

论文题目：纳米材料的溶剂加压热合成、结构及性能

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摘要

建立了在有机溶剂中实现直接反应的技术，将有机溶剂加压热合成发展到制备在水溶液中无法形成的或易氧化、易水解的纳米非氧化物。在国际上首次用此技术在 280℃ 下于苯体系中制备出 30nm GaN, XPS 给出其化学式为 Ga_{0.95}N。所得 GaN 在 370nm 处发光,与块材相同,未表现出量子尺寸效应;与理论计算得 GaN 的激子玻尔半径为 11nm 是一致的。XRD 表明所得的纳米 GaN 大部分为六方纤锌矿相,还含有少量岩盐型亚稳相,文献报道仅利用金刚石砧和同步 X 射线衍射技术在至少 37GPa 下仅证实岩盐型 GaN 的存在,但一旦压力释放,该相重新转化回六方相。本工作国际上首次在低于 5MPa 下制得岩盐型 GaN,并用高分辨电镜直接观察到其存在。在 HRTEM 照片上根据已知的六方相的晶胞参数验证了由 XRD 给出的常压下岩盐型 GaN 的晶胞参数: $a=4.100$ 。在 300℃ 下制备的样品为纤锌矿型、闪锌矿型和岩盐型三相共存的纳米 GaN,给出了闪锌矿型 GaN 的晶胞参数为 $a=4.420$ 。

在聚醚体系中 160℃ 下制备出 10nm InP 和纳米 InAlP 固溶体。所得纳米 InP 在 450nm 处有一弱的宽发光带,与块材相比发生了很大兰移,表现出量子尺寸效应;与量子理论计算得 InP 的激子玻尔半径为 29nm 是一致的。通过对聚醚体系中 InP 团簇的紫外-可见吸收光谱和光致发光光谱的研究,发现溶剂加压热合成法制备纳米材料时经历了团簇→(胶体)→非晶→纳米晶的过程;发现不同的有机溶剂对产物成相和颗粒生长是至关重要的因素;初步认为聚醚类溶剂能够限制纳米 InP 颗粒的生长是由于其不仅能打开 InCl₃ 的二聚体结构,而且具有和中心金属元素形成离子配合物的能力。

利用水热还原反应制备出 160x80nm 短棒状和 80nm 板状 Fe₃O₄,用化学法测定其 Fe(III)/Fe(II)比为 2.13:1。用类似的反应制备出 30nm 球状的 ZnFe₂O₄ 和 NiFe₂O₄ 纳米粉末。利用水热晶化反应制备出 6nm ZnS,红外光谱表明所得纳米 ZnS 在 400-5000cm⁻¹ 范围内基本无吸收,比较对 ZnS 凝胶的水热晶化和普通热处理发现水热晶化过程不仅能提高产物的晶化程度,而且有效地防止了纳米硫化物的氧化。

ABSTRACT

The thesis established a new technique to prepare nanocrystalline phosphides and nitrides in nonaqueous system under pressure, which is named solvothermal process. Benzene-thermal reaction of Li₃N and GaCl₃ under pressure was carried out for preparation of 30nm GaN at

280°C, which is much lower than that of traditional methods. X-ray Photoelectron Spectrum analyses of the sample gave the average composition of Ga_{0.95}N. The Photoluminescence spectrum of as-prepared GaN was similar to that of bulk GaN, exhibiting no quantum size effects, which

is consistent with the Bohr exciton radius of 11nm. The X-ray Powder Diffraction pattern indicated that the sample was mainly hexagonal phase GaN with small amount of rocksalt phase GaN with $a=4.100$ Å. It is the first time that the existence of GaN in rocksalt structure, which previously appeared under pressure at least 37GPa, was observed directly with High Resolution Transmission Electron Microscopy. HRTEM verified the cell parameter of rocksalt GaN and showed that there was a transitional region between the two cubic phases of GaN with zincblende and rocksalt. The sample prepared at 300°C was the wurtzite GaN coexisted with zincblende and rocksalt structure. The cell parameter of zincblende GaN was measured to be $a=4.420$ Å.

10nm InP and nanocrystalline InAlP solid solutions were obtained in 1,2-dimethoxyethane system at 160°C. The PL spectrum of as-prepared InP showed a large blue-shift, exhibiting the quantum size effects, which is consistent with the Bohr exciton radius of 29nm. In the preparation of nanocrystalline InP, InP clusters were observed through UV-Vis absorption spectrum and PL spectrum. A possible mechanism is that the clusters act as the intermediate and combines to form amorphous and finally nanocrystalline InP particles during the solvothermal process. The ability of 1,2-dimethoxyethane that dissociation and the formation of ionic complexes may play an important role in the mechanism to limit the growth of particles.

160x80nm Fe₃O₄ in short-rod shape and 80nm Fe₃O₄ in plate shape were synthesized through hydrothermal reductive reaction. Chemical analyses indicated that the ratio of Fe(III) to Fe(II) was 2.13: 1. 30nm NiFe₂O₄ and ZnFe₂O₄ powders in spherical shape were prepared through a similar process. Hydrothermal crystallization process was used to prepare 6nm ZnS. IR spectrum of as-prepared ZnS showed no absorption in the range from 400 to 5000cm⁻¹. Compared to the normal thermal process, the hydrothermal crystallization process can not only enhance the crystallinity of the products, but also effectively avoid the oxidization of nanocrystalline sulphide.