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高灵敏度下转换光学测温材料：$NaGd(WO_4)_2:Yb^{3+}/Er^{3+}$

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摘要：基于 Er^{3+} 的两个热耦合能级发光强度测量的荧光强度比测温技术由于不受光谱损失和激发强度波动的影响，故能够提供准确的非接触式温度测量。但目前通用的荧光强度比技术都是基于上转换激发，而上转换材料效率较低，测温不准确。考虑到 Er^{3+} 能级可通过不同激发源来布居，本文利用高能光子激发的高效下转换光学测温方法，来解决上转换发光带来的问题，并以具有高测温灵敏度的钨酸盐 $NaGd(WO_4)_2$ 为基质。研究发现，$NaGd(WO_4)_2$ 可成功用于下转换测温，Yb^{3+}/Er^{3+} 共掺样品比 Er^{3+} 单掺拥有更高的测温灵敏度，且下转换测温灵敏度要高于上转换，在掺杂浓度为 20% Yb^{3+}/1% Er^{3+} 时，测温灵敏度高达 $344.6\times10^{-4}\ K^{-1}$。这证明了 $NaGd(WO_4)_2:Yb^{3+}/Er^{3+}$ 是理想的测温材料，也很好地验证了其在高灵敏度下转换测温的可行性，为荧光强度比技术的应用开辟了新的前景。

关 键 词：荧光强度比测温；光学测温；高灵敏度；钨酸盐；上转换；下转换
中图分类号：O482.31 **文献标识码**：A doi：10.3788/CO.20191203.0596

Highly sensitive down-conversion optical temperature-measurement material: $NaGd(WO_4)_2:Yb^{3+}/Er^{3+}$

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Abstract: The fluorescence intensity ratio(FIR) thermometry based on the measurement of luminous intensi-

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ties of two thermal coupling energy levels of Er^{3+} provides high precision for the non-contacted thermometry due to its independency of the spectral loss and excitation intensity fluctuations. However, the common FIR technology is based on the up-conversion(UC) excitation, and its low up-conversion efficiency makes the temperature measurement inaccurate. Considering that the thermalization of population in Er^{3+} can be achieved by different excitation sources, we utilize the efficient down-conversion(DC) optical temperature measurement with a high-energy photon excitation. A tungstate material of $NaGd(WO_4)_2$ with high temperature sensitivity is used as the matrix material. It is found that $NaGd(WO_4)_2$ can be successfully applied for the DC thermometry, and the temperature sensitivity of Yb^{3+}/Er^{3+} co-doped sample is higher than that of Er^{3+} single-doped one. In addition, the DC thermometry possesses higher sensitivity than UC, and the temperature sensitivity of 20% Yb^{3+}/1% Er^{3+} doped sample is up to 344.6×10^{-4} K^{-1}, which demonstrates that $NaGd(WO_4)_2$:Yb^{3+}/Er^{3+} is an ideal temperature measuring material. More importantly, it further proves the feasibility of highly sensitive DC thermometry and opens up new prospects for the utilizations of FIR technology.

Key words: fluorescence intensity ratio(FIR) thermometry; optical thermometry; high sensitivity; tungstate; up-conversion; down-conversion

1　引　言

基于稀土(Rare Earth, RE)掺杂的光学测温由于能够通过荧光强度比进行非接触式测温,近年来引起了广泛关注[1-7]。与传统测温方法相比,基于 RE 离子的两个热耦合能级发光强度测量的 FIR(Fluorescence Intensity Ratio)技术不受光谱损失和激发强度波动的影响,因此它能够提供更为准确的温度测量[8-13]。众多稀土元素中,Er^{3+} 的 $^2H_{11/2}$和$^4S_{3/2}$能级发射符合玻尔兹曼分布,是公认的用于温度探测材料的理想发光中心。FIR 技术为非接触式测温带来了新的前景,但由于测温材料必须具有稳定的物理化学性质、较强的荧光信号和高测温灵敏度,理想的测温材料仍然短缺。稀土掺杂钨酸盐发光材料因具有结构多样性、良好的热稳定性和低声子能量而得到广泛研究,其在光学测温上的应用也被相继报道[14-16]。其中,Yb^{3+}/Er^{3+} 掺杂的 $Ca(WO_4)_2$、$La_2(WO_4)_3$、$NaY(WO_4)_2$ 材料的最高测温灵敏度分别高达 73×10^{-4}、97×10^{-4}和 146×10^{-4} K^{-1}[17-19]。然而,这些常用的 FIR 技术都是基于 980 nm 激发的上转换光学测温技术,而上转换效率较低,其需要较高的激发密度才能产生足够强的发射光[20],但高激发密度相应地会导致温度的升高,会使发光材料本身由于较高无辐射弛豫温度升高,进而使得测温不准确。考虑到 Er^{3+} 的能级可以通过不同激发源来热布居,除了传统的上转换激发方式外,本文认为通过具有高转换效率的下转换激发也可以实现 Er^{3+} 的热布居,进而实现温度探测。

本文利用高能光子激发的高效下转换光学测温方法来解决上转换发光带来的问题,选用高能激发源 X 射线[21-23]作为下转换激发源,并以具有高测温灵敏度的钨酸盐 $NaGd(WO_4)_2$为基质。具体地,先探讨了 1% Er^{3+} 单掺和 1% Yb^{3+}/1% Er^{3+} 共掺样品在 980 nm 激发下的上转换光学测温进行对比,发现不同掺杂的样品均能实现测温,但在共掺条件下上转换测温灵敏度更高。之后,系统地研究了两种测温样品在 X 射线下转换激发下的光学测温特性,研究发现,1% Er^{3+} 单掺和 1% Yb^{3+}/1% Er^{3+} 共掺的 $NaGd(WO_4)_2$的下转换测温灵敏度均高于上转换测温灵敏度,且共掺杂样品拥有较高的测温灵敏度(136.1×10^{-4} K^{-1})。此外,通过改变 Yb^{3+} 的掺杂浓度发现,增加 Yb^{3+} 的掺杂量有利于进一步提高下转换测温灵敏度,当掺杂配比为 20% Yb^{3+}/1% Er^{3+} 时,$NaGd(WO_4)_2$ 下转换测温灵敏度高达 344.6×10^{-4} K^{-1}。这验证了高灵敏下转换测温的可行性,为 FIR 技术的应用开辟了新的前景。

2 实 验

2.1 样品制备

通过高温固相法制备 $NaGd(WO_4)_2$:1% Er^{3+} 以及 $NaGd(WO_4)_2$:x% Yb^{3+}/1% Er^{3+} (x = 1,5,10,15,20)样品,实验所用的试剂有 WO_3(AR)、$NaCO_3$(AR)、Gd_2O_3(AR)、Yb_2O_3(99.99%)和 Er_2O_3(99.99%)。首先,将上述原料按照分子式化学计量比称取,并充分研磨 30 min。混合均匀后,将样品装入高温氧化铝坩埚中,然后在箱式高温炉中加热至 1 000 ℃持续 4 h。自然冷却至室温后取出,均匀研磨即可得到样品。

2.2 实验仪器

样品的晶体结构通过德国布鲁克公司 D8 advance X 射线衍射仪(CuKα,40 kV,40 mA)测定,扫描范围为 10°~80°。实验中所用的上、下转换激发源为 980 nm 连续激光器(最大输出功率为 3 W)和 X-ray 光源(JF-2000 W 靶,40 kV,20 mA)。采用 Andor SR-500i 光谱仪对不同温度下的样品进行发射谱测量。将样品填充在铜样品池中,并且通过电阻线元件将样品温度从 303 K 升至 563 K,埋在样品中的铜恒定热电偶用于监测样品的温度,误差为 ±1.5 K。

3 结果与讨论

3.1 结构表征

图 1 为 $NaGd(WO_4)_2$:1% Er^{3+} 样品以及 $NaGd(WO_4)_2$:1% Yb^{3+}/1% Er^{3+} 样品的 X 射线衍射(X-ray diffraction, XRD)图。可以观察到所有衍射峰的位置与 $NaGd(WO_4)_2$ 标准卡(PDF#25-0829)的位置一致,且未观察到其他的衍射峰,表明合成的样品为纯相。图 2 为 $NaGd(WO_4)_2$:1% Er^{3+} 样品以及 $NaGd(WO_4)_2$:1% Yb^{3+}/1% Er^{3+} 样品的 SEM 图,可以看出,高温固相法得到的样品颗粒尺寸在微米量级。

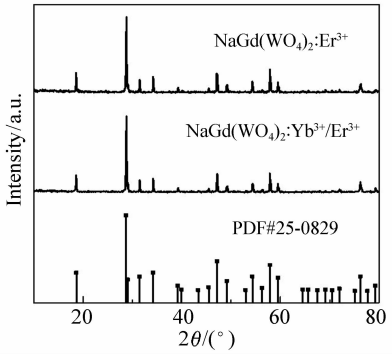

图 1 $NaGd(WO_4)_2$:1% Er^{3+} 及 $NaGd(WO_4)_2$:1% Yb^{3+}/1% Er^{3+} 样品的 XRD 图谱

Fig. 1 XRD spectrum patterns of $NaGd(WO_4)_2$:1% Er^{3+} and $NaGd(WO_4)_2$:1% Yb^{3+}/1% Er^{3+} samples

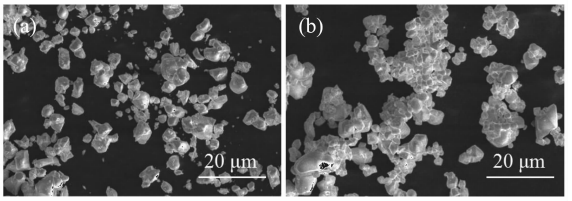

图 2 (a) $NaGd(WO_4)_2$:1% Er^{3+} 的 SEM 图;(b) $NaGd(WO_4)_2$:1% Yb^{3+}/1% Er^{3+} 的 SEM 图

Fig. 2 (a) SEM image of $NaGd(WO_4)_2$:1% Er^{3+}; (b) SEM image of $NaGd(WO_4)_2$:1% Yb^{3+}/1% Er^{3+}

3.2 上转换测温性质分析

图 3(a)和 3(b)给出了 1% Er^{3+} 单掺杂及 1% Yb^{3+}/1% Er^{3+} 共掺杂的 $NaGd(WO_4)_2$ 样品在不同温度(303 K,433 K and 563 K)时的 980 nm 激发上转换绿光发射谱。可以观察到,不同掺杂的样品均具有两个源于 $^2H_{11/2}\rightarrow{}^4I_{15/2}$ 和 $^4S_{3/2}\rightarrow{}^4I_{15/2}$ 辐射跃迁的发射峰,且当温度较低时,二者于 530 nm 绿光强度明显小于 552 nm 绿光发射强度。而当温度升高时,530 nm 强度相对于 552 nm 强度增加明显,即两个绿光的荧光强度比随温度升高逐渐增大。根据文献[24-26]知,两个绿光的荧光强度比可以表示为:

$$R = \frac{I_2}{I_1} = \frac{N_2 A_2 h\nu_2}{N_1 A_1 h\nu_1}, \tag{1}$$

其中,I_2 和 I_1 分别代表 $^2H_{11/2}\rightarrow{}^4I_{15/2}$ 和 $^4S_{3/2}\rightarrow{}^4I_{15/2}$ 跃迁过程产生的 530 nm 和 552 nm 绿色发光的积分强度,N_2 和 N_1 为能级 $^2H_{11/2}$ 和 $^4S_{3/2}$ 上的光子布居

总数,A_2 和 A_1 分别代表 $^2H_{11/2}$ 和 $^4S_{3/2}$ 的自发辐射跃迁几率,ν 是跃迁初态和末态的能量差,h 为普朗克常量。由于能级 $^2H_{11/2}$ 和 $^4S_{3/2}$ 非常接近,$^4S_{3/2}$ 能级上的电子热平衡后会有一部分通过热辐射作用布居 $^2H_{11/2}$ 能级[27],因此 $^2H_{11/2}$ 和 $^4S_{3/2}$ 能级跃迁带来的荧光强度比随温度变化关系可以表示为:

$$R = \frac{I_2}{I_1} = \frac{N_2 A_2 h\nu_2}{N_1 A_1 h\nu_1} = \frac{g_2}{g_1}\exp\left(\frac{-\Delta E}{k_B T}\right)\frac{h\nu_2 A_2}{h\nu_1 A_1} = B\exp\left(\frac{-\Delta E}{k_B T}\right), \quad (2)$$

其中,g_2、g_1 分别代表能级 $^2H_{11/2}$ 和 $^4S_{3/2}$ 的简并度 $2J+1$。为了方便对实验数据进行拟合,对(2)取对数,得到线性关系式

$$\mathrm{Ln}(R) = \alpha - \beta/T, \quad (3)$$

其中,$\alpha = \mathrm{Ln}B$,$\beta = \Delta E/k_B$。因此,温度 T 的倒数与荧光强度比 R 的对数成线性关系,通过数据拟合就可以得到参数 $\alpha = \mathrm{Ln}B$,$\beta = \Delta E/k_B$ 的值,从而得到 B 与 k_B 的值。图 4(a)、4(b)、4(d)、4(e)分别给出了 1% Er^{3+} 及 1% Yb^{3+}/1% Er^{3+} 掺杂样品 980 nm 激发的上转换荧光强度比 R 与绝对温度 T,及 $\mathrm{Ln}(R)$ 与 $1/T$ 的关系和拟合效果图。可以看到,实验数据能用指数和线性函数很好地拟合,单掺杂样品和共掺杂样品的荧光强度比与温度倒数间的关系分别为 $\mathrm{Ln}(R) = 2.01 - 929.6/T$ 和 $\mathrm{Ln}(R) = 3.24 - 1052.52/T$。对于实际应用来说,材料的测温灵敏度,即材料荧光强度比随温度变化的快慢是光学测温的重要参数。将测温灵敏度用 S 表示,则其与 R、T 之间的关系可以表示为:

$$S = \frac{\mathrm{d}R}{\mathrm{d}T} = R\left(\frac{\Delta E}{k_B T^2}\right) = B\frac{\Delta E}{k_B T^2}\exp\left(\frac{-\Delta E}{k_B T}\right). \quad (4)$$

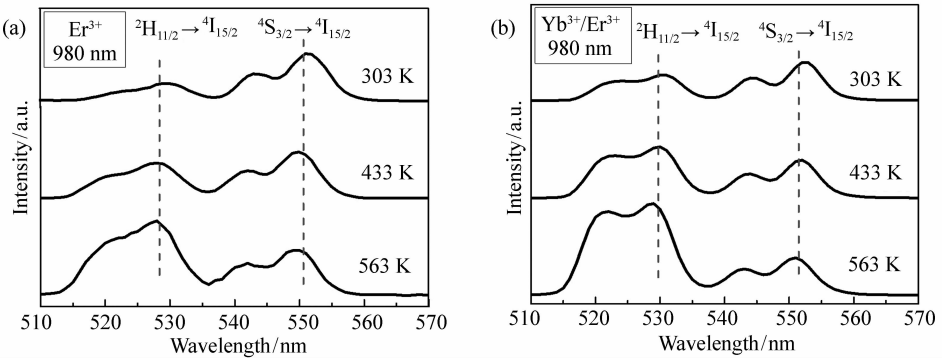

图 3　(a)1% Er^{3+} 单掺杂样品处于不同温度(303 K, 433 K and 563 K)时的 980 nm 激发上转换发射谱;(b)1% Yb^{3+}/1% Er^{3+} 共掺杂样品处于不同温度(303 K, 433 K and 563 K)时的 980 nm 激发上转换发射谱。图中均对 552 nm 处的峰进行了归一化

Fig. 3　(a) UC spectra of 1% Er^{3+}-doped sample at different temperatures (303 K, 433 K and 563 K) excited with 980 nm; (b) UC spectra of 1% Yb^{3+}/1% Er^{3+} co-doped sample at different temperatures (303 K, 433 K and 563 K) excited with 980 nm. The spectra were normalized at 552 nm

图 4(c)和 4(f)分别给出了 1% Er^{3+} 单掺杂样品和 1% Yb^{3+}/1% Er^{3+} 共掺杂样品测温灵敏度 S 与绝对温度 T 之间的变化关系。其中,1% Er^{3+} 单掺杂样品在 467 K 时,达到上转换测温的最高灵敏度:43.54×10^{-4} K^{-1};1% Yb^{3+}/1% Er^{3+} 共掺杂样品在 523 K 时,达到上转换测温的最高灵敏度:133.22×10^{-4} K^{-1}。可见,Yb^{3+} 对 Er^{3+} 存在敏化作用,在共掺条件下上转换测温灵敏度更高。

3.3　下转换测温性质分析

为了探究下转换测温的可行性,本文选用高能激发源 X 射线作为下转换激发源,并以上述 980 nm 激发下的上转换光学测温结果作为对比数据,系统地研究了 1% Er^{3+} 单掺和 1% Yb^{3+}/1% Er^{3+} 共掺的 $NaGd(WO_4)_2$ 材料的下转换光学测温性质。如图 5(a)和 5(b)所示,在 X 射线激发下,两种材料均拥有与 980 nm 激发一样的明亮绿色

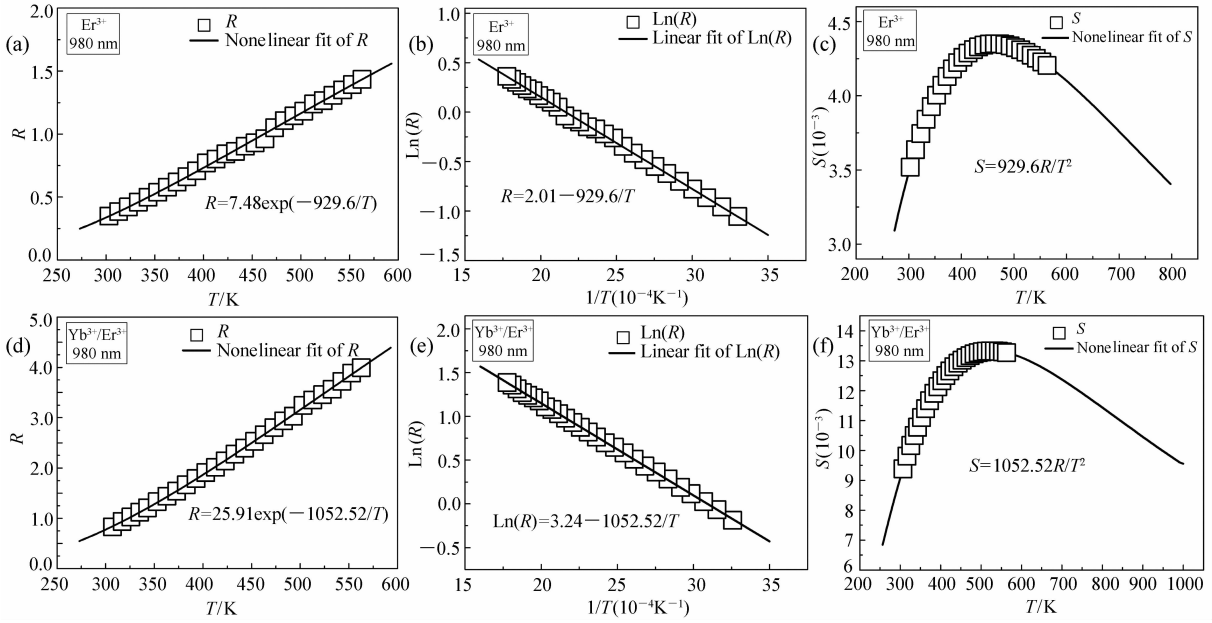

图4 (a)1% Er^{3+} 单掺杂样品在980 nm上转换激发下的荧光强度比 R 与绝对温度 T 之间的曲线关系;(b)1% Er^{3+} 单掺杂样品在980 nm上转换激发下 Ln(R)与1/T 之间的线性关系;(c)1% Er^{3+} 单掺杂样品在980 nm上转换激发下测温灵敏度 S 与绝对温度 T 之间的曲线关系;(d)1% Yb^{3+}/1% Er^{3+} 共掺杂样品在980 nm上转换激发下的荧光强度比 R 与绝对温度 T 之间的曲线关系;(e)1% Yb^{3+}/1% Er^{3+} 共掺杂样品在980 nm上转换激发下 Ln(R)与1/T 之间的线性关系;(f)1% Yb^{3+}/1% Er^{3+} 共掺杂样品在980 nm上转换激发下测温灵敏度 S 与绝对温度 T 之间的曲线关系

Fig. 4 (a) Relationship between R and absolute temperature T of 1% Er^{3+}-doped sample under 980 nm(UC) excitation; (b) Monolog plot of R as a function of reciprocal absolute temperature of 1% Er^{3+}-doped sample under 980 nm(UC) excitation; (c) Sensor sensitivity(S) as a function of the absolute temperature of 1% Er^{3+}-doped sample under 980 nm(UC) excitation; (d) Relationship between R and absolute temperature T of 1% Yb^{3+}/1% Er^{3+} co-doped sample under 980 nm(UC) excitation; (e) Monolog plot of R as a function of reciprocal absolute temperature of 1% Yb^{3+}/1% Er^{3+} co-doped sample under 980 nm(UC) excitation; (f) Sensor sensitivity(S) as a function of absolute temperature of 1% Yb^{3+}/1% Er^{3+} co-doped sample under 980 nm(UC) excitation

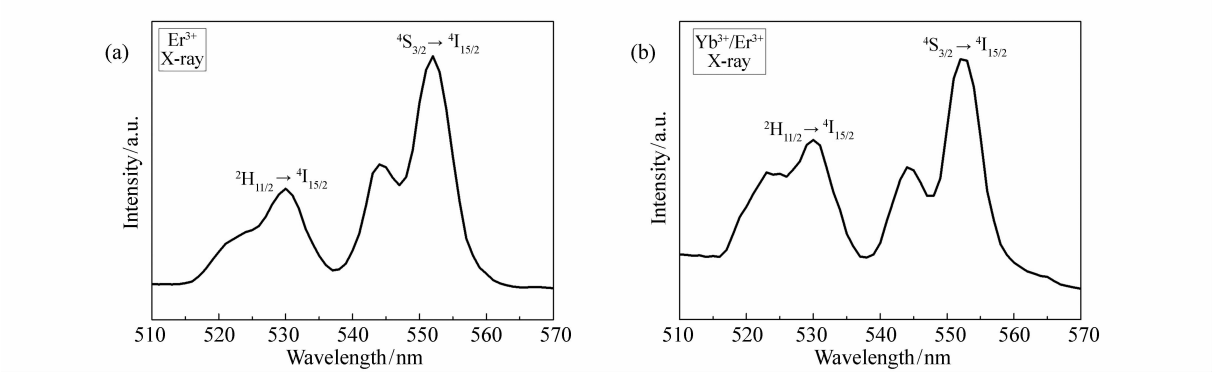

图5 (a)1% Er^{3+} 单掺杂样品的X射线激发下转换发射谱;(b)1% Yb^{3+}/1% Er^{3+} 共掺杂样品的X射线激发下转换发射谱

Fig. 5 (a) DC emission spectrum of 1% Er^{3+}-doped sample excited with X-ray; (b) DC emission spectrum of 1% Yb^{3+}/1% Er^{3+} co-doped sample excited with X-ray

发光,且也均包含 2 个典型的发射峰:530 nm、552 nm。这意味着 X 射线下转换激发也可以成功实现 Er^{3+} 的热布居,也为接下来的下转换测温提供了可能和依据。

由图 6(a)和 6(b)可以观察到,Er^{3+} 单掺杂及 Yb^{3+}/Er^{3+} 共掺杂的 $NaGd(WO_4)_2$ 样品在 X 射线激发下的下转换发射谱随温度变化的规律与上转换一致。如图 7(a)和 7(d)所示,两个绿光的荧光强度比也随温度升高逐渐增大,且下转换得到的荧光强度比都相对高于上转换。此外,通过 $Ln(R)$ 与 $1/T$ 之间的函数关系(图 7(b)和 7(e)),$Ln(R) = 2.52 - 993.97/T$(1% Er^{3+} 单掺杂样品)和 $Ln(R) = 3.3 - 1078.32/T$(1% Yb^{3+}/1% Er^{3+} 共掺杂样品)可以看到,在不同布居方式下得到的拟合结果相近,因此可得通过拟合所得实验结果较为准确,下转换布居进行测温也是可行的。

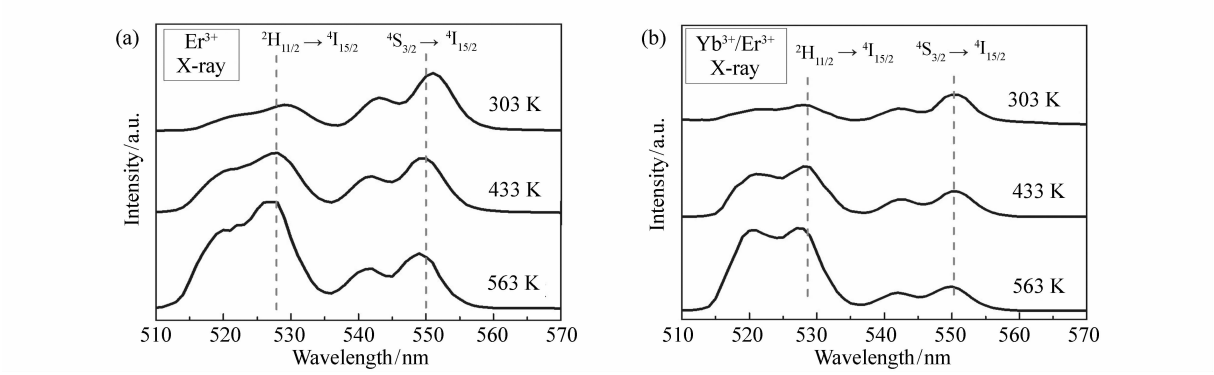

图 6　(a)1% Er^{3+} 单掺杂样品处于不同温度(303 K, 433 K and 563 K)时的 X 射线激发下转换发射谱;(b)1% Yb^{3+}/1% Er^{3+} 共掺杂样品处于不同温度(303 K, 433 K and 563 K)时的 X 射线激发下转换发射谱。图中均对 552 nm 处的峰进行了归一化

Fig. 6　(a) DC spectra of 1% Er^{3+}-doped sample at different temperatures (303 K, 433 K and 563 K) excited with X-ray; (b) DC spectra of 1% Yb^{3+}/1% Er^{3+} co-doped sample at different temperatures (303 K, 433 K and 563 K) excited with X-ray. The spectra were normalized at 552 nm

下转换布居方式下,1% Er^{3+} 单掺杂样品和 1% Yb^{3+}/1% Er^{3+} 共掺杂样品的测温灵敏度 S 与绝对温度 T 之间的关系如图 7(c)和 7(f)所示。值得注意的是,在 X 射线激发,两种材料均具有比上转换激发更高的测温灵敏度。其中,1% Er^{3+} 单掺杂样品在 501 K 时,达到下转换测温的最高灵敏度:67.96×10^{-4} K^{-1};1% Yb^{3+}/1% Er^{3+} 共掺杂样品在 539 K 时,达到下转换测温的最高灵敏度:136.1×10^{-4} K^{-1}。而且当温度高达 1 000 K 时,1% Yb^{3+}/1% Er^{3+} 共掺杂样品依然具有高达 100×10^{-4} K^{-1}的下转换测温灵敏度,这是大多数测温材料所不具备的。此外,1% Yb^{3+}/1% Er^{3+} 共掺杂样品无论在何种布居方式下,都具有比 1% Er^{3+} 单掺杂样品更高的测温灵敏度,但具体作用机理还不太清晰。更为重要的是,通过改变 Yb^{3+} 掺杂浓度发现,增加 Yb^{3+} 的掺杂量有利于进一步提高下转换测温灵敏度(图 8),当掺杂配比为 20% Yb^{3+}/1% Er^{3+} 时,$NaGd(WO_4)_2$ 下转换测温灵敏度高达 344.6×10^{-4} K^{-1}。

这些结果表明,Yb^{3+}/Er^{3+} 共掺杂 $NaGd(WO_4)_2$ 材料在同类型测温材料中均具有较高的测温灵敏度,如表 1 所示,是理想的测温材料。更为重要的是,$NaGd(WO_4)_2$:Yb^{3+}/Er^{3+} 材料不仅具有稳定的物理化学性质,且在 X 射线激发的下转换布居方式下得到的最高测温灵敏度高于上转换布居。这也进一步验证了高灵敏度下转换测温的可行性。又由于 X 射线具有较深的穿透性,因此 X 射线下转换测温也为 FIR 技术在深层次组织中的应用提供了新的可能。

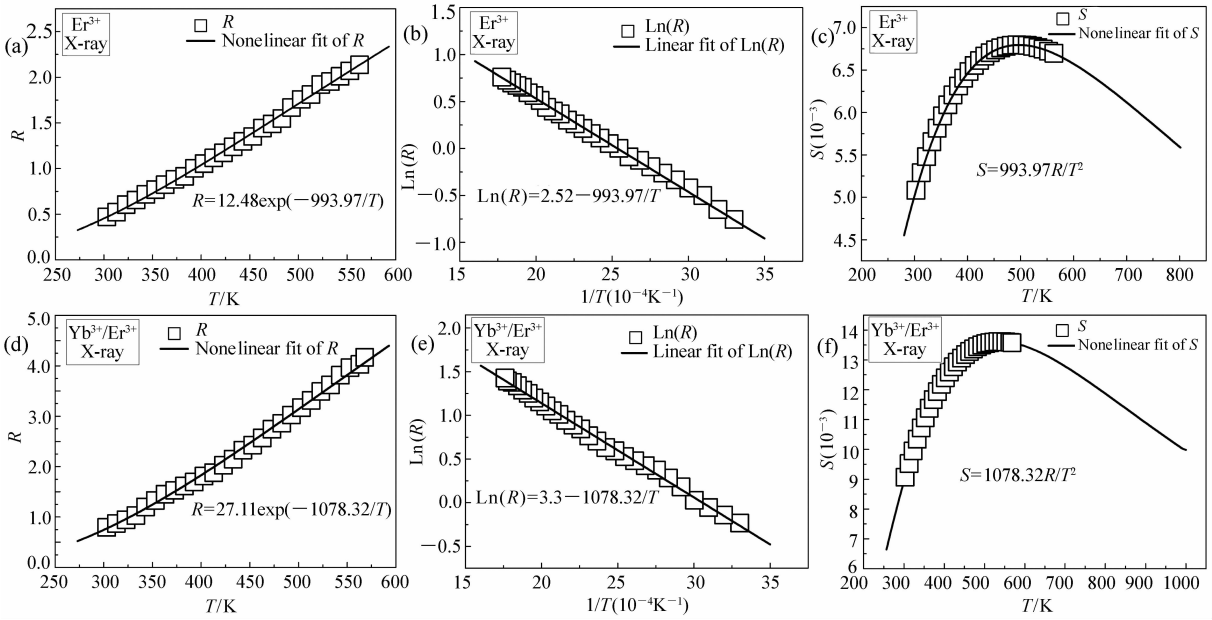

图7 (a)1% Er^{3+}单掺杂样品在X射线下转换激发下的荧光强度比R与绝对温度T之间的曲线关系;(b)1% Er^{3+}单掺杂样品在X射线下转换激发下Ln(R)与1/T之间的线性关系;(c)1% Er^{3+}单掺杂样品在X射线下转换激发下测温灵敏度S与绝对温度T之间的曲线关系;(d)1% Yb^{3+}/1% Er^{3+}共掺杂样品在X射线下转换激发下的荧光强度比R与绝对温度T之间的曲线关系;(e)1% Yb^{3+}/1% Er^{3+}共掺杂样品在X射线下转换激发下Ln(R)与1/T之间的线性关系;(f)1% Yb^{3+}/1% Er^{3+}共掺杂样品在X射线下转换激发下测温灵敏度S与绝对温度T之间的曲线关系

Fig. 7 (a) Relationship between R and absolute temperature T of 1% Er^{3+}-doped sample under X-ray (DC) excitation; (b) monolog plot of R as a function of reciprocal absolute temperature T of 1% Er^{3+}-doped sample under X-ray (DC) excitation; (c) sensor sensitivity (S) as a function of absolute temperature of 1% Er^{3+}-doped sample under X-ray (DC) excitation; (d) relationship between R and absolute temperature T of 1% Yb^{3+}/1% Er^{3+} co-doped sample under X-ray (DC) excitation; (e) monolog plot of R as a function of reciprocal absolute temperature of 1% Yb^{3+}/1% Er^{3+} co-doped sample under X-ray (DC) excitation; (f) sensor sensitivity (S) as a function of the absolute temperature of 1% Yb^{3+}/1% Er^{3+} co-doped sample under X-ray (DC) excitation

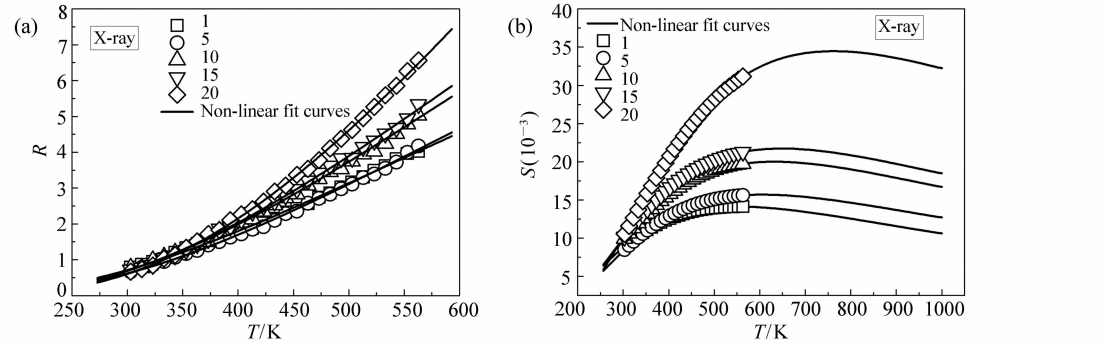

图8 (a)x% Yb^{3+}/1% Er^{3+}(x=1,5,10,15,20)共掺杂样品在X射线下转换激发下的荧光强度比R与绝对温度T之间的曲线关系;(b)x% Yb^{3+}/1% Er^{3+}(x=1,5,10,15,20)共掺杂样品在X射线下转换激发下测温灵敏度S与绝对温度T之间的曲线关系

Fig. 8 (a) Relationship between R and absolute temperature T of x% Yb^{3+}/1% Er^{3+} (x = 1, 5, 10, 15, 20) co-doped samples under X-ray (DC) excitation; (b) sensor sensitivity (S) as a function of absolute temperature for x% Yb^{3+}/1% Er^{3+} (x = 1, 5, 10, 15, 20) co-doped samples under X-ray (DC) excitation

表 1　Er^{3+} 在不同 Yb^{3+}/Er^{3+} 共掺基质中的最高测温灵敏度和计算荧光强度比中涉及到的参数 B 和 $\Delta E/k_B$ 的大小,及每种材料达到最高测温灵敏度时所需温度和激发波长

Tab. 1　The fluorescence intensity ratio parameters and values of the maximum sensitivity of Er^{3+} in different Yb^{3+}/Er^{3+} co-doped hosts, and temperatures for the maximum sensitivity as well as the excitation wavelength

Host	B	$\Delta E/k_B$(K)	S_{MAX}(K^{-1})	T/K	Excitation wavelength/nm	Ref.
$NaZnPO_4$	12.8	1 218.4	0.005 7	612	980	28
Ba_2LaF_7	1.56	396.88	0.004 3	298	980	29
CaF_2	6.79	1 263.6	0.003 1	625	980	30
KLu_2F_7	10.86	1 242	0.004 7	620	980	31
$La_2(WO_4)_3$	18.12	1 018.39	0.009 7	510	980	18
$NaY(WO_4)_2$	29.2	1 073.6	0.014 5	530	980	19
$NaLa(MO_4)_2$	24.78	1 035	0.013 1	510	980	32
$NaYF_4$	4.89	1 117.4	0.002 4	560	980	33
GdF_3	3	1 127	0.004	575	980	34
$NaGdF_4$	7.71	1 135	0.003 7	580	980	35
silicate glass	3.65	592.6	0.003 3	286	978	36
Yttrium silicate powders	3.65	817	0.005 6	400	975	37
$NaGd(WO_4)_2$	27.11	1 178.32	0.034 46	539	X-ray	本文

4　结　论

本文报道了一种新型的基于高灵敏度测温材料 $NaGd(WO_4)_2$可用于深层次高效测温的 FIR 技术,利用 X 射线下转换激发方式实现了光学温度探测。具体地,先探讨了 Er^{3+} 单掺和 Yb^{3+}/Er^{3+} 共掺样品在 980 nm 激发下的上转换光学测温结果作为对比数据,又进一步探讨了二者在 X 射线下转换激发下的测温性质。研究发现,Er^{3+} 单掺和 Yb^{3+}/Er^{3+} 共掺样品通过不同的激发方式,均可以实现布居,进而实现光学测温,但共掺杂样品无论在 980 nm 激发的上转换测温还是 X 射线激发的下转换测温中,都拥有比 Er^{3+} 单掺杂样品更高的测温灵敏度。重要的是,下转换测温灵敏度均高于上转换测温灵敏度。此外,通过改变 Yb^{3+} 掺杂浓度发现,增加 Yb^{3+} 的掺杂量有利于进一步提高下转换测温灵敏度,当掺杂配比为 20% Yb^{3+}/1% Er^{3+} 时,$NaGd(WO_4)_2$ 的下转换测温灵敏度高达:344.6×10^{-4} K^{-1}。这验证了高灵敏下转换测温的可行性,为 FIR 技术的应用开辟了新的前景。

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