

## 直接沉淀法合成 $\text{Sc}_2\text{O}_3$ 纳米粉

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**摘 要:** 研究了直接沉淀法合成 $\text{Sc}_2\text{O}_3$  纳米粉的工艺。以硝酸钪 $[\text{Sc}(\text{NO}_3)_3]$  为母盐, 氨水 $(\text{NH}_3 \cdot \text{H}_2\text{O})$  作沉淀剂, 采用直接沉淀法合成出网状的前驱沉淀物, 同时分析了前驱体的热分解过程。通过X射线衍射和红外光谱对前驱体的物相组成进行了定性分析, 结果表明, 该前驱沉淀物为 $\gamma\text{-ScOOH} \cdot n\text{H}_2\text{O}$  与 $\text{NH}_4\text{Sc}_3(\text{SO}_4)_2(\text{OH})_6 \cdot n\text{H}_2\text{O}$  的两相混合物。前驱体经过微化处理, 在 $1\,000\,^\circ\text{C}$  的温度下煅烧, 生成的 $\text{Sc}_2\text{O}_3$  纳米粉具有纯度较高、颗粒粒度小( $40\,\text{nm}$ )、粒度分布窄、近似球形 $\text{Sc}_2\text{O}_3$  的性能, 但是粉体产生了轻微团聚的现象。

**关键词:**  $\text{Sc}_2\text{O}_3$ ; 纳米粉; 直接沉淀法; 微化处理; 硝酸盐

中图分类号: O611.3 文献标识码: A 文章编号: 1674-3962(2011)04-0054-04

## Synthesis of $\text{Sc}_2\text{O}_3$ Nanopowders by Direct Precipitation Process

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**Abstract:** Synthesis of  $\text{Sc}_2\text{O}_3$  nanopowders by direct precipitation approach has been investigated. The netlike precursor was synthesized taking ammonia as precipitant and scandium nitrate solution as mother liquor. Phase transformation of the precursor upon calcination was analyzed. The results show that  $\text{Sc}_2\text{O}_3$  nanopowders calcined at  $1\,000\,^\circ\text{C}$  are spherical, ultrafine ( $40\,\text{nm}$ ), and of high purity and narrow particle size distribution.

**Key words:**  $\text{Sc}_2\text{O}_3$ ; nanopowders; direct precipitation process; micro processing; nitrate

### 1 前 言

$\text{Sc}_2\text{O}_3$  是一种稀土氧化物, 广泛地应用于航天、激光、导弹等尖端科学领域, 也广泛地应用于工业生产与日常生活中。

以 $\text{Sc}_2\text{O}_3$  为原料制成的钪钠灯作为一种新型光源, 以其节能、光性能优良和长寿等特点而逐渐取代其它光源;  $\text{Sc}_2\text{O}_3$  还可作为二氧化锆陶瓷的稳定剂以及氮化硅陶瓷的烧结助剂; 将其掺杂到 $\text{CO}_2$ ,  $\text{NO}_2$  传感器中或掺杂到阴极射线管中, 可以起到提高分辨率和提高亮度的

作用; 将它掺杂到钆镓石榴石(GGG)中制得的钆镓钪石榴石(GSGSS), 可以显著提高其发射功率;  $\text{Sc}_2\text{O}_3$  还用于制造基于张弛振荡器的铁电陶瓷, 如钽酸铅钪(PST)和铌酸铅钪(PSN); 含 $\text{Sc}_2\text{O}_3$  的 $\text{LiNbO}_3$  晶体的二次光折射率降低, 适于制造参数频率选择器、波导管和光导开关; 此外,  $\text{Sc}_2\text{O}_3$  用来制备 $\text{Sc}_2\text{O}_3$  透明陶瓷、YSAG透明陶瓷及激光透明陶瓷等。<sup>[1-10]</sup>

本文以硝酸钪为母盐, 氨水作沉淀剂, 研究了直接沉淀法制备 $\text{Sc}_2\text{O}_3$  纳米粉的工艺并表征了粉体的相关性能。

### 2 实 验

#### 2.1 实验原理

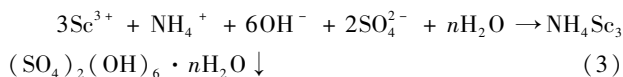
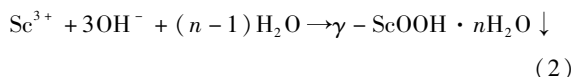
本实验, 通过各种测试分析, 推测反应过程如下:



收稿日期: 2010-10-90

基金项目: 国家自然科学基金资助项目(50672014); 国家高技术  
研究发展计划资助项目(2007AA06Z116)

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煅烧前驱沉淀物, 经过一系列脱水、脱羟基、脱铵、脱硫的过程, 最终形成  $\text{Sc}_2\text{O}_3$  粉体。

## 2.2 溶液的配置

(1) 90 ~ 110 °C 的温度下, 将  $\text{Sc}_2\text{O}_3$  粗粉溶于过量的浓硝酸溶液中, 然后将溶液蒸干以除去过量的硝酸。将所得的白色固体, 溶解在蒸馏水中配成 300 mL 浓度为 0.1 mol/L 的  $\text{Sc}(\text{NO}_3)_3$  溶液, 加入 4 g  $(\text{NH}_4)_2\text{SO}_4$  作为分散剂, 同时加入 3 g 聚乙二醇 1000 作为表面活性剂, 搅拌使之溶解; (2) 配制浓度为 0.8 mol/L 的  $\text{NH}_3 \cdot \text{H}_2\text{O}$  溶液作为沉淀剂。

## 2.3 粉体的合成

室温下, 将上述配置好的  $\text{NH}_3 \cdot \text{H}_2\text{O}$  溶液正向滴加到  $\text{Sc}(\text{NO}_3)_3$  溶液中, 同时快速搅拌, 滴定速度大约为 5 mL/min, 滴定终点的 pH 值至 8.0。反应结束后生成胶状物, 继续搅拌 1 h 得到前驱沉淀物。前驱沉淀物用蒸馏水离心清洗数次, 再用无水乙醇洗涤两次。将清洗后的前驱沉淀物超声 15 min, 然后在 80 °C 真空干燥。干燥后的前驱体在万能粉碎机中粉碎, 过 74  $\mu\text{m}$  的筛网, 并用玛瑙研钵研细。将产物放入高温电阻炉中, 在 1 000 °C 的温度下煅烧 4 h, 升温速率为 5 °C/min, 中间取出一次湿磨 5 h。

## 2.4 粉体的表征

采用美国 TA 公司产的 SDT Q 600 型热分析系统分析前驱体的热分解过程, 测试样品的质量为 6.261 0 mg, 升温速率为 10 °C/min, 气氛为流动  $\text{O}_2$ 。

采用美国 PerkinElmer proclisely 公司产的 Spectrum One 红外光谱仪对前驱体及煅烧产物的化学组成进行定性分析。采用荷兰 Pypw3040-60 型 X 射线衍射仪 ( $\text{CuK}\alpha$  辐射, Ni 滤波, 分析前驱沉淀物和煅烧产物的物相组成。采用 JME-2010 型高分辨透射电镜 (HRTEM) 观察前驱沉淀物及其在 1 000 °C 的温度下煅烧后得到的粉体形貌。

# 3 性能测试结果与讨论

## 3.1 前驱体煅烧过程的 DTA/TG 分析

图 1 表示的是前驱体 DTA/TG 曲线。从 TG 曲线上可以看出, 这种前驱体分解成为氧化物主要分 3 个阶段。第 1 阶段 (300 °C 以下) 主要是由于脱水 (包括吸附水和结晶水), 失重率为 -7.0%; 第 2 阶段 (300 ~ 460 °C) 主要是由于脱铵, 失重率为 -21.9%; 第 3 阶段 (460 ~

750 °C) 是由于脱羟基, 失重率为 -27.8%; 第 4 阶段 (750 °C 以上) 主要是由于脱硫, 失重率达到 36.55%。从 DTA 曲线上可以看出, 温度在 350 °C 有 1 个明显的放热峰, 可能是由于分解出的气体 (主要是氨气) 燃烧生成氮氧化物而放出的热量。在 454 °C 有 1 个明显的吸热峰, 说明在此温度下开始大量脱羟基; 而在 800 °C 微弱的吸热峰则是由于脱硫造成的, 这与 TG 分析的结果是一致的。

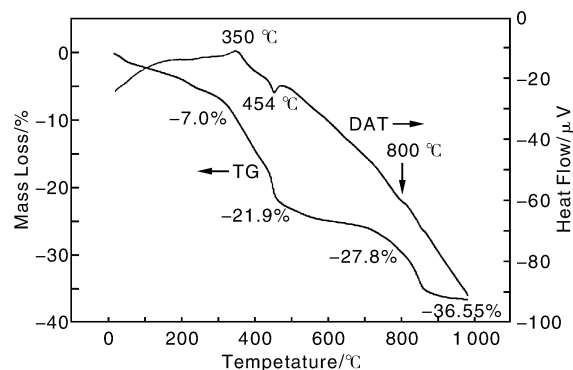


图 1 前驱体的热分解过程 DTA/TG 分析曲线

Fig. 1 DTA/TG curves of decomposition process of the precursor

## 3.2 红外光谱分析

通过红外光谱法 (IR) 对沉淀前驱体及 1 000 °C 的煅烧产物的化学组成作了定性分析 (图 2)。前驱体在波数

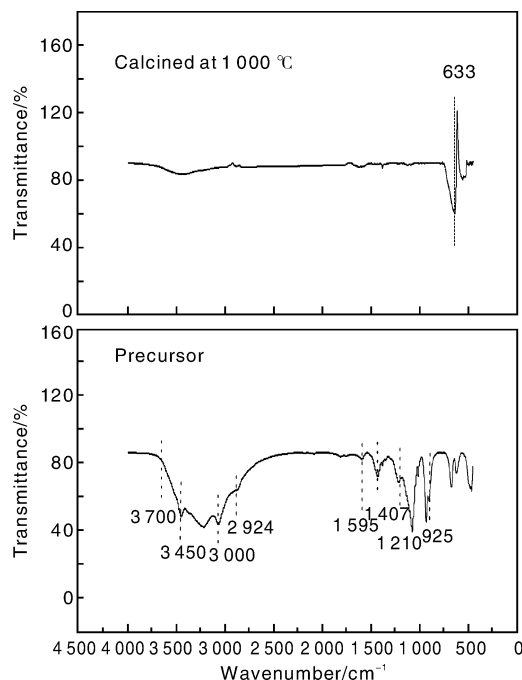


图 2 前驱体和 1 000 °C 的煅烧产物的红外光谱

Fig. 2 Infrared spectra showing the precursor and calcined powders at 1 000 °C

为  $1\,595$ ,  $3\,450$ ,  $3\,750\text{ cm}^{-1}$  左右的峰分别为水分子的剪式、对称和反对称的振动峰特征(由于水分子的振动自由度为:  $3 \times 3 - 6 = 3$ , 故水分子具有 3 种基本振动形式)。在  $3\,000 \sim 3\,700\text{ cm}^{-1}$  处为自由羟基(与 Sc 离子相连的羟基而不是水中的羟基)的振动峰。在  $2\,924$ ,  $1\,407\text{ cm}^{-1}$  处的峰是铵的振动峰。在  $925 \sim 1\,210\text{ cm}^{-1}$  的多频带为硫酸根的振动峰。所以, 前躯体的成分为:  $\gamma\text{-ScOOH} \cdot n\text{H}_2\text{O}$  与  $\text{NH}_4\text{Sc}_3(\text{SO}_4)_2(\text{OH})_6 \cdot n\text{H}_2\text{O}$  的两相混合物, XRD 的分析结果(图 3)也证实了这一点。在温度为  $1\,000\text{ }^\circ\text{C}$  煅烧后的粉体中仅有  $633\text{ cm}^{-1}$  处的振动峰, 该峰为 Sc-O 的振动峰。可见, 这说明在此温度下前躯体的分解反应已经基本结束, 生成的  $\text{Sc}_2\text{O}_3$  的纯度较高。IR 的分析结果与 DTA/TG 的分析结果是一致的。

### 3.3 XRD 射线分析

通过 XRD 对前躯体及  $1\,000\text{ }^\circ\text{C}$  的煅烧产物进行了定性分析(图 3)。结果表明, 主要成分为:  $\gamma\text{-ScOOH} \cdot n\text{H}_2\text{O}$  与  $\text{NH}_4\text{Sc}_3(\text{SO}_4)_2(\text{OH})_6 \cdot n\text{H}_2\text{O}$  的两相混合物。通过对前躯体的 XRD 衍射峰的分析表明, 部分衍射峰较尖锐, 对应结晶性良好的晶相  $\text{NH}_4\text{Sc}_3(\text{SO}_4)_2(\text{OH})_6 \cdot n\text{H}_2\text{O}$ 。另一部分低强度的衍射峰是  $\gamma\text{-ScOOH} \cdot n\text{H}_2\text{O}$  相。在  $1\,000\text{ }^\circ\text{C}$  的煅烧产物的 XRD 衍射峰与  $\text{Sc}_2\text{O}_3$  的立方晶相一致, 并未检测出其它晶相的存在, 衍射峰强度大且尖锐, 说明此温度下的煅烧产物的晶体性好, 晶体

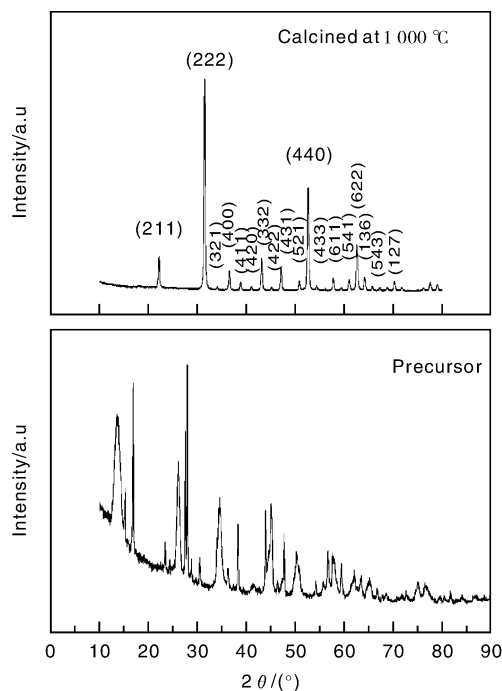


图 3 XRD 测定的前躯体及煅烧产物的图谱

Fig. 3 XRD patterns of precursor and powder calcined at  $1\,000\text{ }^\circ\text{C}$

缺陷少。XRD 分析的结果与 DTA/TG 分析和 IR 分析的结果是一致的。

### 3.4 前躯体及煅烧产物

图 4 是沉淀前躯体和  $\text{Sc}_2\text{O}_3$  纳米粉的粒子形态。由图 4a 可以看出, 前躯体多呈网状结构, 由图 4b 可以看出, 煅烧后的纳米粒子的颗粒粒度小(大约为  $40\text{ nm}$ )、粒度分布窄、近似球形, 但是粉体分散性稍差, 产生了轻微的团聚现象。这是因为由该方法合成出的前驱沉淀物类似于胶状, 很难洗涤, 且干燥后产生了较大的收缩并发生了强烈的团聚现象, 前躯体用研钵很难研碎, 所以应该在煅烧之前对前躯体进行微化分散处理。本实验采用粉碎细度为  $350 \sim 74\text{ }\mu\text{m}$  的高速万能粉碎机将此硬块粉碎、过筛、并用研钵研细, 然后在煅烧过程中取出一次湿磨, 以起到分散粉体的目的。但是由于前躯体的团聚过于强烈, 煅烧后的粉体始终还是无法彻底打开, 产生了轻微的团聚现象。

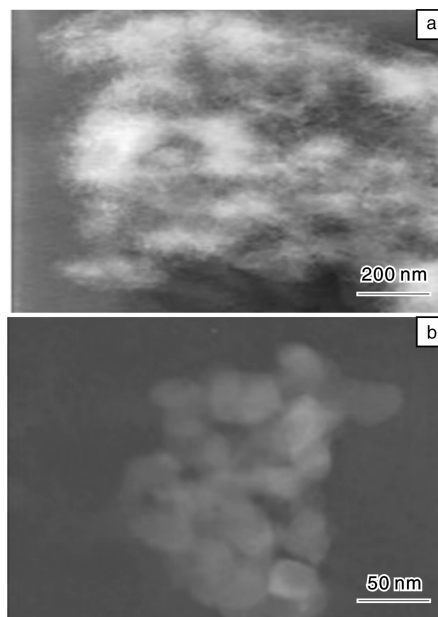


图 4 前躯体及煅烧产物的 TEM 照片: (a) 前躯体, (b)  $1\,000\text{ }^\circ\text{C}$  煅烧后的产物

Fig. 4 TEM micrographs of precursor (a) and powder (b) calcined at  $1\,000\text{ }^\circ\text{C}$  for 4 h

## 4 结 论

(1) 在室温下, 通过正向滴定的方法合成出了网状结构的前躯体。

(2) 前躯体经微化处理、煅烧后合成出粒度约为  $40\text{ nm}$  左右的  $\text{Sc}_2\text{O}_3$  纳米粉。该制备工艺合成的  $\text{Sc}_2\text{O}_3$  纳米粉具有纯度较高、颗粒粒度小、粒度分布窄、近似球形的性能。

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## Dutch Researchers Identify Huge Potential of Nanocrystals in Fuel Cells

The addition of extremely small crystals to solid electrolyte material has the potential to considerably raise the efficiency of fuel cells. Researchers at TU Delft were the first to document this accurately. Their second article on the subject in a very short time was published in the scientific journal, *Advanced Functional Materials*.

The researchers at the Faculty of Applied Sciences at TU Delft were concentrating their efforts on improving electrolyte materials. This is the material between two electrodes, for example in a fuel cell or a battery. The better the characteristics of the electrolyte, the better, more compactly or more efficiently the fuel cell or battery works.

The electrolyte is usually a liquid, but this has a number of drawbacks. The liquid has to be very well enclosed, for example, and it takes up a relatively large amount of space. "It would therefore be preferable to have an electrolyte made of solid matter," says PhD student Lucas Haverkate. "Unfortunately though, that has disadvantages as well. The conductivity in solid matter is not as good as it is in a liquid."

"In a solid matter you have a network of ions, in which virtually every position in the network is taken. This makes it difficult for the charged particles (protons) to move from one electrode to another. It's a bit like a traffic jam on a motorway. What you need to do is to create free spaces in the network."

One of the ways of achieving this, and therefore of increasing conductivity in solid electrolytes, is to add nanocrystals (of seven nanometres to around fifty nanometres), of Titanium Dioxide. "A characteristic of these  $\text{TiO}_2$  crystals is that they attract protons, and this creates more space in the network." The nanocrystals are mixed in the electrolyte with a solid acid ( $\text{CsHSO}_4$ ). This latter material 'delivers' the protons to the crystals. "The addition of the crystals appears to cause an enormous leap in the conductive capacity, up to a factor of 100," concludes Haverkate.

This remarkable achievement by TU Delft has already led to two publications in the scientific journal *Advanced Functional Materials*. Last December, Haverkate published an article on the theory behind the results. His fellow PhD student, Wing Kee Chan, is the main author of a second item that appeared in the same publication this week. Chan focused on the experimental side of the research. "The nice thing about these two publications is that the experimental results and the theoretical underpinning strongly complement each other," says Haverkate.

Chan carried out measurements on the electrolyte material using the neutron diffraction method. This involves sending neutrons through the material. The way in which the neutrons are dispersed makes it possible to deduce certain characteristics of the material, such as the density of protons in the crystals. Haverkate: "It is the first time that measurements have been taken of solid-material electrolytes in this way, and on such a small scale. The fact that we had nuclear research technologies at the Reactor Institute Delft at our disposal was tremendously valuable."

However, the combination of  $\text{TiO}_2$  and  $\text{CsHSO}_4$  does not mark the end of the search for a suitable solid-material electrolyte. Other material combinations will be tested that may achieve better scores in the area of stability, for example. Professor Fokko Mulder, who is Haverkate's and Chan's PhD supervisor, says. "At this stage, we are more concerned about acquiring a fundamental understanding and a useful model, than the concrete issue of finding out what the most suitable material is. It is important that we identify the effect of nanocrystals, and give it a theoretical basis. I think there is great potential for these electrolytes. They also have the extra benefit of continuing to function well over a wide range of temperatures, which is of particular relevance for applying them in fuel cells."

(From: <http://www.physorg.com/news/2011-03-dutch-huge-potential-nanocrystals-fuel.html>)