Synthesis and Characterization of Pr$_2$S$_3$ Binary Compound

Natalia Q$^1$, Sonia Gaona Jb$^2$ and Alfonso Ramírez Sa$^1$

$^1$Department of Chemistry, University of Cauca, Popayán, Colombia
$^2$Department of Physics, University of Cauca, Popayán, Colombia

Submission: May 09, 2017; Published: June 29, 2017

*Corresponding author: Alfonso Ramírez Sa, Department of Chemistry, University of Cauca, Popayán, Colombia, Tel: 8209900; Email: aramirez@unicauca.edu.co

Abstract
In the current work it is shown that the synthesis method that consists in direct reaction of praseodymium and sulfur in its elemental form, using heat as a treatment, with relatively low temperatures and reaction time of one week, allows the preparation of Pr$_2$S$_3$ compound, with a purity of about 92%. The respective characterization of resultant materials was carried out using powder XRD, whereby it was determined that the thermal treatment used, effectively leads to the binary sulfide of interest, a compound known to be a semiconductor.

Keywords: Praseodymium sulfide; Thermal treatment; Semiconductor

Introduction
In the last years, the optical properties of semiconductor compounds (which in most cases are limited to TiO$_2$, zinc oxides and cadmium) have been investigated, as well as the magnetism of ferrites, superconducting ceramics, and related compounds. In this regard, it is important to take into account that compounds with semiconductor and paramagnetic properties have not been widely studied, despite the interest in multifunctional materials, where the same compound can have two useful properties simultaneously. That is why there is a special interest on rare earth sulfides [1].

According to different studies, sulfides belonging to the TR$_2$S$_3$ system (TR$^3+$ = rare earth ion) are known to be potential materials as magnetic semiconductors, given that they have a band gap of approximately 2.5-3eV. An example of this is the binary compound Pr$_2$S$_3$ with a band gap of approximately 2.75eV. Also, these types of materials are usually characterized by a high resistivity ($\rho$=1010 $\Omega$cm) and a wide transparency in the visible spectral range [2]. The presence of rare earth ions with incomplete 4f sublevels in these compounds is the responsible for the magnetic properties and the relatively large magnitude of optical effects [2].

However, the preparation of such sulfides is often a problem, because TR$^3+$ ions are considered as strong hard acids, whereas sulfide ions are known to exhibit soft base properties, which leads to the desired compounds, being chemically unstable [1]. Known methods for the synthesis of such sulfides can be divided in two groups: first, the reaction of the rare earth oxide with carbon disulfide and second, the prior isolation of a precursor, consisting of a rare earth/ligand complex, with subsequent thermal decomposition, either in solid state or in suspension in a high boiling solvent, to give rise to the desired sulfide [1].

For example, Selishchev AV et al. [1]. A reports the synthesis of TR$_2$S$_3$ compounds, using the reaction of precursor NH$_2$Et$_2$[Pr(Dttc)4] (Dttc=diethyl dithiocarbamate) with excess carbon disulfide (CS$_2$), giving rise to a material with semiconductor properties [1]. Although sulfur represents a less toxic alternative compared to its analogue, hydrogen sulfide, the high volatility, represents a limitation to use sulfurization as a method [3]. Additionally, another known method for the preparation of TR$_2$S$_3$ compounds is using the direct reaction of the rare earth oxide with CS$_2$, however, in some cases it is possible to find oxygen incorporated as impurity in the final product, affecting the purity of the resulting phase [4].

On the other hand, Jabua et al. reports the preparation of Pr$_2$S$_3$ crystalline films, by direct reaction of the elements, using thermal evaporation in a vacuum chamber, and pyroceramics and...
mono crystalline silicon as substrates. Although in this case the reaction is direct and complexes are not required as precursors, the application of this method requires more sophisticated equipment, which results impractical.

Considering the importance and potential application of this type of sulfides, the current work has two purposes: first, synthesize the compound (Pr$_2$S$_3$) by using direct reaction of the elements, but in this case, using very simple equipment; and secondly, present the characterization of the sample, using powder X-ray diffraction. The details of such processes are described in the experimental section and analysis of results.

**Experimental Section**

Synthesis 0.7043g of praseodymium (rods, 99.9995%, Alfa Aesar) and 0.2405g of sulfur (powder, 99.998%, Alfa Aesar) were mixed in a quartz tube, applying an oxygen/nitrogen flame under vacuum condition, to prevent a possible oxidation of the praseodymium along the heating. The reaction was carried out in a box type furnace and the following treatment was applied:

The tube with the mixture was heated to 200°C (0.5 °C/min) and held for 24h, then the reaction was raised to 400 °C (0.5 °C/min), keeping the temperature for 24h, subsequently it was raised to 600 °C (1 °C/min), keeping the temperature constant for a period of 4 days. Once the thermal treatment finished, the sample was removed from the furnace and the tube, and then reserved for proper characterization. Characterization by XRD. The sample obtained using the above treatment, was very well homogenized and then analyzed to determine the composition and purity, using a 2θ range between 10 and 90°. The analysis was carried out with a PANalytical X’pert powder diffracto meter.

**Results and Analysis**

With the XRD analysis it was found that the sample actually corresponds to binary compound Pr$_2$S$_3$. The diffracto gram that corresponds to the synthesized sulfide is shown in Figure 1. Based on the analysis made to the polycrystalline sample, it was found that 91.7% corresponds to the compound Pr$_2$S$_3$ with orthorhombic structure and space group Pnma (PDF 01-087-1643). In both cases, the diffracto gram of Figure 1 and the PDF, it is possible to identify the characteristic peak of this compound (the higher intensity), corresponding to 2θ=25, 60.

The remaining 8.3% corresponds to a small fraction of unreacted praseodymium, which is identified, according to peaks located in 2θ: 29.80, 34.55, 49.65 and 59.05, corresponding to the same ones in PDF 01-071-6539 (29.81, 34.56, 49.68 and 59.03). Based on these results, it could be said that binary phase obtained has a high purity. Additionally, using the Scherrer equation and the diffracto gram data, it was determined that the diameter of the crystals in the sample corresponds to:

According to this result, the average particle size is much smaller compared to the crystals reported for the ligand decomposition method, where the crystal size varies between 22 and 26nm. Considering that the band gap of the larger particles (26nm) is 2.58eV and for the smaller particles (22nm) is 2.75eV, it could be predicted that the binary compound synthesized by having a much smaller particle size (14, 93nm) would possibly present a change in the band gap width, which would modify its properties as a semiconductor material, especially if we bear in mind that these materials have a band in the range 0.1-2eV.

These types of compounds usually crystallize with the Th$_4$P$_4$ structure type, an arrangement where the praseodymium ions are located in the centers of each octahedron (formed by the ions S$_6$), belonging to the non-centro symmetric point group S$_6$. Also, Pr$_{2+}$ ions occupy 8/9 of the possible central positions, while the remaining 1/9 of these sites are vacant.

Considering the complications that arise when working with sulfur, given its high vapor pressure; the simplicity of this method represents a great advantage compared to other commonly used methods, such as the reaction of rare earth oxides with sulfides, where extremely high temperatures of up to 1250K are required [5]. The use of a direct mixture of the elements through this heat treatment (with much lower temperatures), reduces the activation energy of the compound, favoring the obtaining of the binary sulfide and consequently its application in different fields. In addition to this, by not using oxides and sulfides as CS$_2$ or HS$_2$ as starting reagents, (as mentioned in traditional methods) the incorporation of impurities into the resulting phase is reduced, making this method a simple and efficient option for the production of rare earth sulfides.

**Conclusion**

The direct combination of praseodymium and sulfur, by using as thermal treatment a furnace heating and low temperatures, allows the preparation of binary sulfide Pr$_2$S$_3$, proving to be a practical and simple method in comparison with other traditional methods, where the use of sophisticated tools and equipment is required, in addition to very high temperatures. With the
characterization made to the compound, it was possible to find that the achieved binary phase has a high purity, given that only a small percentage of the reagents remained unreacted. From the grain size determined for this compound, one can conjecture that the material has a significant improvement in its semiconductor properties, in comparison with other reported materials, which have a much larger diameter.

Acknowledgment

We thank to Professor Robin T. Macaluso at the University of Texas at Arlington for allowing us to use the laboratories to carry out the synthesis and make possible this research. We also thank to Adriana Paola Sotelo, Ph.D. student at the same university, for her collaboration and suggestions, which contributed to the development of the current work. Finally, we thank to the VRI of the University of Cauca ID-4391 for the support to this project.

References

1. Selishchev A, Pavlishchuk V (2014) Effect of Formation Conditions on the Size, Shape and Spectral Properties of EuS and Pr$_2$S$_3$ Nanoparticles. Theoretical and Experimental Chemistry 50(1): 39-45.

2. Krichevtsov B (2001) Anisotropy of the linear and quadratic magnetic birefringence in rare-earth semiconductors ($\gamma$-Ln$_2$S$_3$ (Ln= Dy$^{3+}$, Pr$^{3+}$, Gd$^{3+}$, La$^{3+}$)). Journal of Experimental and Theoretical Physics 92(5): 830-839.

3. Michihiro OH, Habin Y, Hirai S, Uemura Y, Shimakage K, et al. (2004) Preparation of R$_2$S$_3$ (R: La, Pr, Nd, Sm) powders by sulfurization of oxide powders using CS$_2$ gas. Journal of alloys and compounds 374(1): 112-115.

4. OHTA M, Hini S, Zucai MA, Nishimura T, Uemun Y, et al. (2006) Phase transformation and microstructures of Ln$_2$S$_3$ (Ln= La, Sm) with different impurities content of oxygen and carbon. Journal of alloys and compounds 408-412: 551-555.

5. Ohta M (2008) Thermoelectric properties of Th$_3$P$_4$-type rare-earth sulfides Ln$_2$S$_3$ (Ln= Gd, Tb) prepared by reaction of their oxides with CS$_2$ gas. Journal of Alloys and Compounds 451(1): 627-631.

Your next submission with Juniper Publishers will reach you the below assets

• Quality Editorial service
• Swift Peer Review
• Reprints availability
• E-prints Service
• Manuscript Podcast for convenient understanding
• Global attainment for your research
• Manuscript accessibility in different formats (Pdf, E-pub, Full Text, Audio)
• Unceasing customer service

Track the below URL for one-step submission

https://juniperpublishers.com/online-submission.php

This work is licensed under Creative Commons Attribution 4.0 License
DOI: 10.19080/JOJMS.2017.02.555582

How to cite this article: Natalia Q, Sonia G J, Alfonso R S. Synthesis and Characterization of Pr$_2$S$_3$ Binary Compound. JOJ Material Sci. 2017; 2(2): 555582. DOI: 10.19080/JOJMS.2017.02.555582