

US 20230217971A1

(19) **United States**(12) **Patent Application Publication**
Qadri et al.(10) **Pub. No.: US 2023/0217971 A1**(43) **Pub. Date: Jul. 13, 2023**(54) **NANO-STRUCTURED ALUMINUM NITRIDE (ALN) IN A PURE FORM AND IN THE WURTZITE PHASE OF ALN FROM NUT SHELLS**(71) Applicant: **The Government of the United States of America, as represented by the Secretary of the Navy, Arlington, VA (US)**(72) Inventors: **Syed B. Qadri, Fairfax Station, VA (US); Bhakta B. Rath, Oakton, VA (US); Edward P. Gorzkowski, III, Odenton, MD (US)**(73) Assignee: **The Government of the United States of America, as represented by the Secretary of the Navy, Arlington, VA (US)**(21) Appl. No.: **18/118,921**(22) Filed: **Mar. 8, 2023****Related U.S. Application Data**

(62) Division of application No. 17/081,216, filed on Oct. 27, 2020, now Pat. No. 11,602,158, which is a division of application No. 16/406,969, filed on May 8, 2019, now abandoned, which is a division of application No. 15/786,180, filed on Oct. 17, 2017, now Pat. No. 10,292,411.

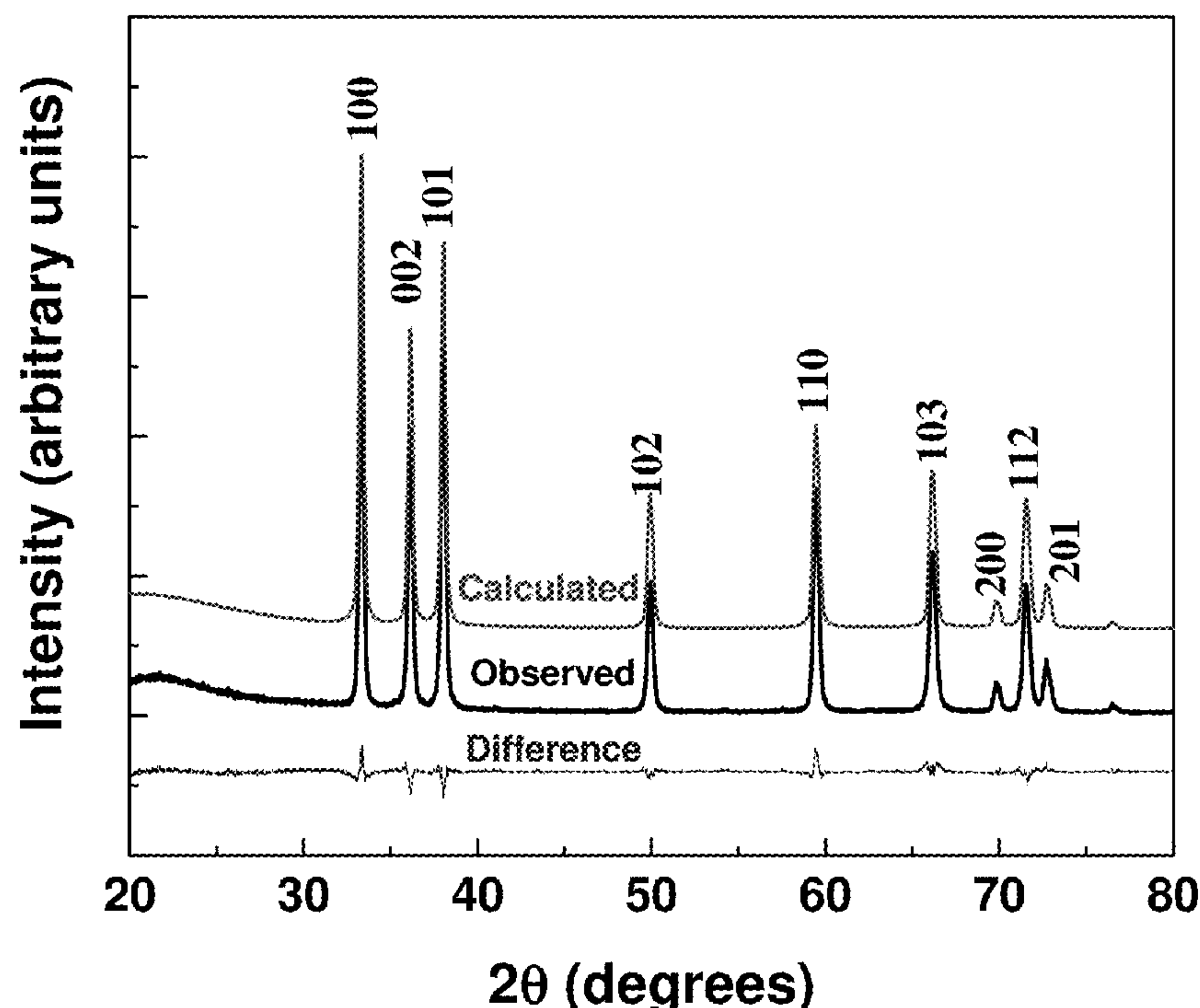
(60) Provisional application No. 62/422,793, filed on Nov. 16, 2016.

Publication Classification(51) **Int. Cl.****A23L 25/00** (2016.01)**B02C 17/20** (2006.01)**C01B 21/072** (2006.01)**B82Y 30/00** (2011.01)(52) **U.S. Cl.**CPC **A23L 25/00** (2016.08); **B02C 17/20** (2013.01); **C01B 21/0726** (2013.01); **B82Y 30/00** (2013.01); **C01P 2002/82** (2013.01); **C01P 2004/04** (2013.01); **C01P 2002/72** (2013.01)

(57)

ABSTRACT

Nano-structures of Aluminum Nitride and a method of producing nano-structures of Aluminum Nitride from nut shells comprising milling agricultural nuts into a fine nut powder, milling nanocrystalline Al_2O_3 into a powder, mixing, pressing the fine nut powder and the powder of nanocrystalline Al_2O_3 , heating the pellet, maintaining the temperature of the pellet at about 1400°C ., cooling the pellet, eliminating the residual carbon, and forming nano-structures of AlN. An Aluminum Nitride (AlN) product made from the steps of preparing powders of agricultural nuts using ball milling, preparing powders of nanocrystalline Al_2O_3 , mixing the powders of agricultural nuts and the powders of nanocrystalline Al_2O_3 forming a homogenous sample powder of agricultural nuts and Al_2O_3 , pressurizing, pyrolyzing the disk, and reacting the disk and the nitrogen atmosphere and forming AlN.

Almond

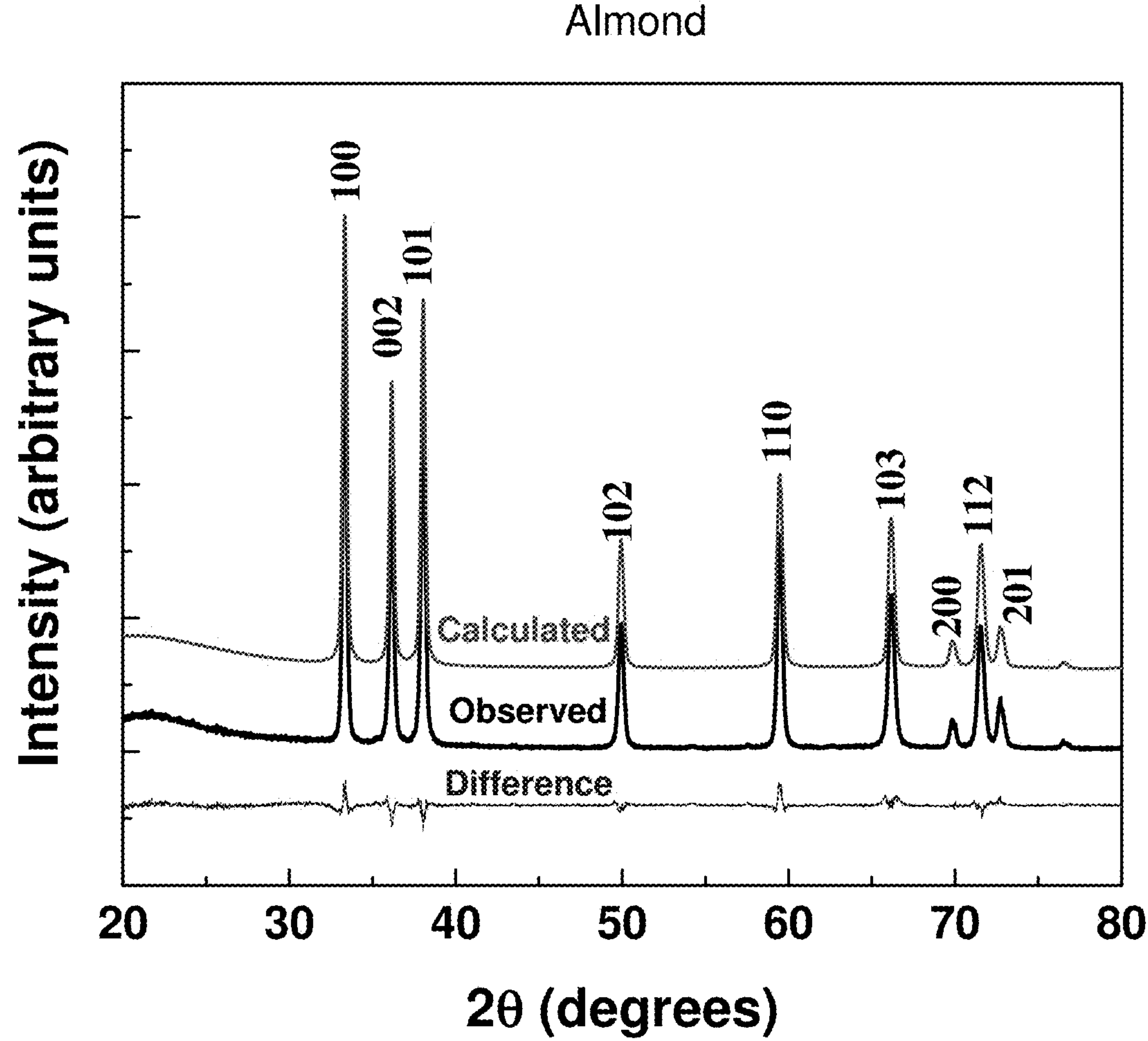


FIGURE 1

FIG. 2A

(a) Almond

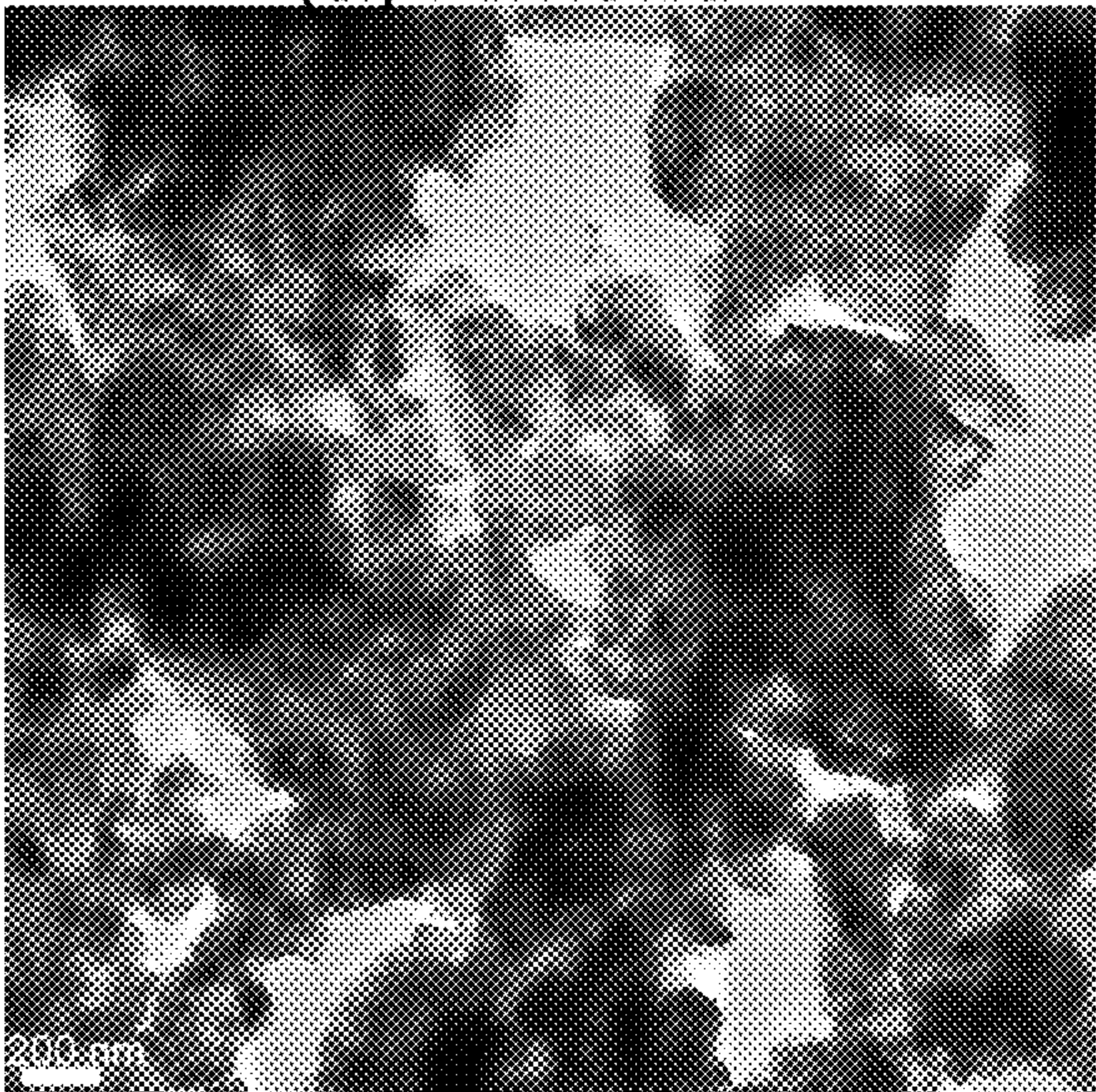
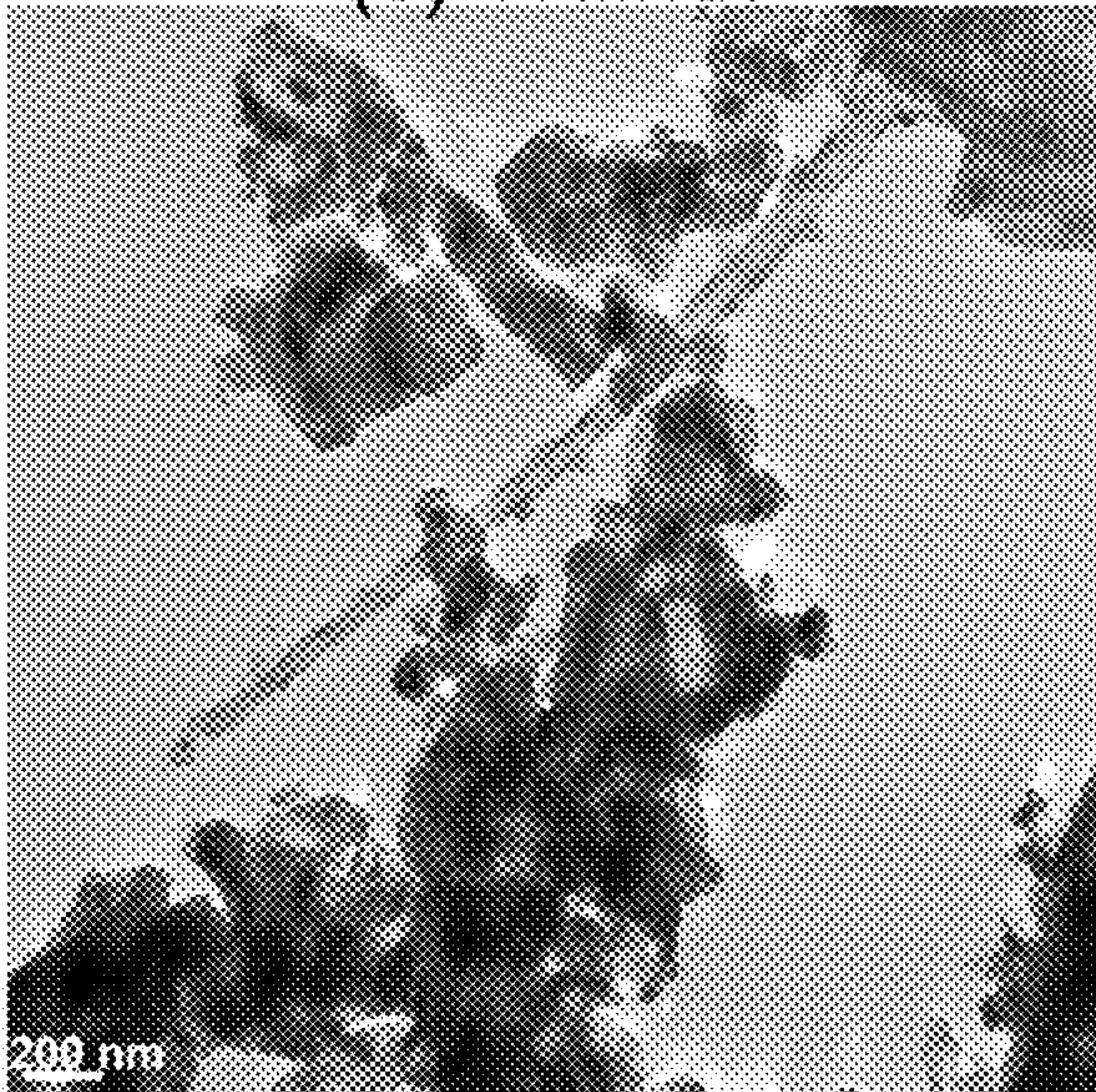
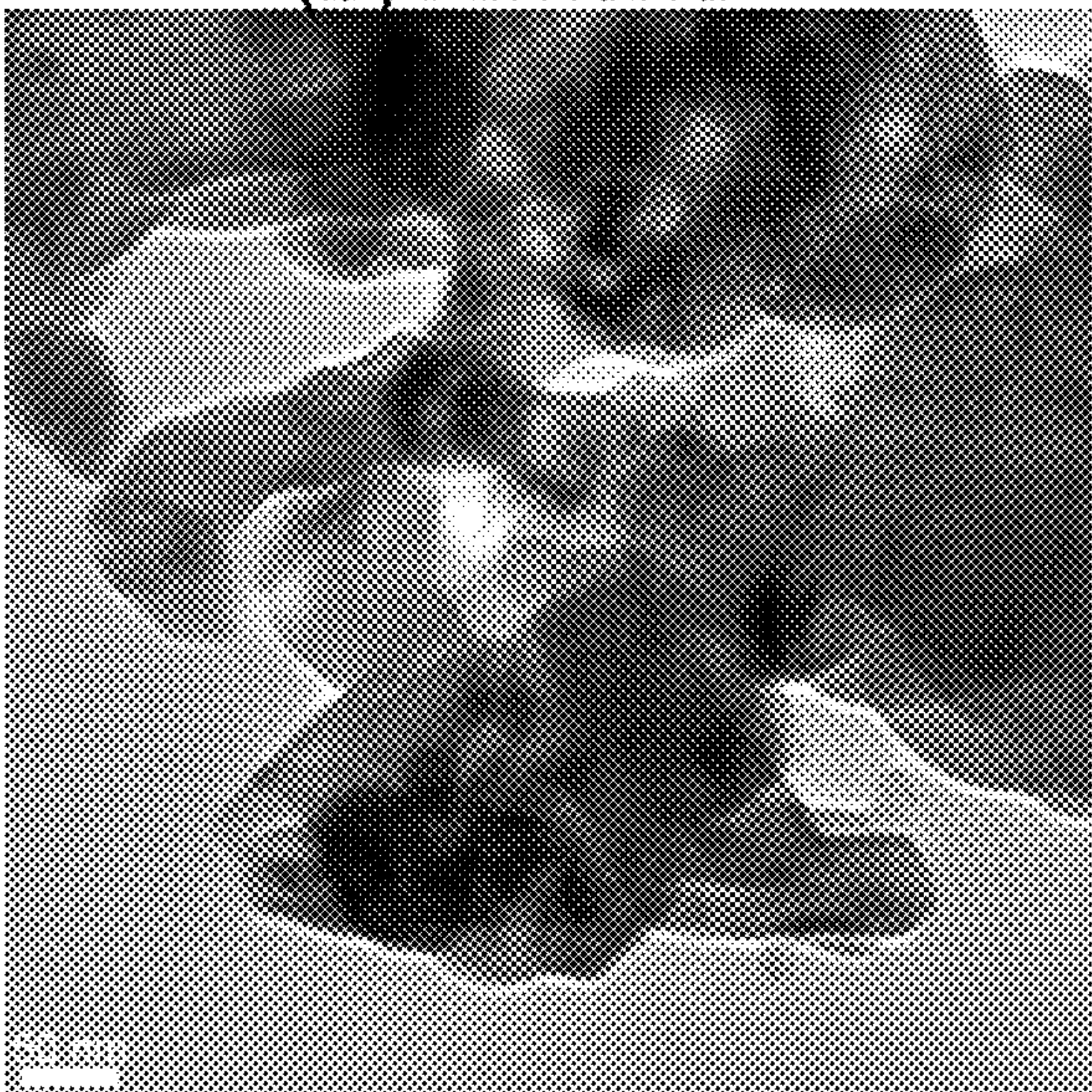


FIG. 2C

(c) Walnut



(b) Almond



(d) Walnut

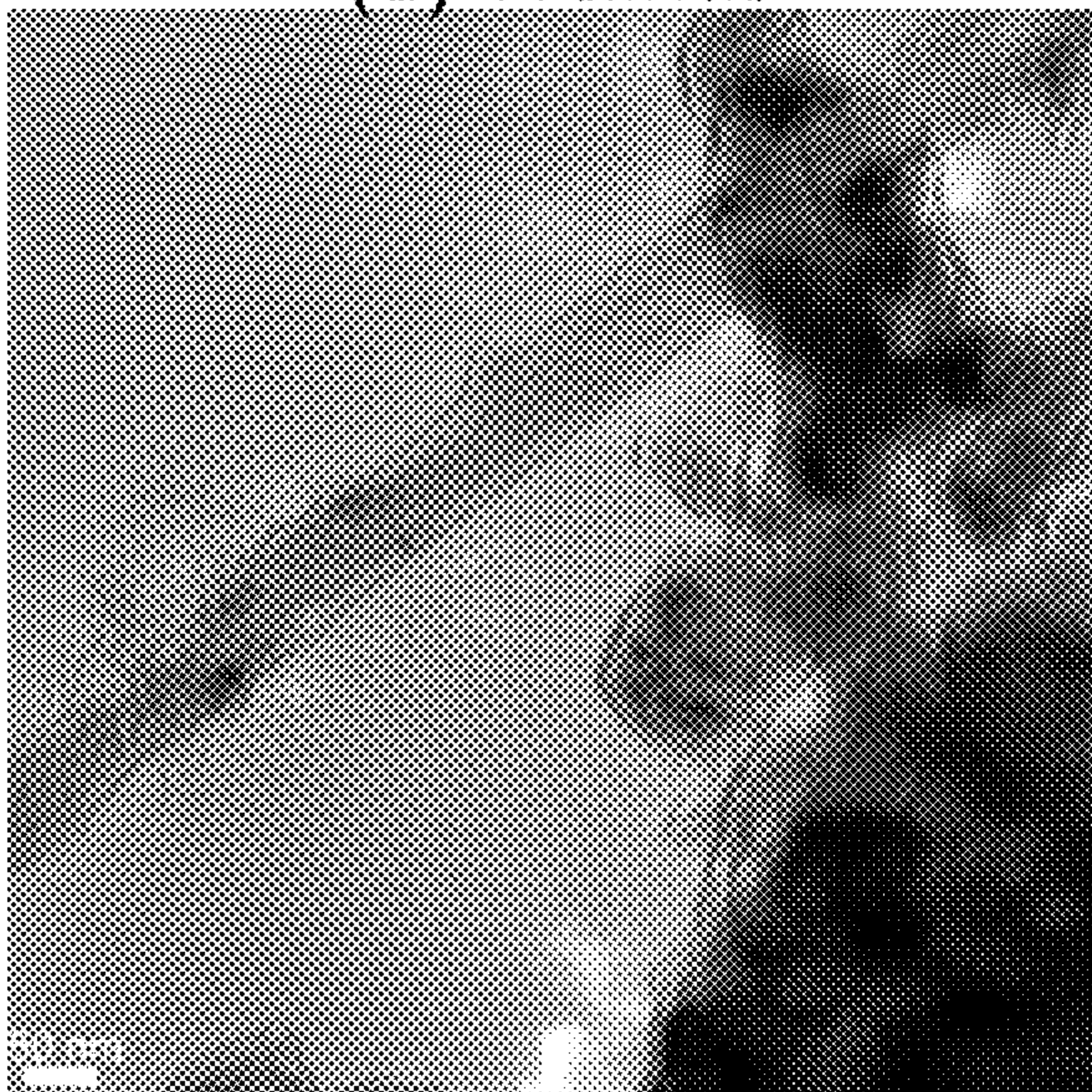


FIG. 2B

FIG. 2D

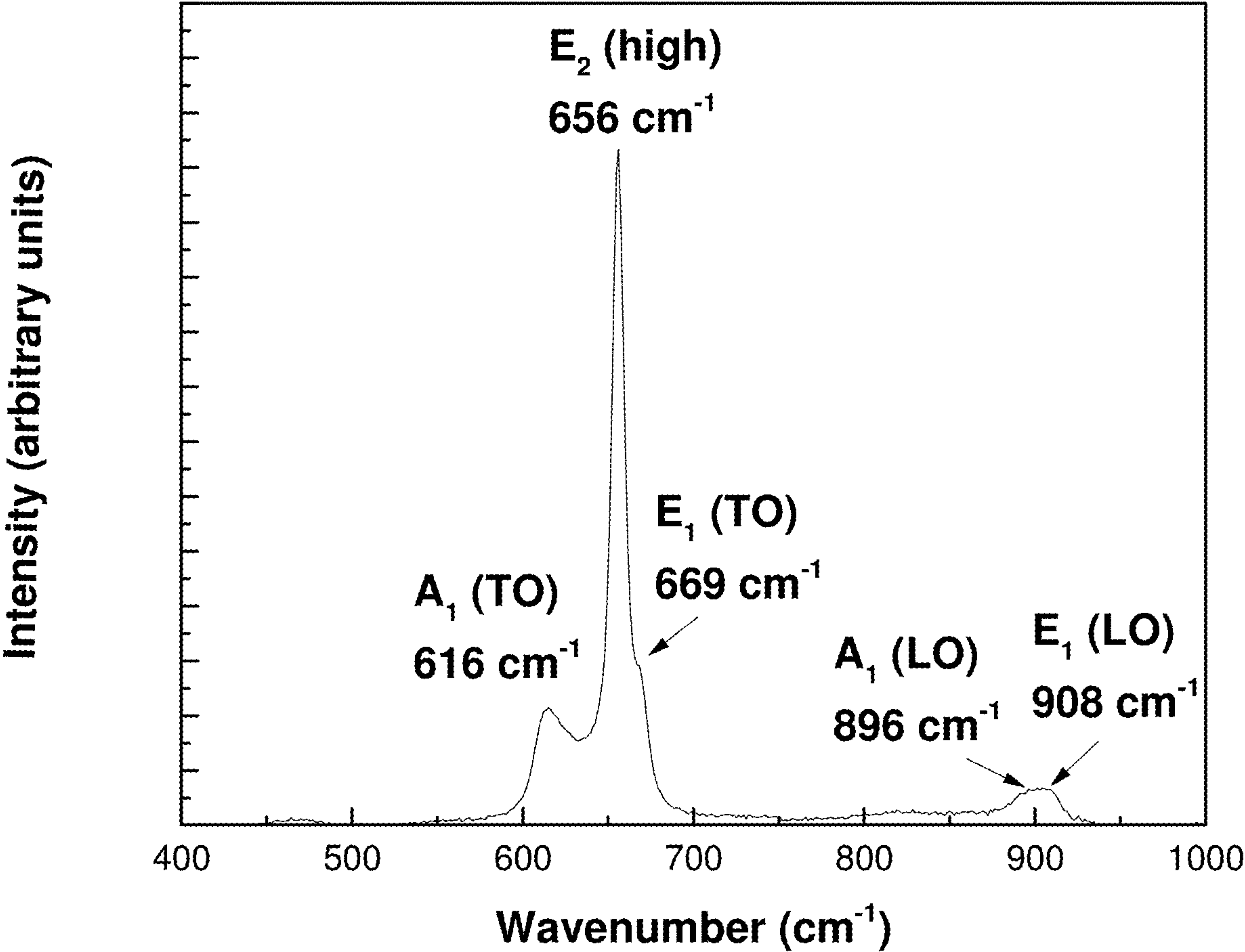


FIGURE 3

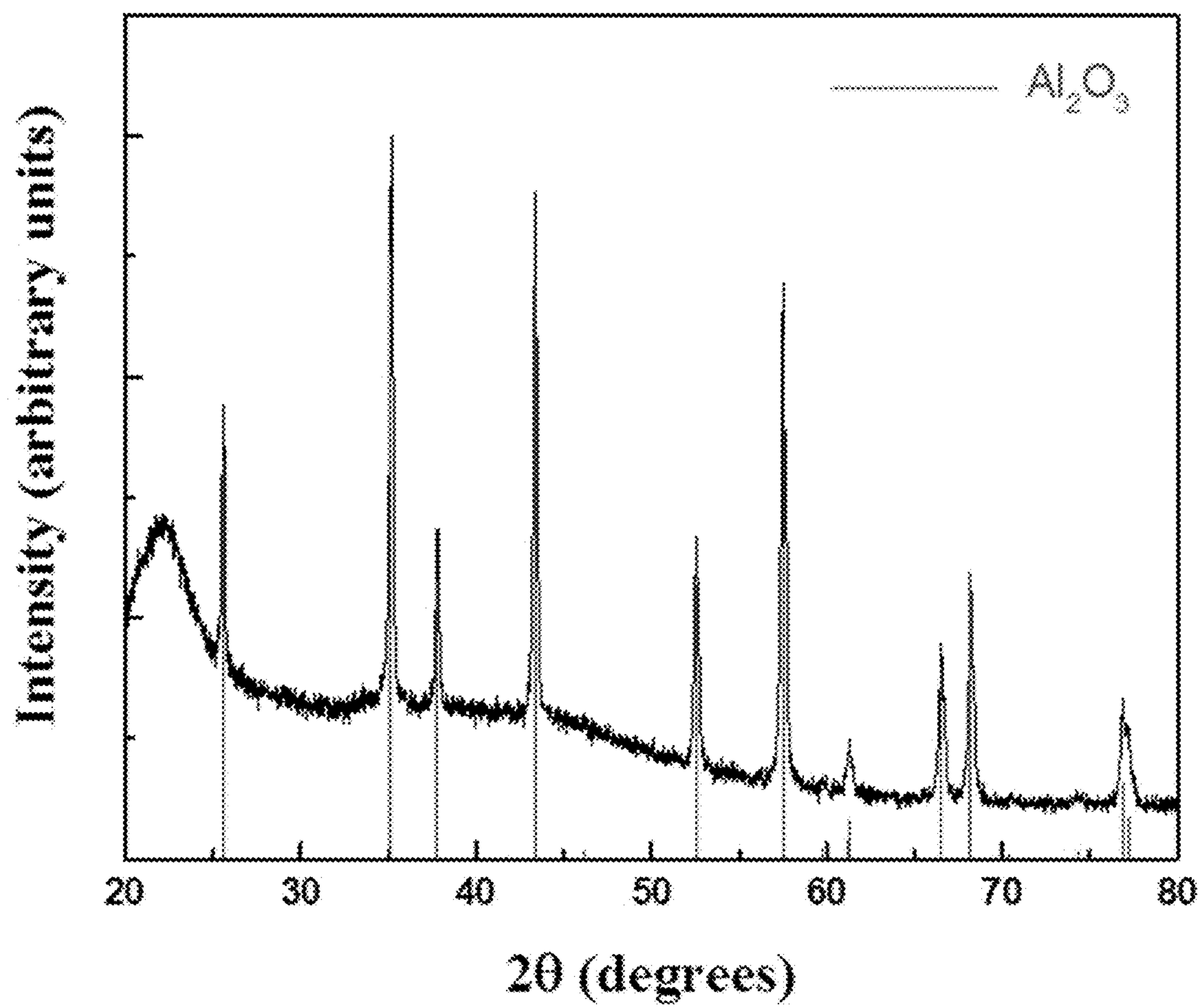


FIGURE 4A

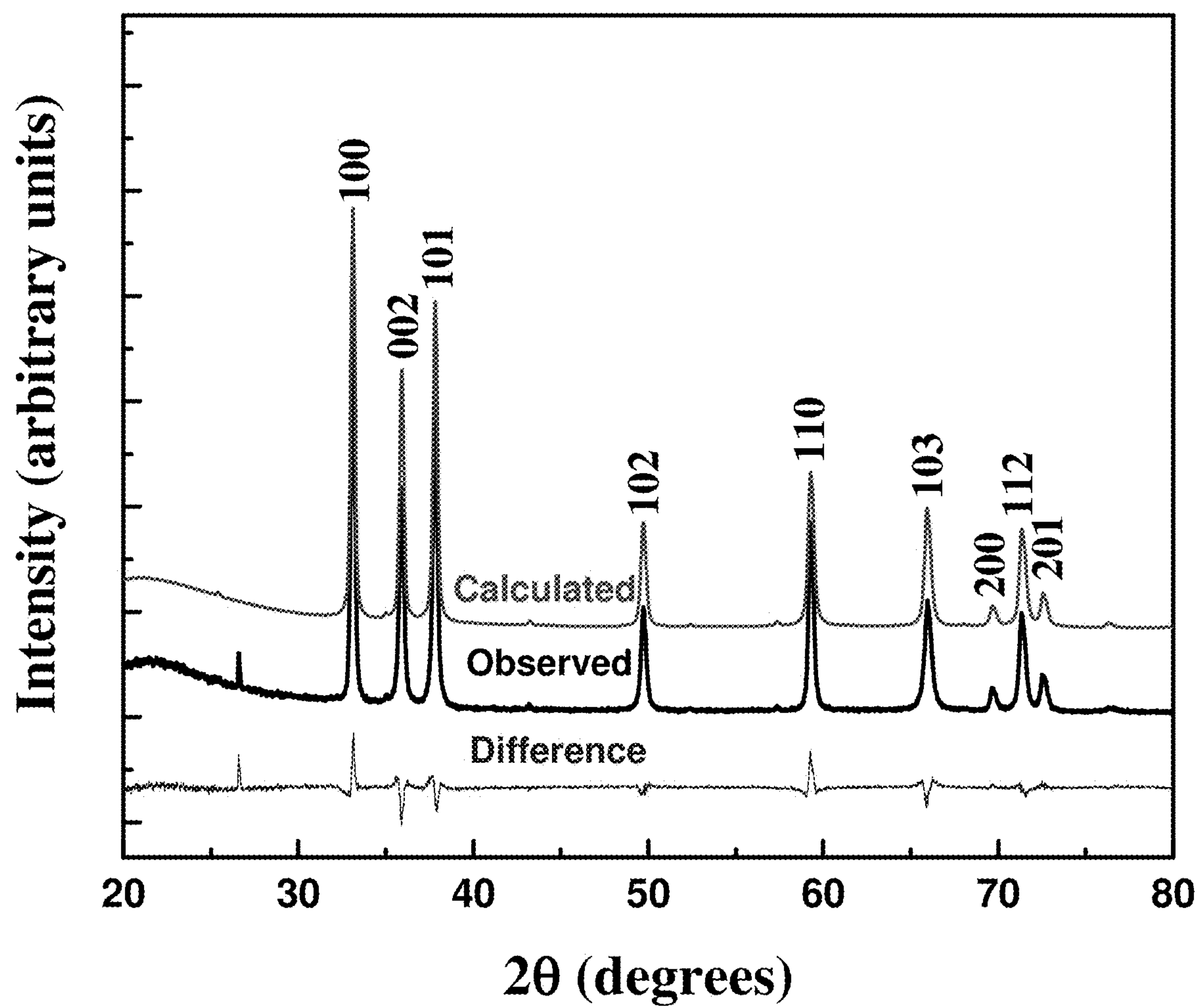


FIGURE 4B

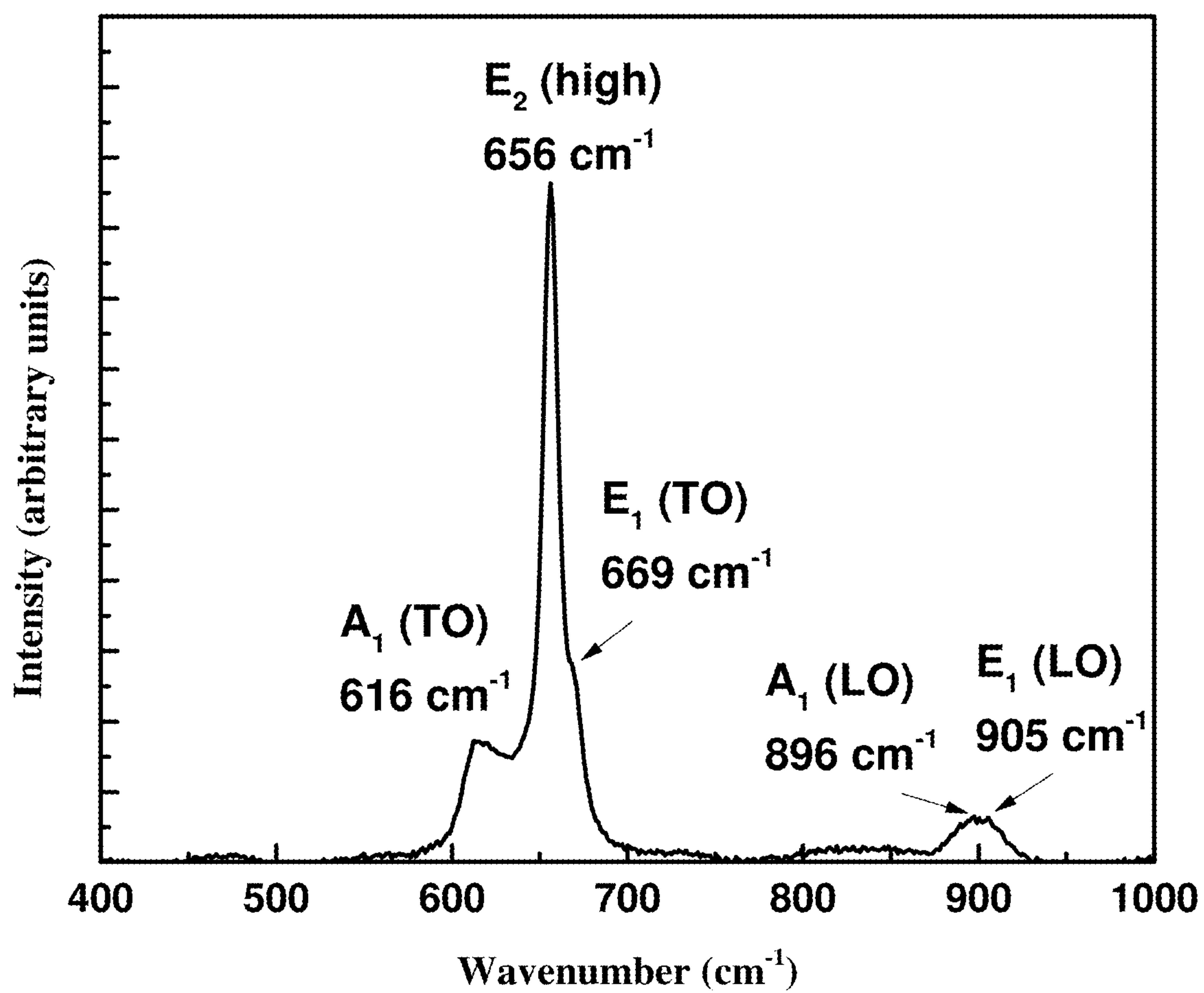


FIGURE 5A

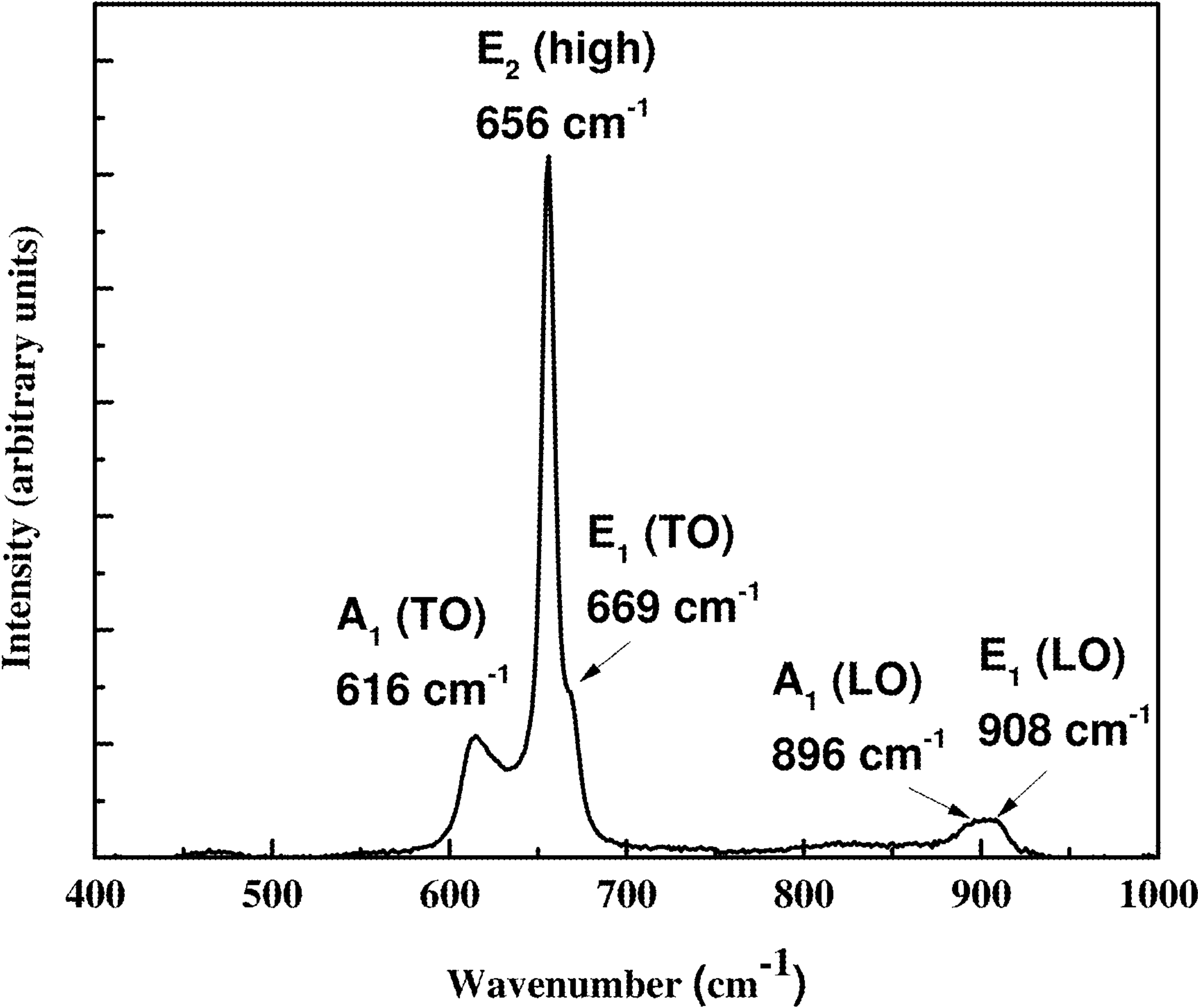


FIGURE 5B

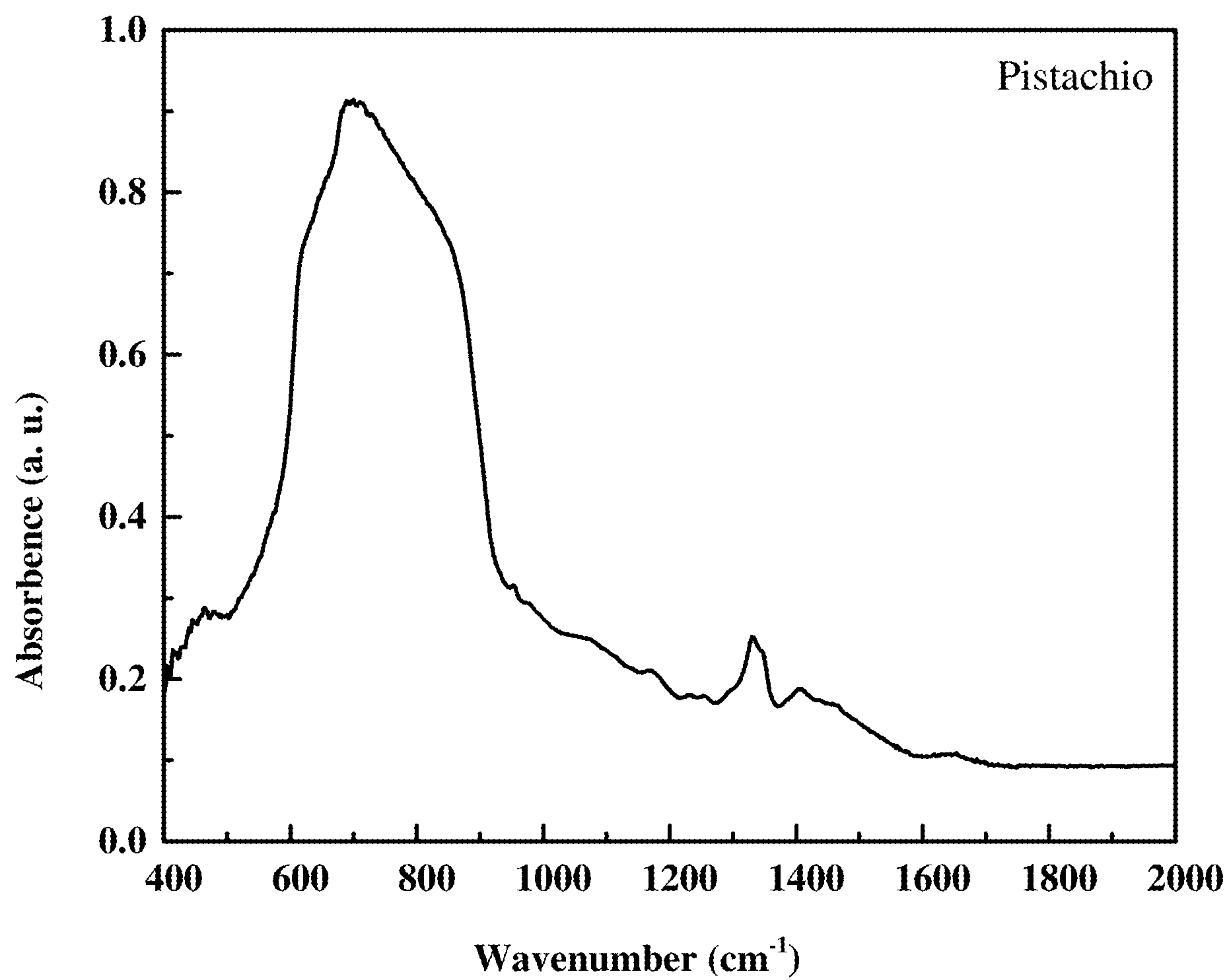


FIGURE 5C

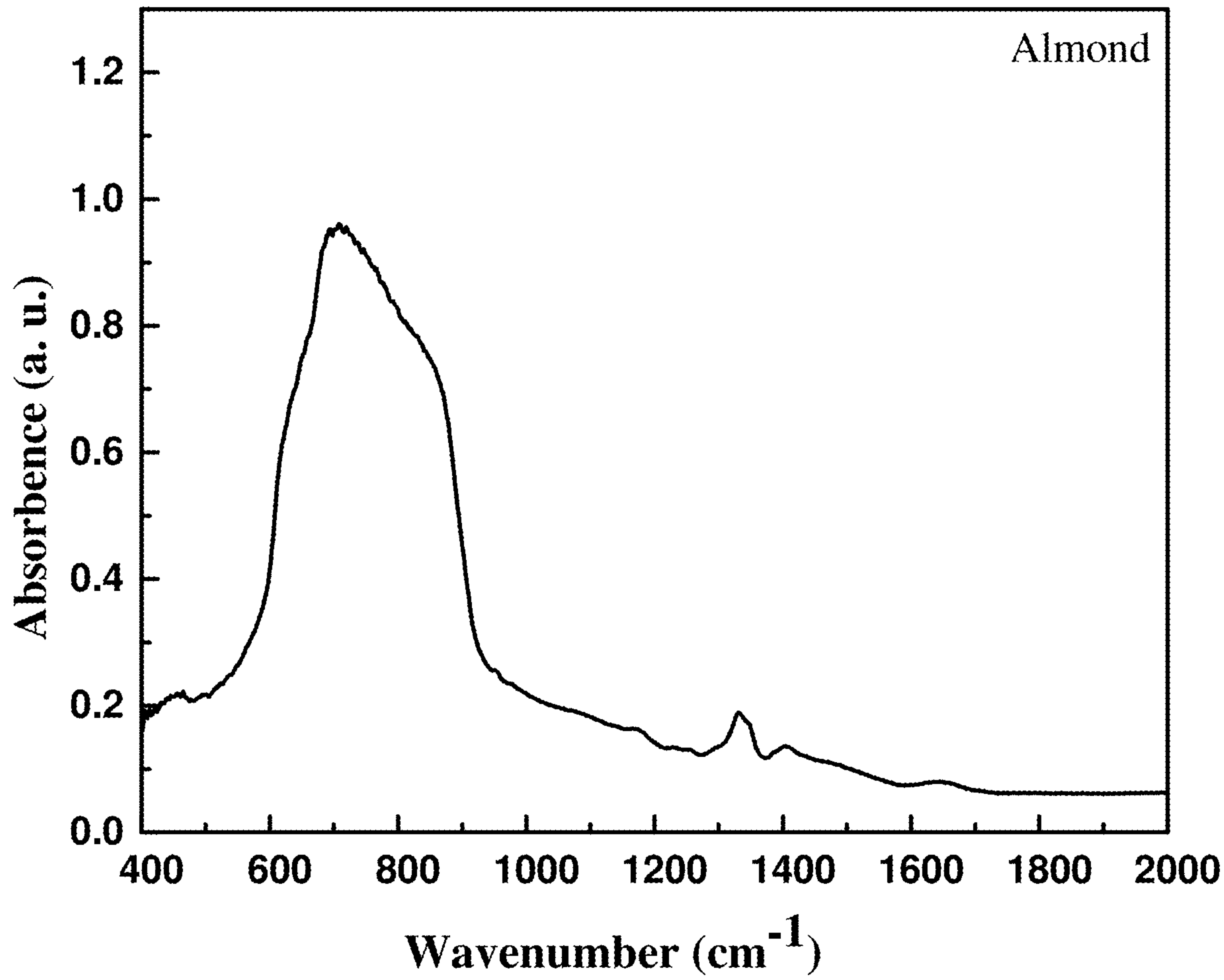


FIGURE 5D

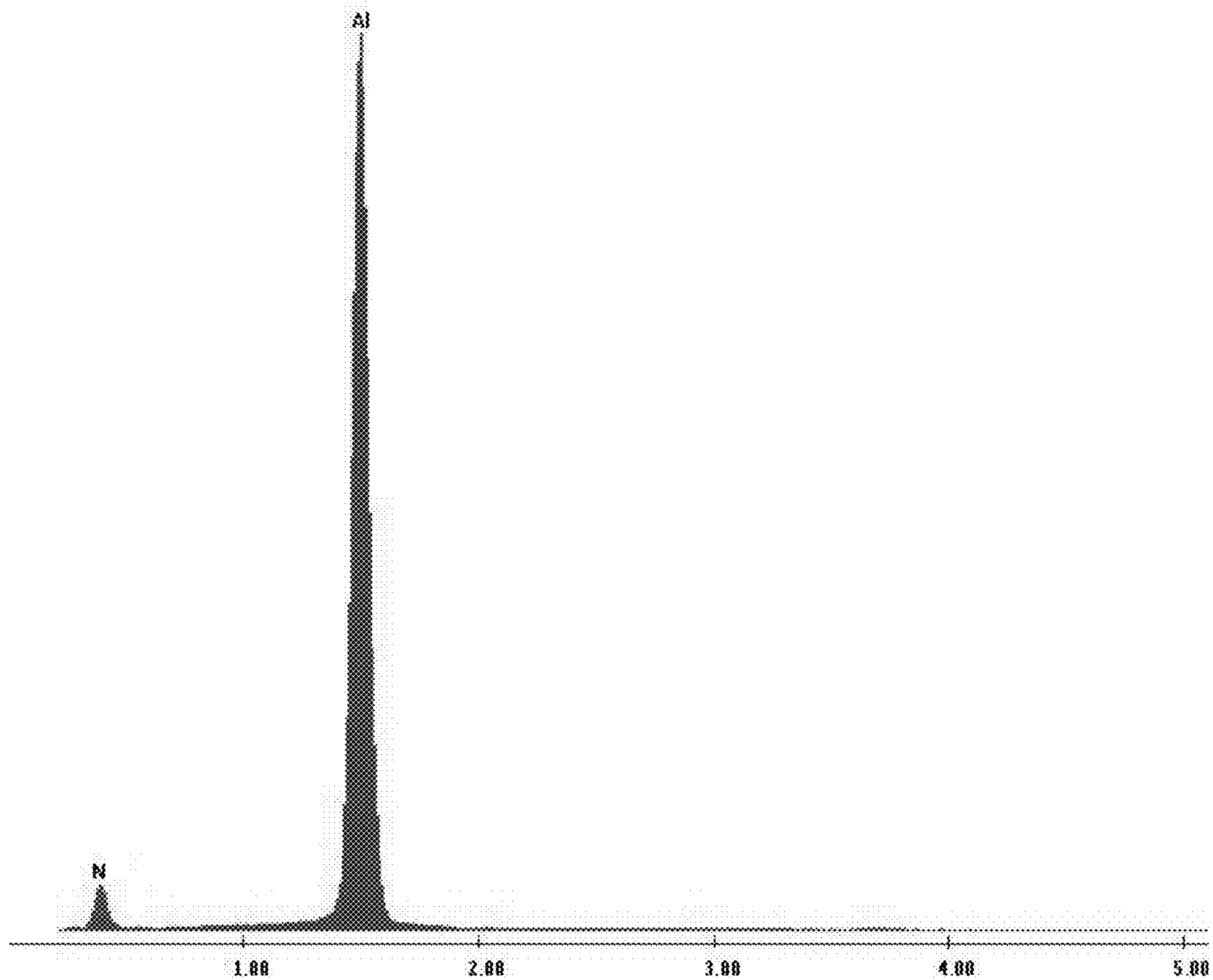


FIGURE 6

NANO-STRUCTURED ALUMINUM NITRIDE (ALN) IN A PURE FORM AND IN THE WURTZITE PHASE OF ALN FROM NUT SHELLS

REFERENCE TO RELATED APPLICATION

[0001] This application is a non-provisional of, and claims priority to and the benefits of, U.S. Patent Application No. 62/422,793 filed on Nov. 16, 2016 and U.S. patent application Ser. No. 15/786,180 filed on Oct. 17, 2017 and U.S. patent application Ser. No. 16/406,969 filed on May 8, 2019, and U.S. patent application Ser. No. 17/081,216 filed on Oct. 27, 2020, the entirety of each is hereby incorporated by reference.

BACKGROUND

[0002] This invention concerns a new method for the formation of abundant quantities of Aluminum Nitride (AlN) from a thermal treatment of a mixture of aluminum oxide (Al_2O_3) and shells of almond, cashew, coconuts, pistachio, and walnuts in a nitrogen atmosphere at temperatures in excess of 1450°C .

[0003] This new method of synthesizing Aluminum Nitride from various Nut Shells uses conventional heating or microwave heating to produce nano-structures.

[0004] Billions of pounds of agricultural waste of nut shells such as those of almonds, pistachios, walnuts, cashew, coconuts, macadamia etc. are generated every year all over the world.

[0005] Aluminum Nitride (AlN) is a very useful material for industrial and electronic applications due to its unique physical properties.

[0006] AlN is an insulator in electronic device applications because of high electrical resistivity, low thermal expansion, resistance to erosion and corrosion, excellent thermal shock resistance and chemical stability in air up to 1380°C . with surface oxidation occurring at 780°C .

[0007] Surface acoustic wave sensors (SAWs) can be deposited on silicon wafers because of AlN's piezoelectric properties and AlN can be used as an RF filter for mobile phones.

[0008] AlN is synthesized in the bulk form by the carbo-thermal reduction of aluminum oxide in the presence of gaseous nitrogen or ammonia or by direct nitridation of aluminum. In order to get a fully dense form, Y_2O_3 or CaO are required as additives during the hot pressing.

[0009] Aluminum nitride is a wide gap semiconductor with band gap between 6.01-6.05 eV at room temperature. It crystallizes in wurtzite phase and has many potential applications in microelectronics due to its relatively high thermal conductivity ($70\text{--}210\text{ NV}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $285\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). In addition, other unique properties that make it an attractive for applications include high electrical resistivity, low thermal expansion, resistance to erosion and corrosion, excellent thermal shock resistance and chemical stability in air up to 1380°C . with surface oxidation occurring at 780°C .

[0010] Epitaxially grown thin film crystalline aluminum nitride is used for surface acoustic wave sensors (SAWs) deposited on silicon wafers because of AlN's piezoelectric properties. Another important application for AlN is its application as an RF filter which is widely used in mobile phones, which is also called a thin film bulk acoustic resonator (FBAR). AlN is synthesized in the bulk form by

the carbothermal reduction of aluminum oxide in the presence of gaseous nitrogen or ammonia or by direct nitridation of aluminum. In order to get fully dense form, Y_2O_3 or CaO are required as additives during the hot pressing.

[0011] Among the agriculture waste products, there are two types, one containing silica and carbonaceous matter and the other one contains mostly carbonaceous matter and no silica. The first kind includes rice husk, wheat husk, and peanut shells. We have demonstrated that they can be utilized to produce industrially important materials such as SiO_2 , SiC, Si_3N_4 , and zinc silicate by pyrolyzing them in air, argon or in nitrogen atmospheres.

[0012] The second kind of agriculture residues are nut shells which contain only carbonaceous matter such as almond, walnuts, pistachio, coconuts, macadamia, cashew, etc. Billions of pounds of nut shells are produced annually all over the world and will be available if they can be harnessed in the synthesis of industrially important materials. Recently, it was reported that mixed phases of SiC and Si_3N_4 can be produced by carbothermal reduction and nitridation of a mixture of silica and macadamia powder.

[0013] We have demonstrated in our recent work that by adding ZnO to powder of wheat or rice husk, pure zinc silicate can be produced with photo-luminescent properties.

[0014] Here, we have developed the formation of AlN from the nut shells powder by adding nanocrystalline powders of Al_2O_3 to the nut shells powder of almond, walnut, coconut, macadamia, pistachio and cashew and pyrolyzing them in nitrogen atmosphere at 1400 to 1500°C .

[0015] Energy dispersive X-ray fluorescence technique was used to determine the elemental composition of the nuts with very slight variation among them. The formation of pure wurtzite phase of AlN was confirmed by x-ray diffraction and Rietveld analysis and Raman spectroscopy. Transmission electron microscopy was used to confirm the nanocrystallinity of AlN and to characterize the size distribution.

SUMMARY OF DISCLOSURE

Description

[0016] A new method of making Aluminum Nitride from Nut Shells involving the formation of abundant quantities of MN from a thermal treatment of a mixture of aluminum oxide (Al_2O_3) and shells of almond, cashew, coconuts, pistachio, and walnuts in a nitrogen atmosphere at temperatures in excess of 1450°C .

DESCRIPTION OF THE DRAWINGS

[0017] The following description and drawings set forth certain illustrative implementations of the disclosure in detail, which are indicative of several exemplary ways in which the various principles of the disclosure may be carried out. The illustrated examples, however, are not exhaustive of the many possible embodiments of the disclosure. Other objects, advantages and novel features of the disclosure will be set forth in the following detailed description when considered in conjunction with the drawings.

[0018] FIG. 1 illustrates X-ray diffraction patterns taken with $\text{CuK}\alpha$ radiation of AlN synthesized from Almond powder and aluminum oxide powder in nitrogen at a temperature of 1450°C . showing the wurtzite phase.

[0019] FIG. 2A illustrates a TEM micrograph of AlN samples fabricated from almond showing the nanocrystalline nature.

[0020] FIG. 2B illustrates a TEM micrograph of AlN samples fabricated from almond showing the nanocrystalline nature.

[0021] FIG. 2C illustrates a TEM micrograph of AlN samples fabricated from walnut showing the nanocrystalline nature.

[0022] FIG. 2D illustrates a TEM micrograph of AlN samples fabricated from walnut showing the nanocrystalline nature.

[0023] FIG. 3 illustrates Raman Spectra of the AlN sample derived from almond confirming the wurtzite phase.

[0024] FIG. 4A illustrates X-ray diffraction scan of Al_2O_3 mixed with almond showing peaks corresponding to corundum phase. The vertical lines correspond to the expected peaks of alumina.

[0025] FIG. 4B illustrates a Rietveld whole profile analysis of the diffraction pattern for the AlN sample derived from almond after pyrolysing in a nitrogen atmosphere followed by treatment in air at 800° C.

[0026] FIG. 5A illustrates Raman spectra of AlN derived from pistachio showing the different Raman active modes.

[0027] FIG. 5B illustrates Raman spectra of AlN derived from almond showing the different Raman active modes.

[0028] FIG. 5C illustrates FTIR spectra of AlN derived from pistachio showing a broad band of 699 cm^{-1} .

[0029] FIG. 5D illustrates FTIR spectra of AlN derived from almond showing a broad band of 698 cm^{-1} .

[0030] FIG. 6 illustrates EDX of AlN derived from almond nut shell after pyrolysing in N_2 and followed by heat treatment in O_2 to remove excessive carbon.

DETAILED DESCRIPTION OF THE INVENTION

[0031] A method of making Aluminum Nitride Synthesis from Nut Shells.

[0032] Here, the inventors have discovered a method of forming pure AlN by carbothermal reduction of Al_2O_3 with raw nuts of almonds, coconuts, macadamia, pistachios, and walnuts in the presence of a N_2 atmosphere to produce nano-tubes and nanoparticles previously not formed by other processing then purified in an O_2 atmosphere in a Al_2O_3 crucible.

Example 1

[0033] The production process involves preparing samples from powders of raw nuts of almonds, coconuts, macadamia, pistachios, and walnuts after mixing them with nanocrystalline Al_2O_3 powder using ball milling with a SPEX 8000M including stainless steel milling media.

Example 2

[0034] The Al_2O_3 sample along with the specific nut shell was combined and milled to obtain a uniform powder. A hydraulic press was used to pressurize the homogenous powder into 1 cm diameter disks with a 2.5-3 mm depth.

[0035] The pellets were heat treated (pyrolysed) in a conventional furnace at temperatures exceeding 1400° C. for an interval of 5-6 hours in a nitrogen atmosphere.

[0036] In order to eliminate the residual carbon, the pellets were then placed in air at 670° C.

Example 3

[0037] XRD scans were obtained using a Rigaku 18 kW rotating anode generator and a high resolution powder diffractometer. The diffraction scans were collected using monochromatic $\text{CuK}\alpha$ radiation.

[0038] Raman spectra were collected on an inVia Raman Microscope (Renishaw) using a 514 nm laser line.

[0039] Scans were obtained at ca. 15 mW laser power at the sample and an integration period of 30 seconds.

[0040] Fourier Transform Infrared (FTIR) spectra were collected using Thermo Scientific Nicolet FT-IR spectrometer with Diffuse Reflectance Infrared Transform Spectroscopy (DRIFTS) accessory.

Example 4

[0041] In order to conduct the TEM analysis, ethyl alcohol was mixed with the pyrolyzed sample; the mixture was then set in an ultrasonic cleaner.

[0042] A carbon covered 200 mesh copper grid was submerged into the mixture to collect AlN particles.

[0043] A FEI Tecnai G2 TEM was utilized to examine the sample at 300 kV.

[0044] Nuts have very little SiO_2 uptake from the ground but still is a carbon source. Therefore nuts are a great candidate to mix with oxides to form a carbide and/or a nitride with further processing. The result is a pure nitride (in this case AlN) that is made in a simple cost effective process.

[0045] AlN made from nuts such as almonds, pistachios, walnuts, cashew, coconuts, macadamia etc. can be made fully dense without the use of other dopants like AlN made in other ways. This provides a more pure bulk form of AlN.

[0046] Due to its unique properties, it is extremely useful for the Navy. AlN its applications have been developed mainly for military aeronautics and transport fields.

[0047] Other applications of AlN lie in refractory composites for handling of aggressive molten metals, and high efficiency heat exchange systems.

[0048] The formation of pure AlN from nut shells offers a simple route as compared to complicated reactions currently being used involving carbon rich agents and at elevated temperatures.

[0049] Moving to more environmentally greener processes is important. This process should become the standard processing for obtaining Pure AlN.

[0050] The above examples are merely illustrative of several possible embodiments of various aspects of the present disclosure, wherein equivalent alterations and/or modifications will occur to others skilled in the art upon reading and understanding this specification and the annexed drawings. In addition, although a particular feature of the disclosure may have been illustrated and/or described with respect to only one of several implementations, such feature may be combined with one or more other features of the other implementations as may be desired and advantageous for any given or particular application. Also, to the extent that the terms “including”, “includes”, “having”, “has”, “with”, or variants thereof are used in the detailed description and/or in the claims, such terms are intended to be inclusive in a manner similar to the term “comprising”.

What we claim is:

1. A nano-structured Aluminum Nitride (AlN) in a pure form and in the wurtzite phase of AlN from nut shells made from the steps of:

preparing powders of agricultural nuts using ball milling including stainless steel milling media;
 preparing powders of nanocrystalline Al_2O_3 using ball milling including stainless steel milling media;
 mixing the powders of agricultural nuts and the powders of nanocrystalline Al_2O_3 using ball milling including stainless steel milling media and thereby forming a homogenous sample powder of agricultural nuts and Al_2O_3 ;
 pressurizing the homogenous sample powder of agricultural nuts and Al_2O_3 into a disk;
 heat treating or pyrolyzing the disk in a nitrogen atmosphere; and
 reacting the disk and the nitrogen atmosphere and forming AlN;
 wherein the AlN is nano-structured AlN and in a pure form and in the wurtzite phase of AlN.

2. The nano-structured Aluminum Nitride (AlN) in a pure form and in the wurtzite phase of AlN from nut shells of claim 1 further comprising the step of:
 eliminating residual carbon by placing the disk in air after the step of reacting the disk and the nitrogen atmosphere and forming AlN.

3. The nano-structured Aluminum Nitride (AlN) in a pure form and in the wurtzite phase of AlN from nut shells of claim 2
 wherein the step of heat treating or pyrolyzing the disk comprises temperatures exceeding 1400°C . for an interval of 5-6 hours in a nitrogen atmosphere.

4. The nano-structured Aluminum Nitride (AlN) in a pure form and in the wurtzite phase of AlN from nut shells of claim 1
 wherein the step of eliminating the residual carbon by placing the disk in air involves a temperature of 670°C .; and
 wherein the step of heat treating or pyrolyzing the disk comprises a conventional furnace.

5. A nano-structured Aluminum Nitride product from nut shells in a pure form and in the wurtzite phase from the steps comprising:
 milling agricultural nuts into a fine nut powder;
 milling nanocrystalline Al_2O_3 into a powder;
 mixing the fine nut powder with the powder of nanocrystalline Al_2O_3 ;
 pressing the fine nut powder and the powder of nanocrystalline Al_2O_3 into a pellet;
 providing a nitrogen atmosphere;

heating the pellet to a temperature of about 1400°C .;
 maintaining the temperature of the pellet at about 1400°C .;
 cooling the pellet in air to a temperature of about 670°C .;
 eliminating the residual carbon; and
 forming nano-structures of AlN.

6. A nano-structured Aluminum Nitride product from nut shells in a pure form and in the wurtzite phase from the steps comprising:
 milling agricultural nuts into a fine nut powder;
 milling nanocrystalline Al_2O_3 into a powder;
 mixing the fine nut powder with the powder of nanocrystalline Al_2O_3 ;
 wherein the fine nut powder of agricultural nuts is prepared using ball milling with a SPEX 8000M including stainless steel milling media;
 wherein the powder of nanocrystalline Al_2O_3 is prepared using ball milling including stainless steel milling media;
 wherein the fine nut powder of agricultural nuts and the powder of nanocrystalline Al_2O_3 are mixed using ball milling including stainless steel milling media and thereby forming a homogenous sample powder of agricultural nuts and Al_2O_3 ;
 pressing the fine nut powder and the powder of nanocrystalline Al_2O_3 into a pellet;
 providing a nitrogen atmosphere;
 heating the pellet to a temperature of about 1400°C .;
 wherein the step of heating the pellet comprises a conventional furnace; and
 wherein the step of pressing utilizes a hydraulic press;
 maintaining the temperature of the pellet at about 1400°C .;
 cooling the pellet in air to a temperature of about 670°C .;
 eliminating the residual carbon; and
 forming nano-structures of AlN;
 wherein the AlN is nano-structured AlN and in a pure form and in the wurtzite phase of
 wherein an 18 kW rotating anode generator and a high resolution powder diffractometer characterize the structure of the nano-structured AlN in a pure form and in the wurtzite phase with monochromatic $\text{CuK}\alpha$ radiation and further using a 514 nm laser line to obtain Raman spectra on an inVia Raman Microscope and scanning at about 15 mW laser power and an integration period of 30 seconds.

* * * * *