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Whalen et al.

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(54) **ARTICLE COMPRISING A SEMICONDUCTING MATERIAL**

(58) **Field of Classification Search**
CPC C30B 29/46
See application file for complete search history.

(71) Applicant: **The Florida State University Research Foundation, Inc.,**
Tallahassee, FL (US)

(56) **References Cited**

(72) Inventors: **Jeffrey Whalen, Tallahassee, FL (US); Theo Siegrist, Tallahassee, FL (US)**

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(73) Assignee: **The Florida State University Research Foundation, Inc.,**
Tallahassee, FL (US)

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 63 days.

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(21) Appl. No.: **14/674,567**

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(22) Filed: **Mar. 31, 2015**

Electronic properties of barium chalcogenides from first-principals calculations: Tailoring wide-band-gap II-VI semiconductors. G.Q. Lin et al. Physical Letters B, vol. 71, 085203, pp. 1-5, 2005.*

(65) **Prior Publication Data**

US 2015/0203992 A1 Jul. 23, 2015

(Continued)

Related U.S. Application Data

(63) Continuation of application No. PCT/US2013/067045, filed on Oct. 28, 2013.

Primary Examiner — Douglas B Call

(60) Provisional application No. 61/718,945, filed on Oct. 26, 2012.

(74) *Attorney, Agent, or Firm* — Robert J. Varkonyi; Smith & Hopen, P.A.

(51) **Int. Cl.**

(57) **ABSTRACT**

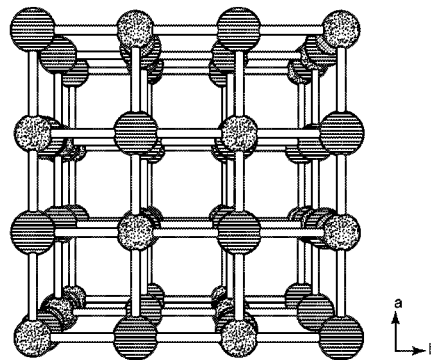
C30B 29/46 (2006.01)
H01B 1/10 (2006.01)
C30B 9/10 (2006.01)
H01B 1/08 (2006.01)
C30B 9/12 (2006.01)
C30B 29/22 (2006.01)

Single crystals of the new semiconducting oxychalcogenide phase were synthesized using a novel crystal growth method. The crystals had low defects and homogeneous composition as characterized by single crystal X-ray diffraction and scanning electron microscopy, respectively. Heat capacity and resistivity measurements were in agreement with the calculated band structure calculations indicating semiconductivity, with a band gap of about 3 eV.

(52) **U.S. Cl.**

CPC **C30B 29/46** (2013.01); **C30B 9/10** (2013.01); **C30B 9/12** (2013.01); **C30B 29/22** (2013.01); **H01B 1/08** (2013.01); **H01B 1/10** (2013.01)

14 Claims, 6 Drawing Sheets



● BARIUM
● TELLURIUM
● OXYGEN

(56)

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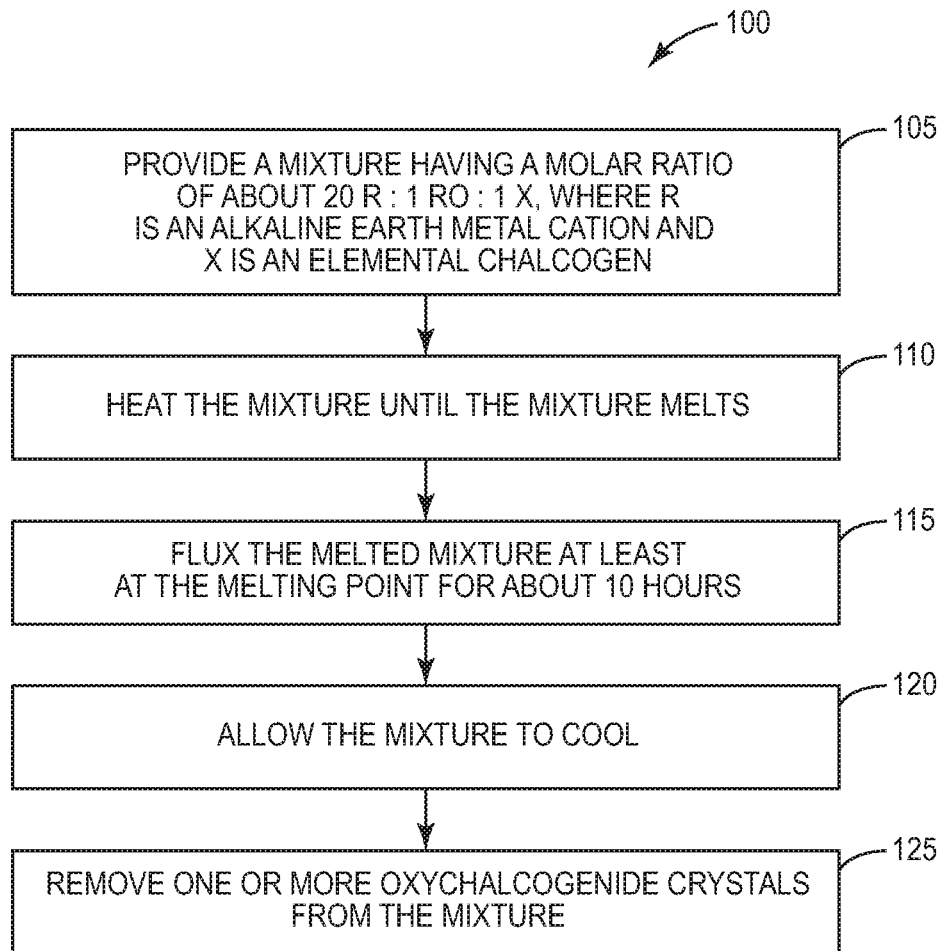


FIG. 1

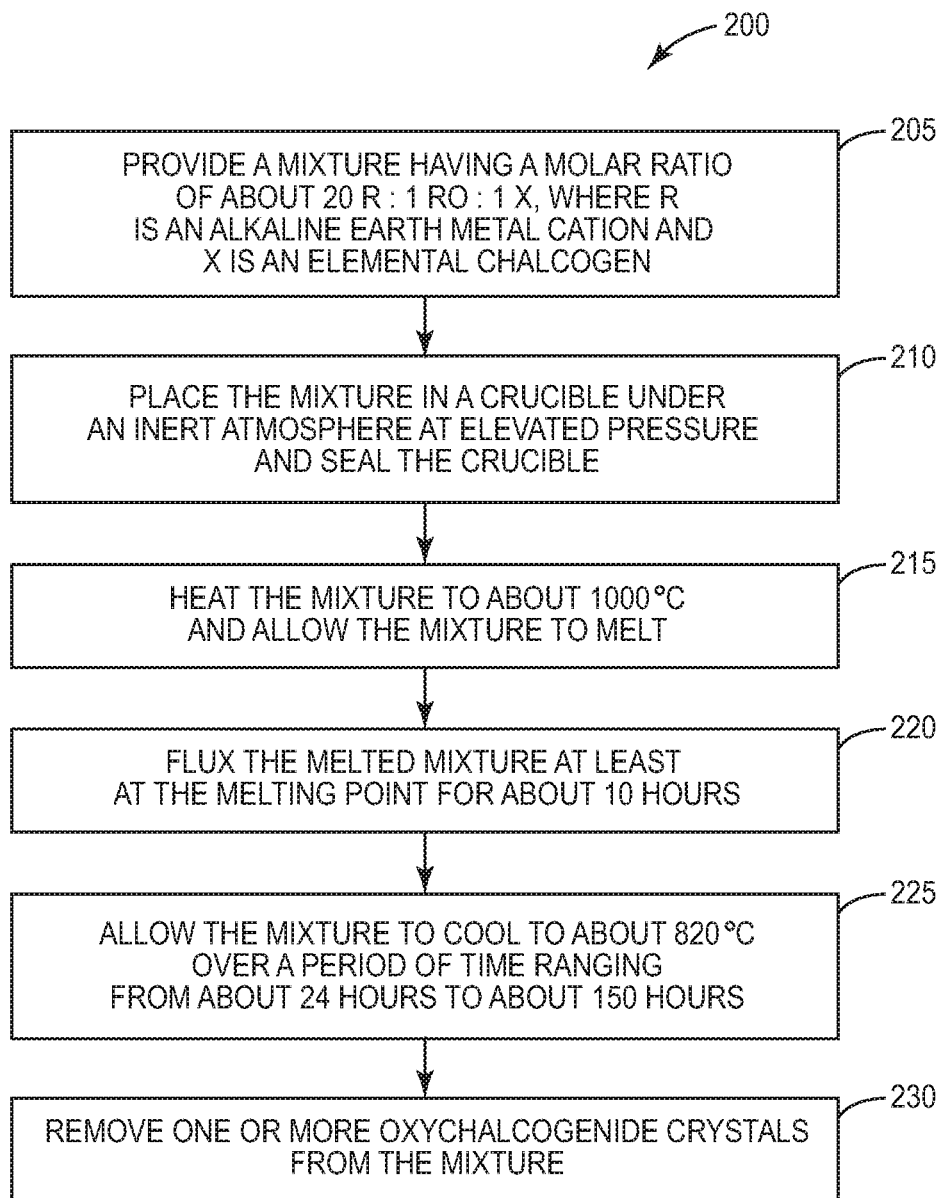


FIG. 2

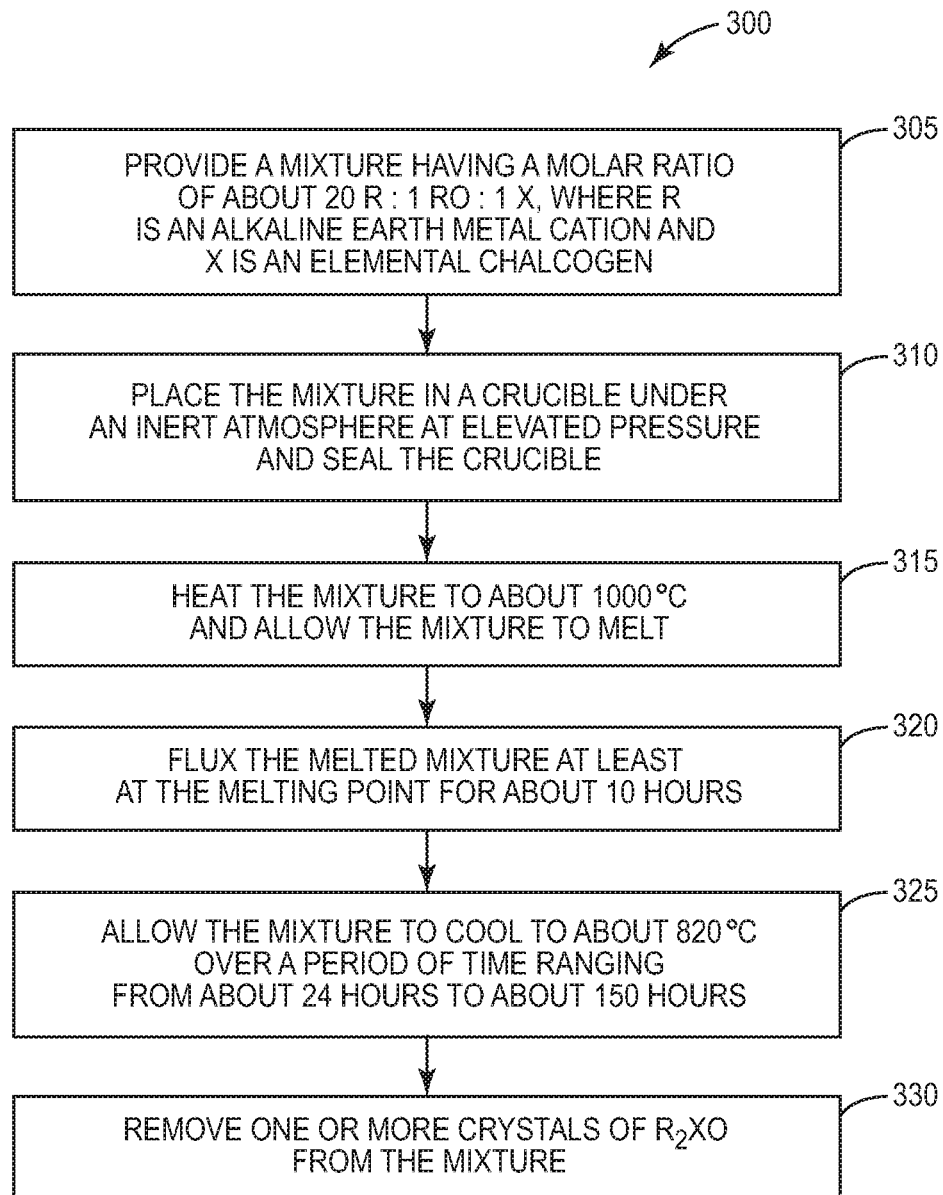


FIG. 3

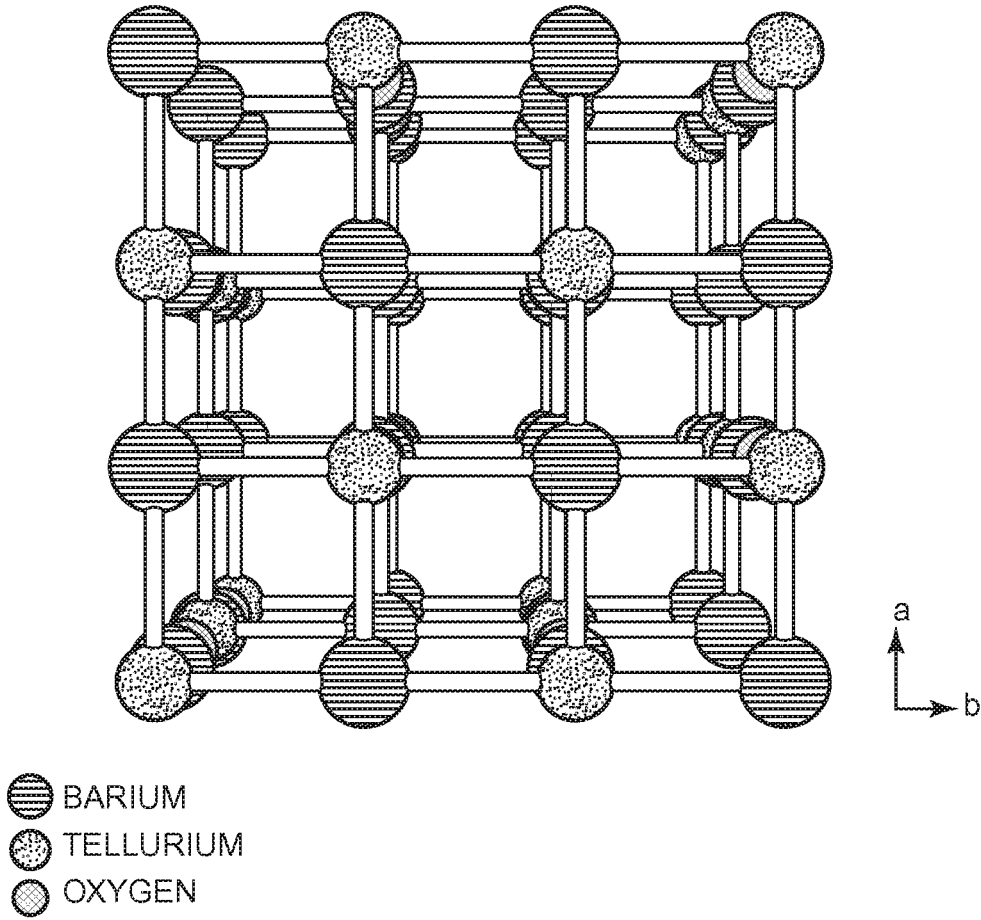
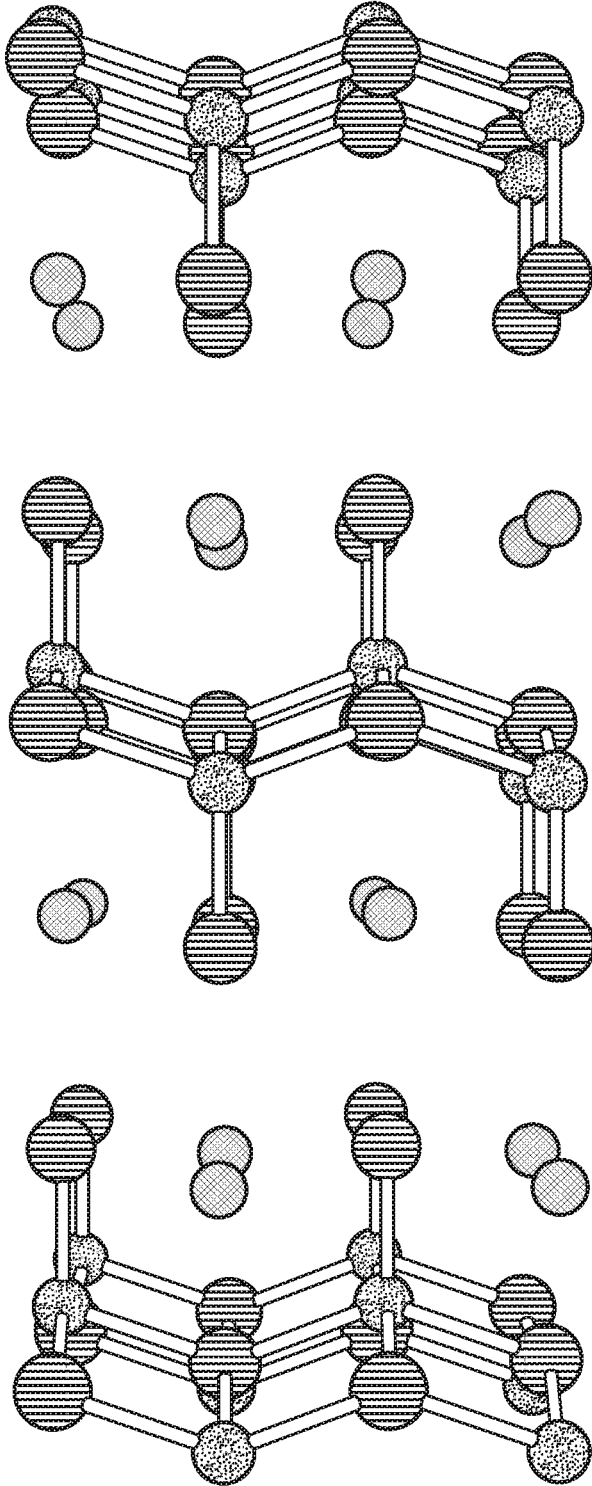


FIG. 4






-  BARIUM
-  TELLURIUM
-  OXYGEN

FIG. 5

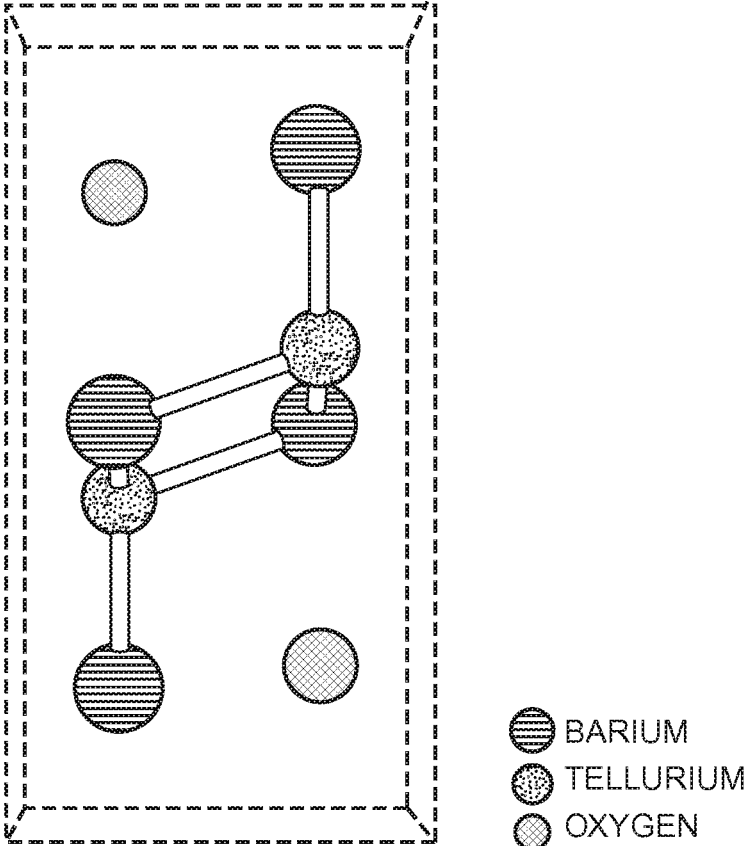


FIG. 6

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ARTICLE COMPRISING A SEMICONDUCTING MATERIAL

CROSS-REFERENCE TO RELATED APPLICATIONS

This nonprovisional application is a continuation of currently pending PCT Application PCT/US2013/067046 filed Oct. 28, 2013, which claims priority to provisional application No. 61/718,945, entitled "Semiconducting Oxytelluride Single Crystal BA₂TEO," filed on Oct. 26, 2012 by the same inventors, and is incorporated by reference in its entirety.

STATEMENT OF GOVERNMENT SUPPORT

This invention was made with government support under C & E funds from the National High Magnetic Field Laboratory. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to novel semiconductor materials. More specifically, the invention relates to oxychalcogenide crystal compositions.

2. Brief Description of the Prior Art

There exists many more reported crystal structures of tellurates/tellurites containing cationic Te^{3+/4+}, than for oxytellurides containing anionic Te²⁻. Yet, semiconducting oxytelluride systems may have promise in the field of commercialized optoelectronic applications like transparent semiconductors. The complex orbital hybridizations in anion-ordered multinary crystals like oxytellurides can give rise to unique physical properties. These systems are the cutting edge of applied semiconductor technology research, but further exploration for better suited materials could result in more efficient and/or more effective functional materials. In such a raw materials intensive market, though, a semiconductor that is comprised of the most abundant and/or inexpensive elements may be of the greatest commercial interest and have the most potential for large scale applications.

The copper-based oxychalcogenides (Liu 2007, Zakutayev 2010; Ueda, et al., *Thin Solid Films* 496 (2006) 8-15; Ohta, et al., *Solid-State Electronics* 47 (2003) 2261-2267), such as LaCuOX (X=S, Se) and La₂O₂CdSe₂, are classes of materials which may have commercial applications. (Ueda, et al., *Applied Physics Letters* 77 (2000) 2701-2703; Huang, et al., *Journal of Solid State Chemistry* 155 (2000) 366-371; Kamioka, et al., *Journal of Luminescence* 112 (2005) 66-70; Ramasubramanian, et al., *Journal of Applied Physics* 106 (2009) 6). Transition metal oxysulfides like Sm₂Ti₂S₂O₅ have also been identified as stable catalysts for photo-oxidation and reduction of water. (Ishikawa, et al., *Journal of the American Chemical Society* 124 (2002) 13547-13553; Meignen, et al., *Journal of Solid State Chemistry* 178 (2005) 1637-1643).

BRIEF SUMMARY OF THE INVENTION

The long-standing but heretofore unfulfilled need for oxychalcogenides compounds containing both anionic chalcogenides and oxygen, and methods for manufacturing these compounds, is now met by a new, useful, and nonobvious invention.

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The oxychalcogenide compounds may comprise a tetragonal crystal of repeating units of RX and RO where R is an alkaline earth metal cation, X is an anionic chalcogens, and O is oxygen. The anionic chalcogens may be tellurium, selenium or sulfur, and the alkaline earth metal cation is beryllium, magnesium, calcium, strontium, barium, radium or mixtures thereof, with the alkaline earth metal cation of RO is integrated into a crystalline structure with the unit of RX. Additionally, the molar ratio of the alkaline earth metal cation and the anionic chalcogens is 2:1.

These and other important objects, advantages, and features of the invention will become clear as this disclosure proceeds.

BRIEF DESCRIPTION OF THE DRAWINGS

For a fuller understanding of the invention reference should be made to the following detailed description, taken in connection with the accompanying drawings, in which:

FIG. 1 is a general flow chart of an exemplary method for producing oxychalcogenide crystals.

FIG. 2 is a general flow chart of an exemplary method for producing oxychalcogenide crystals.

FIG. 3 is a general flow chart of an exemplary method tier producing oxychalcogenide crystals.

FIG. 4 is an illustration of a crystalline structure.

FIG. 5 is an illustration of a crystalline structure having tetragonal symmetry.

FIG. 6 is an illustration of a single unit of a crystalline structure having tetragonal symmetry.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

As used herein, "about" means approximately or nearly and in the context of a numerical value or range set forth means about ± 15 percent of the numerical.

Oxytellurides (OR₂Te) may be better suited as transparent conductors due to their high hole mobilities. Doping of the 5p orbitals of Te increases hole mobility and conduction in LnCuOTe (Ln=La, Ce, Nd) phases more than doping of the 3p/4p orbitals of S/Se in the corresponding LaCuO (S/Se) phases.

Using metal fluxes to grow oxide single crystals may generate an advantageous chemical growth environment since oxygen is a minority constituent of the system, with the metal flux acting as a reducing agent. Good oxygen solubility in the metal flux may therefore be beneficial, and preliminary synthesis experiments have indicated high oxygen solubility in alkaline earth fluxes. In addition, low growth temperatures are desirable for discovery activities, especially coupled with low cost crucible materials. The molten alkaline flux reactions create a unique single crystal oxide growth environment and may further allow control of dopant substitution, electron transfer, and phase selectivity. Since alkaline earth metals readily form solid solutions with lanthanide metals as well as group IIIB and IVB metals, complex intermetallic phases have been grown (Stojanovic, M. and Lattner, S. E. Growth of new ternary intermetallic phases from Ca/Zn eutectic flux. *J. Solid State Chem.* 180, 907-914 (2007); Lattner, S. E., Bilc, D., Mahanti, S. D. and Kanatzidis, M. G. R₃Au₆+xAl₂6T (R=Ca, Sr, Eu, Yb; T=Early Transition Metal): a Large Family of Compounds with a Stuffed BaHg₁₁ Structure Type Grown from Aluminum Flux. *Inorg. Chem.* 48, 1346-1355 (2009); Lattner, S. E. and Kanatzidis, M. G. RE(AuAl₂)_nAl₂(AuxSil-x)₂: A New Homologous Series of Quaternary Intermetallics

Grown from Aluminum Flux. Inorg. Chem. 47, 2089-2097 (2008)). The alkaline earth flux can be further modified to include transition element, expanding the possibilities of discovery of new phases.

Investigating the oxygen solubility in alkaline earth fluxes showed, surprisingly, that single crystal oxide growth is possible in this unique environment, and may allow for control of dopant substitution, electron transfer, and phase selectivity.

Slow cooling of the alkaline earth metal flux from about 1000° C. may kinetically force oxygen anion-metal cation organization that is high in cation concentration due to the presence of the flux. This bonding in the liquid flux may be relatively weak compared to more oxygen-rich combinations of the same ion pairs, which may allow for crystal growth. The use of eutectic mixtures therefore may allow for a temperature reduction well below the critical precipitation temperature for most oxide phases, effectively pitting thermal kinetic energy losses in competition with increased crystal lattice energies. This balance of equilibrium factors, combined with quick removal of the liquid solvent environment (quench), may lead to exclusive stabilization and isolation of metastable phases not formed at ambient temperatures and pressures.

FIG. 1 illustrates an exemplary method 100 for producing oxychalcogenide crystals according to various embodiments. At step 105, a mixture may be provided that may have a molar ratio of about 20 R:1 RO:1 X, where R is an alkaline earth metal cation and X is an elemental chalcogen. In various embodiments, the alkaline earth metal cation may comprise barium (Ba), supplied as chunks or rods (99+ percent, Acros Organics), and the RO may comprise barium oxide (BaO), supplied in powder form (99+ percent, Cerac). The elemental chalcogen may be provided, for example, as tellurium powder (99.999 percent, Puratronic, AlfaAesar). The mixture may then be heated until the mixture melts (step 110), forming a molten barium flux. At step 115, the mixture may be fluxed for about 10 hours while holding the mixture at a temperature of at least the melting point of the mixture. The mixture may then be allowed to cool (step 120), at which point one or more oxychalcogenide crystals may be removed from the mixture (step 125).

In various embodiments, doping may occur during the fluxing step in which a portion of the chalcogen anions in the crystal phase are replaced with a different anion. For example, a Group 15 pnictogen may be used to dope the material. In various embodiments, the pnictogen may be bismuth. The doping concentration may be on the order of Ba₂OTe_{0.8}Bi_{0.2}. The doping anion may substitute up to about 20 atomic percent of the chalcogen anions. Experimentation has indicated that doping with bismuth may change the electronic conductivity of the material making the material more conductive, which may be useful for transparent semiconductor applications. In addition, the doped material may absorb light in the ultraviolet range, and may be suitable for an ultraviolet light emitting device.

FIG. 2 illustrates an exemplary method 200 for producing oxychalcogenide crystals according to various embodiments. Similar to method 100, a mixture may be provided that may have a molar ratio of about 20 R:1 RO:1 X, where R is an alkaline earth metal cation and X is an elemental chalcogen (step 205). At step 210, the mixture may be placed in a crucible under an inert atmosphere at elevated pressure, then the crucible may be welded shut. The crucible may also be sealed in quartz tubing under vacuum. The inert atmosphere may comprise argon gas at a pressure of about 1.5 atm. One Skilled in the art will readily recognize that other

gas environments (comprising a single gas or mixture of gases) may be used in place of argon, and that other pressures may be used that are higher or lower than 1.5 atm. The mixture may then be heated to about 1000° C., and the mixture allowed to melt (step 215). The mixture may then be allowed to flux at about 1000° C. (or at least the melting point of the mixture) for about 10 hours (step 220). The mixture may then be allowed to cool to about 820° C. over a period of time ranging from about 24 hours to about 150 hours (step 225). The crucible may be opened in an inert atmosphere glovebox, and then one or more oxychalcogenide crystals may be removed from the mixture (step 230).

FIG. 3 illustrates a further exemplary method 300 for producing oxychalcogenide crystals in the form of R₂XO according to various embodiments. Similar to method 100, a mixture may be provided that may have a molar ratio of about 20 R:1 RO:1 X, where R is an alkaline earth metal cation and X is an elemental chalcogen (step 305). At step 310, the mixture may be placed in a crucible under an inert atmosphere at elevated pressure, then the crucible may be welded shut. The crucible may also be sealed in quartz tubing under vacuum. The inert atmosphere may comprise argon gas at a pressure of about 1.5 atm. One skilled in the art will readily recognize that other gas environments (comprising a single gas or mixture of gases) may be used in place of argon, and that other pressures may be used that are higher or lower than 1.5 atm. The mixture may then be heated to about 1000° C., and the mixture allowed to melt (step 315). The mixture may then be allowed to flux at about 1000° C. (or at least the melting point of the mixture) for about 10 hours (step 320). The mixture may then be allowed to cool to about 820° C. over a period of time ranging from about 24 hours to about 150 hours (step 325). The crucible may be opened in an inert atmosphere glovebox, and then one or more crystals of R₂XO may be removed from the mixture (step 330).

Elemental analysis using EDS in a JEOL 5900 scanning electron microscope indicated the stoichiometry of an exemplary oxychalcogenide with the formula Ba₂TeO having a molar Ba:Te ratio of 2:1 to within about 5 atomic percent as shown in Table 1. The crystals had a platelet morphology and micaceous cleavage.

TABLE 1

Result of Elemental Analysis					
Element	Line	Intensity (c/s)	Error 2-sig	Atomic %	
O	Ka	0.00	0.000	0.000 [†]	
Cu	Ka	3.13	1.119	0.334	
Te	La	286.76	10.707	31.859	
Ba	La	553.93	14.882	67.807	
				100.000	Total

[†]Element not detected because the atomic electron values were below the detection limits for the device.

The crystals were structurally characterized by single crystal x-ray diffraction using an Oxford-Diffraction Xcalibur2 CCD system. The as-grown crystals were transferred from the glovebox under Paratone-N oil on a glass slide. The crystals were cleaved in the oil and shards of appropriate size were selected and mounted in cryoloops then aligned in a nitrogen stream for data collections at 200 K. Reflections were recorded, indexed and corrected for absorption using the Oxford-Diffraction CrysAlis software. Subsequent struc-

ture determination and refinement was carried out using SHELXTL. (Sheldrick, 2000).

A Quantum Design PPMS system was used to measure the zero-field heat capacity between 2 K and room temperature, with crystals embedded in grease. Electrical resistance was tested using 4-point contacts at room temperature. The optical reflectivity spectra of the crystals were collected with a 0.75 m focal length spectrometer and back-illuminated CCD configured to provide a spectral resolution of 1.2 nm, with a polished aluminum surface serving as a reference.

Atomic Structure and Chemical Stability

Ba₂TeO is structurally comprised of one BaTe unit combined with one BaO unit. The normal structure type for both BaTe and BaO is the cubic "NaCl" structure type (Fm-3 m, #225). Single crystalline Ba₂TeO was obtained in platelet form and had a metallic color. The crystals averaged about 4 mm×4 mm×0.5 mm and were mildly air sensitive, showing signs of decomposition within a few hours on the benchtop.

The atomic structure of Ba₂TeO is tetragonal symmetry as illustrated in FIG. 4. FIG. 5 shows an exploded view of the Ba₂TeO crystal structure to better illustrate the tetragonal symmetry and the placement of the oxygen atoms within the structure. FIG. 6 illustrates a single unit of tetragonal symmetry for the Ba₂TeO structure. The structure may have puckered square layers of BaO and 2D BaTe layers alternating in the a-b plane. There may be a shorter than expected bond between the Ba and O atom at 2.44 Å, which may be the result of the linking bond between the BaO and BaTe layers.

The disclosures of all publications cited above are expressly incorporated herein by reference, each in its entirety, to the same extent as if each were incorporated by reference individually.

Glossary Of Claims Terms

a-b plane: An atomic plane in a crystal lattice.

Alkaline earth metal: Metallic elements found in the second group (also known as Group IIA) of the periodic table, comprising beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). Generally, very reactive metals that do not occur freely in nature.

Anionic: Having a negative electrical charge, such as an ion with more electrons than protons.

Ba₂TeO: A semiconducting oxytelluride compound containing barium.

Barium: Chemical element (Ba) with atomic number 56. Barium is an alkaline earth metal.

Cation: An ion having fewer electrons than protons, thus having a positive charge.

Chalcogen: The elements sulfur (S), selenium (Se), and tellurium (Te).

Chalcogenide: A compound containing a chalcogen.

Crucible: A container that can withstand very high temperatures and is used for metal, glass, and pigment production as well as various other modern laboratory processes.

Crystal: Solid material whose constituent atoms, molecules, or ions are arranged in an orderly, repeating pattern extending in all three spatial dimensions.

Doping: The process of intentionally introducing impurities into a semiconductor to change the electrical properties of the semiconductor.

Fluxing: A process by which molten metals are brought into contact with one another to form an alloy. The flux may act as a reducing agent.

Oxychalcogenide: A compound containing a chalcogen ion and oxygen.

Oxygen: Chemical element (O) with atomic number 8.

Oxytelluride: A compound containing a telluride ion (Te²⁻) and oxygen.

Pnictogen: Elements found in the fifteenth group (also known as Group VA) of the periodic table, comprising nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), and bismuth (Bi).

Selenium: Chemical element (Se) with atomic number 34.

Sulfur: Chemical element (S) with atomic number 16.

Tellurium: Chemical element (Te) with atomic number 52.

Tetragonal structure: A crystalline structure with a four-fold symmetry axis.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall there between.

What is claimed is:

1. An oxychalcogenide composition, comprising: a tetragonal crystalline material, further comprising: an anionic chalcogen, where the chalcogen is tellurium, selenium, sulfur, a combination of tellurium and a pnictogen, a combination of selenium and a pnictogen, or a combination of sulfur and a pnictogen; wherein the pnictogen is up to 20 atomic % of the chalcogen anions; oxygen; and R, where R is an alkaline earth metal cation, where the alkaline earth metal cation is beryllium, magnesium, calcium, strontium, barium, radium, or mixtures thereof; wherein the molar ratio of the alkaline earth metal cation to the anionic chalcogen is about 2:1.
2. The oxychalcogenide composition of claim 1, wherein the alkaline earth metal cation is barium.
3. The oxychalcogenide composition of claim 1, wherein the molar ratio of the alkaline earth metal cation to the anionic chalcogen to the oxygen is about 2:1:1.
4. The oxychalcogenide composition of claim 1, wherein the composition is Ba₂TeO.
5. The oxychalcogenide composition of claim 1, wherein the composition comprises one unit of RX and one unit of RO; where X is an anionic chalcogen.
6. The oxychalcogenide composition of claim 5, wherein the composition comprises puckered layers of RO and 2D layers of R-anionic chalcogen alternating along the c-axis.
7. The oxychalcogenide composition of claim 1, wherein the chalcogen comprises tellurium.
8. The oxychalcogenide composition of claim 1, wherein the pnictogen is nitrogen, phosphorus, arsenic, antimony, or bismuth.
9. The oxychalcogenide composition of claim 8, wherein the pnictogen comprises bismuth.
10. An oxychalcogenide composition, comprising: a tetragonal crystal of repeating units of RX and RO; wherein R is an alkaline earth metal cation, X is an anionic chalcogen, and O is oxygen; where the anionic chalcogen is sulfur, selenium, or telluride; where the alkaline earth metal cation is beryllium, magnesium, calcium, strontium, barium, radium, or mixtures thereof; where the alkaline earth metal cation of RO is integrated into a crystalline structure with the unit of RX; and wherein the R:X molar ratio is about 2:1.

11. The oxychalcogenide composition of claim **10**, wherein the composition is Ba_2TeO .

12. The oxychalcogenide composition of claim **10**, further comprising a unit of RY integrated in the crystalline structure of the oxychalcogenide composition; 5

where Y is non-chalcogen anion;

wherein the unit of RY replaces a unit of RX in the crystal;

and

wherein RY comprises up to 20 atomic percent of RX.

13. The oxychalcogenide composition of claim **12**, 10 wherein the non-chalcogen anion comprises a pnictogen.

14. The oxychalcogenide composition of claim **13**, wherein the pnictogen comprises bismuth.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 9,777,405 B2
APPLICATION NO. : 14/674567
DATED : October 3, 2017
INVENTOR(S) : Jeffrey Whalen and Theo Siegrist

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

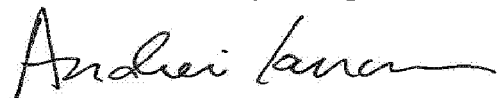
In the Specification

Column 1, Lines 14-19, should read:

STATEMENT OF GOVERNMENT SUPPORT

This invention was made with government support under grant number DE-SC0008832 awarded by the Department of Energy. The government has certain rights in the invention.

Signed and Sealed this
Seventeenth Day of April, 2018



Andrei Iancu
Director of the United States Patent and Trademark Office