, it is still a big challenge to obtain new IR NLO materials, which could balance the demand of large second-harmonic generation (SHG) and high laser damage threshold. As a NLO material, the non-centrosymmetrical structure is the prerequisite condition, and mix-metal chalcogenides have attracted much attention since their structures exhibit a variety of acentric units arising from the combination of different center metals, which show different sizes, coordination preferences, and packing characteristics. Previous investigations indicate that the introduction of alkali and alkali earth metals is good for obtaining large band gap because they may avoid the d-d and f-f electron transition like popular LiGaS_2 , BaGa_4S_7 etc. Moreover, compared with sulfides, selenides produce larger SHG responses. Therefore, in this work, in aim at the balanced optical properties, we selected electricity-positive alkali metal Li, alkali earth metal Ba, silicon in IVA group and selenium as the raw materials. Through high temperature flux method, we have obtained a metal-mixed selenide $\text{Li}_2\text{BaSiSe}_4$.

The raw materials are weighted with the molar ratio of 2:1:1:4, and then loaded into the graphite crucible, finally sealed in a silicon tube under ethane-oxygen flame. The tube is put in a program-computed furnace with the temperature program as blow: (1) heat from room temperature to 190°C in 3 h and keep at this temperature for 300 min; (2) heat from 190 to 450°C in 10 h and keep at this temperature for 20 h; (3) heat from 450 to 850°C in 10 h and keep at this temperature for 30 h; (4) cool from 850 to 400°C in 100 h and turn down the furnace. Optical characterizations contain single crystal X-Ray diffraction (XRD), powder XRD, Raman spectrum, UV-vis-NIR diffuse reflection spectrum, and SHG responses measurement at 2.09 μm . Moreover, theoretical calculations have also made to further investigate the relationship between properties and structure, including band structure, density of states, birefringence and SHG coefficients.

Single crystals with millimeter sizes used for single crystal XRD and Raman spectrum are picked from the synthesized polycrystal under a microscope. The powder samples used for powder XRD characterization and UV-vis-NIR diffuse reflection are obtained from the ground polycrystals. The powder SHG responses are measured with sieved crystals in six different size ranges: 38–55, 55–88, 88–105, 105–150, 150–200, 200–250 μm , with AgGaS_2 in the same particle size ranges as the references. The band gap of $\text{Li}_2\text{BaSiSe}_4$ is obtained from UV-vis-NIR diffuse reflection data converted by Kubelka-Munk function, which is measured to be 2.47 eV, which is larger than AgGaSe_2 (1.83 eV). The SHG response is measured with 2.09 μm laser, and the result shows that $\text{Li}_2\text{BaSiSe}_4$ is type-I phase matchable and is equal to that of commercially applied AgGaS_2 . In conclusion, the introduction of Li and Ba could enlarge the band gap compared with classical AgGaSe_2 , but the SHG response need more rational designation to maintain at a high level.

infrared, nonlinear optical, second-harmonic generation, crystal

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