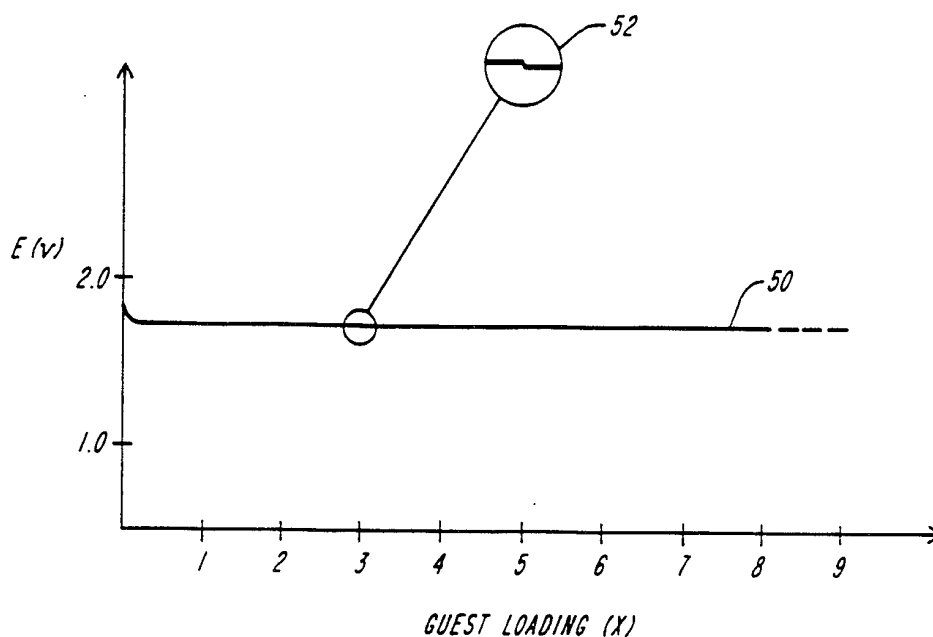




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(54) Title: LAYERED CRYSTALLINE MATERIAL CAPABLE OF HIGH GUEST LOADING



(57) Abstract

A crystalline material capable of high guest loading greater than three and exhibiting independence of the Gibbs free energy function from guest concentration and a method for its manufacture is provided. The crystalline material may belong to the class of Me_yCh_z , where Me is selected from the group consisting of Bi and Sb, Ch is selected from the group consisting of Te, Se and S, y is 1 or 2 and z is in the range of 1 to 3, such that the material has a defect density which is sufficiently low to permit intercalation of at least 3 moles of lithium within van der Waals channels per one mole of said material without significant distortion of the lattice. An intercalated material with guest loading up to 10 mole/mole host is provided.

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5 Layered Crystalline Material Capable of High Guest Loading

This application is a continuation-in-part application of U.S.S.N. 07/784,525 filed October 29, 1991.

10 Background of the Invention

The present invention relates to highly defect-free mono-crystalline materials capable of intercalating high levels of guest species and a method of making the same. The present invention further relates to a highly intercalated layered crystalline material.

15 Layered crystalline materials (hosts) can accommodate foreign species (guests) in the channels between the layers thereby forming intercalated materials. Intercalation compounds, such as graphite and transition metal chalcogenides, have been intensively investigated over the last two decades and have found utility in a number of fields,
20 including batteries, photovoltaic cells, superconductivity and hydrogen accumulation.

The hosts of interest to this application have anisotropic lamellar structures separated by van der Waals channels which are capable of accommodating small guest particles, such a lithium or hydrogen.

25 Because of the weakness of a van der Waals attractive force, the van der Waals channels can readily accept guest species, which can be neutral or charged. The guest species fill the channel until no more sites are energetically available. The amount of guest species which occupy sites in the van der Waals channel is the loading capacity of the
30 guest. "Loading" or "loading capacity" is defined herein as moles guest species per mole host material; "species" is defined as ions or uncharged atoms of elements. It is recognized that for many applications, increased loading capacity of the guest into the layered material would significantly improve device performance.

35 Distortion of a layered crystalline material has been used to increase the channel width and thereby increase guest loading. U.S.

4,288,508 reports a cathode active material for a battery having the preferred formula $\text{Li}_z\text{Na}_y\text{TiS}_2$, where y is in the range of 0.15-0.20 and z can be as high as 3.25. However, increased loading in these materials is accomplished by using the larger sodium atom to pry open the van der Waals channels. This results in significant distortion of the TiS_2 lattice.

U.S. 4,309,491 reports a solid solution containing a bismuth halcogenide for use as a cathode active material. The guest loading process in the bismuth chalcogenide is reported to require up to six Faradays of electrons, suggesting that six moles of guest are intercalated. However, it is also reported that there is substantial dependence of the discharge voltage on the guest concentration. Additionally, there is no indication that the bismuth chalcogenide has been prepared in a highly defect-free form with controlled lattice parameters.

Accordingly, it is the object of the present invention to provide a mono-crystalline material capable of intercalating extremely high loads of a guest species in which a change in the Gibbs free energy (ΔG) of the material is substantially independent of intercalant concentration. Under these conditions, properties dependent upon ΔG , such as working potential of an electrochemical cell, remain unchanged.

It is a further object of the invention, to provide a highly intercalated crystalline material having controlled lattice parameters.

It is yet a further object of the invention to provide a method of making a highly defect-free mono-crystalline material with controlled lattice parameters capable of high guest loading.

Summary of the Invention

The present invention overcomes the limitations of the prior art by providing a highly defect-free material with controlled lattice characteristics. When used in devices such as a battery it provides superior performance over prior art devices.

In one aspect of the invention, a layered mono-crystalline material is provided having a defect density which is sufficiently low to permit intercalation of at least 3 moles of lithium within van der Waals channels per one mole of the material without significant distortion of the lattice. The material is further characterized in that its change in Gibbs free energy is substantially independent of the lithium intercalation concentration.

In another aspect of the present invention, a mono-crystalline material having the formula, Me_yCh_z , is provided where Me is selected from the group consisting of Bi and Sb, Ch is selected from the group consisting of Te, Se and S, y is 1 or 2 and z is 1, 2, or 3. The material has a defect density which is sufficiently low to permit intercalation of at least 3 moles of lithium within van der Waals channels per one mole of the material without significant distortion of the lattice. The material is further characterized in that ΔG is substantially independent of the lithium intercalation concentration. Further detail concerning intercalation compounds and devices using these compounds are given in the following applications, filed on equal date as "Layered Crystalline Material Capable of High Guest Loading", and incorporated herein by reference: "Energy Storage Device", "Electrolytic Double Layer Capacitor", and "Capacitive Thermoelectric Device".

In preferred embodiments, the material has a hexagonal crystal lattice structure, a defect density of less than $10^{12}/\text{cm}^3$ and a gradient of impurity defect distribution in the van der Waals channel inversely proportional to the direction of lithium intercalation. The mono-crystalline materials can be further characterized in that a condensation of lithium occurs at a loading capacity of approximately three. The condensation is from a lattice gas to a quasi-liquid. The lattice structure may be rhombohedral or hexagonal. The mono-crystalline material is preferably a single crystal. In preferred embodiments, the defect density is minimized and perfection of the lattice crystal is accomplished by using careful processing controls. In

other preferred embodiments, the mono-crystalline material is used in a battery, a capacitor or a thermal electric device; although the mono-crystalline material may be ground into a powder for some device applications.

5 In another aspect of the invention, a method of preparing a highly purified bismuth chalcogenide consists of the following steps: an ampoule is charged with stoichiometric quantities of a chalcogenide element and bismuth; the ampoule is provided with an atmosphere selected to prevent oxidation and sealed; the sealed ampoule is heated
10 at a temperature in the range of 5°C to 10°C above T_{liq} of the bismuth chalcogenide, the temperature is controlled to within a range of ± 0.5 along the length of the ampoule and for a time sufficient to melt the component materials and react to form the bismuth chalcogenide, whereby the ampoule is agitated during heating to ensure homogeneous
15 mixing of the component materials; the material is cooled to room temperature at a controlled rate to form a homogeneous polycrystalline bismuth chalcogenide; the polycrystalline bismuth chalcogenide is placed in surface contact with a seed crystal of a specific crystal lattice structure; the seed crystal and polycrystalline bismuth chalcogenide are
20 heated to a temperature which is in the range of 30°C to 40°C below T_{liq} of the bismuth chalcogenide; a zone of the polycrystalline bismuth chalcogenide adjacent to the seed crystal is heated to a temperature which is in the range of 0°C to 15°C above T_{liq} of the bismuth
25 chalcogenide; the zone is moved along the length of the polycrystalline chalcogenide at rate in the range of 2 to 10 mm/hr, whereby a single crystal highly defect-free bismuth chalcogenide is formed; and the single crystal bismuth chalcogenide is cooled to room temperature at the controlled cooling rate.

30 In another aspect of the present invention, a highly intercalated crystalline material is provided having a guest capacity in the range of three to ten moles within van der Waals channels per one mole of said intercalated material without significant distortion of the lattice. The

guest selected from the group consisting of Group IA and Group IIA metals. The intercalated material is further characterized in that ΔG is substantially independent of the guest concentration. The intercalated material may have the formula, $G_xMe_yCh_z$, where G is selected from the group consisting of Group IA and Group IIA metals, Me is selected from the group consisting of Bi and Sb, Ch is selected from the group consisting of Te, Se and S, x is in the range of 3 to 10, y is 1 or 2 and z is in the range of 1 to 3.

Brief Description of the Drawing

10 In the Drawing;

Figure 1 is a schematic illustration of the localized sites in the van der Waals channels for the crystal lattice structures used in the present invention;

15 Figure 2 is a cross-sectional schematic illustration of the zone-refinement apparatus used in preparing single crystals of the present invention; and

Figure 3 is a discharge curve of a battery using the crystalline material of the present invention.

Description of the Preferred Embodiment

20 The present invention has identified that highly defect-free crystalline layered materials with appropriate impurity distribution are capable of intercalating high loads of guest species into van der Waals channels of the material.

Structure. A family of highly defect-free compounds of the formula, Bi_yCh_z , where Ch is Te, Se or S, y is 1 or 2 and z is in the range of 1 to 3, have been identified which permit extremely high loading capacity of the guest species, well beyond the loading capacity conventionally predicted by the lattice structure of the crystal and the model of the lattice gas. Solid solutions of these compounds, *i.e.*,
30 $Bi_2(Te_{1-x}Se_x)_3$, are also within the scope of the invention. Importantly, high loading is achieved without significant distortion of the crystal lattice and without significant dependence of ΔG of the material on the

intercalant concentration. ΔG has been correlated with the operating performance of the crystalline material when used in devices such as a cathode material in a galvanic cell.

Although discussions are directed to a bismuth chalcogenide, it is contemplated that any layered material of requisite crystalline lattice parameters, guest loading capacity and thermodynamic behavior is within the scope of the present invention.

The bismuth chalcogenide family is known to crystallize in rhombohedral and hexagonal lattices. The hexagonal and rhombohedral crystal lattices possess two types of energetically accessible sites which permit localization of the guest species within the van der Waals channel. The basis for this observation has been presented in a co-pending application U.S.S.N. 07/784,525 of which this application is a continuation-in-part and which is herein incorporated by reference.

Figure 1 is a schematic representation of the two types of guest sites. A first site 22 is in the plane of the center of the channel, while a remaining site 24 localizes the guest species along walls 26 of the channel. Total loading of the channel by guest is predicted to be three. Occupation of sites 22 is more energetically favorable at the beginning of intercalation than of sites 24. However, relative energy levels change during the intercalation process. All sites are sufficiently close in energy that "hopping" of guests from one to another site of differing energy is possible. The guest species behave as a "lattice gas".

The conventional model would seem to suggest, therefore, that the upper limit to guest loading without distortion of the lattice is three. However, we have discovered that much higher loading is possible. For the specified lattice types shown in Fig. 1, orbital interaction in a filled van der Waals channel results in increased guest-guest interaction and a decrease in the average guest-guest interatomic distance. This conversion from occupation of localized energy minima to free movement throughout the van der Waals channel is equivalent to a

phase change. The lattice gas condenses into a high density state, which is defined herein as a "quasi-liquid phase".

Because the new phase has a smaller average interatomic distance, additional guests can be introduced without distortion of the crystal lattice. Hence, a loading capacity of three is no longer a
5 limitation to the system and rapid and high levels of guest loading is now possible. Loading capacity of lithium of up to eight and nine have been observed in the bismuth chalcogenide compounds of this invention. We estimate that the loading capacity in this system can be even
10 higher, in particular, capacity of up to ten is considered possible.

The class of compounds of the present invention has stable crystalline phases of hexagonal or rhombohedral symmetry which can be prepared with minimal defect densities and the appropriate impurity distribution. It is known in the prior art that the Bi_2Ch_3 class of
15 compounds may crystallize in a rhombohedral unit cell of space group D_{3d}^5 ($R\bar{3}m$, $a_0=9.83 \text{ \AA}$; $\alpha=24.4^\circ$ for bismuth selenide) containing five atoms. This crystal structure consists of layers formed by equal atoms in hexagonal arrangement. It is also given in prior art that a hexagonal unit cell for bismuth selenide ($a_0=4.14 \text{ \AA}$; $c_0=28.55 \text{ \AA}$) also has
20 been identified.

In a battery, the discharge curve is directly correlated to ΔG of the cathode material (a bismuth chalcogenide). The following thermodynamic parameters which are related to ΔG must be considered when evaluating a guest/host combination: the entropy of distribution of
25 the host/guest atoms, the energy of guest-guest and guest-host interactions, the change in the Fermi energy (ΔF_e), and the lattice distortion (L_D).

The lattice gas to quasi-liquid condensation of the system prevents significant distortion of the lattice. In the present case,
30 loading over the range of intercalation from 0 to 8 or 9 results in distortion only in the range of 2-3%. Such distortion does not contribute significantly to the Gibbs free energy of the system. In the

invention, distortion is held not exceed 10%. In contrast, in prior art TiS_2 intercalation of Lithium, the c -axis of the intercalated Li_xTiS_2 , *i.e.*, the axis perpendicular to the intercalated van der Waals channel, has been shown to increase by 10% in response to as little intercalation as $x=0$ to $x=1$. The change in entropy (ΔS) is significant only in the early stages of the intercalation process. ΔS is therefore very small over the course of the process and need not be considered in the Gibbs free energy equation.

The characteristics of the crystal lattice have a great effect on the remaining two thermodynamic parameters, however. The energy of interaction, E_{int} , is a measurement of guest-guest and guest-host interactions. Both of these are greatly affected by lattice crystalline characteristics. If the crystal lattice contains significant levels of defects and/or dislocations or has sufficiently uneven distribution of defects, the energy minima associated with the localized sites will be disrupted and filling is not uniform along the length of the channel. Fermi energy level of the crystal is also effected by the interstitial and lattice site impurities and the lattice structure. The defect or impurity distribution is important in identifying acceptable crystalline purity. If all defects are clustered near the entrance to van der Waals channels, no guests can enter and guest capacity is low even though crystalline lattice purity is high. It is apparent therefore, that careful crystal growth is important to preparing layered crystalline materials capable of the high loading of the present invention.

Process. The following detailed description is presented to provide details of the crystal growth process providing highly defect-free layered crystalline materials with the specific lattice characteristics, such as defect distribution, of the present invention. The description which follows is for the bismuth chalcogenide family; however, it is contemplated that any layered material of requisite crystalline lattice parameters, guest loading capacity and thermodynamic behavior is within the scope of the present invention.

Stoichiometric quantities of highly purified (99.9999% pure) bismuth and chalcogenide are charged into a quartz ampoule. If necessary, the materials are zone refined before use. Off-stoichiometry results in an n- or p-doped material with characteristic degradation of the lattice structure and the associated performance. The ampoule is evacuated to 10^{-7} mmHg and backfilled to a pressure of 10^{-3} mmHg with a small amount of inert gas, such as argon, or a reducing gas, such as hydrogen (3-10 cycles), and then sealed. Hydrogen is particularly preferred because it reacts with oxygen during processing to prevent oxidation and decrease the segregation of chalcogenide by reducing its vapor pressure.

A highly homogeneous polycrystalline material is prepared in a first processing step. The sealed ampoule is placed in a furnace at room temperature and heated to a temperature 5-10°C above its melting point. The ramp rate, temperature and reaction time are selected for the final compound. The reaction conditions are listed in Table I for the preparation of polycrystalline Bi_2S_3 , Bi_2Se_3 , and Bi_2Te_3 . The temperature of the furnace over the entire length of the ampoule is controlled to within $\pm 0.5^\circ\text{C}$. Careful and accurate control of the temperature is important because of the high volatility of chalcogenides. Temperature variation along the ampoule length causes segregation of chalcogenide which leads to off-stoichiometry. To optimize the temperature control along the length of the ampoule, a long furnace can be used. Additional heating coils can be used at furnace ends to reduce the temperature gradient at the furnace exits.

Table I. Processing conditions for polycrystalline material.

	processing conditions	Bi ₂ Te ₃	Bi ₂ Se ₃	Bi ₂ S ₃
5	heating rate to T _{liq} (°C/h)	30	20	15
	exposure time (h)	10	15	20
	at T _{liq} + 10°C			
10	cooling rate (°C/h)	50	40	35

During the last hour of reaction time, the ampoule is agitated or vibrated to insure complete mixing of the ampoule components. The ampoule vibration preferably is in the range of 25-100 Hz and is accomplished by fixing one end of the ampoule to an oscillation source. Any conventional vibration means is contemplated by the present invention. After reaction is complete, the ampoule is cooled at a slow controlled rate.

Once a homogeneous polycrystalline material is obtained, it can be further processed into a highly defect-free bismuth chalcogenide single crystal. Any known method of growing single crystals can be used, such as Bridgeman techniques, Czochralski process and zone refinement techniques (recrystallization). In particular zone refinement has proved to be highly effective in obtaining high purity single crystals.

Referring to Fig. 2, zone refinement is carried out in a quartz boat 40 containing a seed crystal 42 of the desired lattice structure. It is recommended that clean rooms levels of Class 100 be maintained. The seed crystal 42 is oriented in the boat such that crystal layers 43 are horizontal. The entire apparatus should be shock-mounted to insulate against environmental vibrations. The boule 44 of polycrystalline material is positioned in surface contact with the seed crystal.

The furnace comprise two parts, an outer furnace 46 for maintaining an elevated temperature along the entire boule length and

a narrow zone 47 movable in the direction of arrow 48 for heating a small portion of the polycrystalline material. For production of hexagonal structure, the outer furnace 46 is maintained at 35°C below the melting point, and the zone 47, which is 2-3 cm in length, is held at 10°C above the melting point of the polycrystalline material. Unlike for the preparation of the polycrystalline material in the first processing step, the boule can in this step be rapidly heated to the operating temperature. The zone is initially positioned at the seed crystal/boule interface and this region is heated to the melting point of the material. The zone 47 is then moved slowly down the length of the boule. Zone travel rate is selected according to the particular composition and recommended rates are shown, along with other processing parameters, in Table II. Zone travel rate is an important processing parameter. If the rate is too great, crystallization is incomplete and defects are formed. If the rate is too slow, layer distortions result. The lower portion of the heat-treated boule in contact with the quartz boat is preferably removed before use. The process produces a single crystalline material having less than $10^{12}/\text{cm}^3$ defect density and an impurity distribution which is inversely proportional to the intended direction of intercalation. The single crystal typically contains 10^6 layers/mm with a spacing of 3-4 Å/layer.

Table II. Processing conditions for hexagonal single crystal growth.

processing conditions	Bi_2Te_3	Bi_2Se_3	Bi_2S_3
25 boule temperature 35°C	$M_p - 35^\circ\text{C}$	$M_p - 35^\circ\text{C}$	$M_p -$
30 zone temperature 10°C	$M_p + 10^\circ\text{C}$	$M_p + 10^\circ\text{C}$	$M_p +$
zone travel rate	8 mm/hr	6 mm/hr	3 mm/hr
35 cooling rate	50 °C/hr	40°C/hr	35°C/hr

The above process can be modified slightly to produce crystals of rhombohedral structure, in which case a rhombohedral seed crystal is

employed in the zone refinement process. In addition, to produce rhombohedral crystals, the furnace temperature is held at 30°C below the melting point and the zone is maintained at the melting point of the polycrystalline material.

5 Depending on the composition of the material, there is a preference for either hexagonal or rhombohedral lattice structure. This is summarized below in Table III.

Table III. Preferred lattice structure for bismuth chalcogenide.

10 lattice structure	Bi_2Te_3	Bi_2Se_3	Bi_2S_3
15 rhombohedral	-	-	X
hexagonal	X	X	-

The above process provides a highly defect-free single crystalline material. The crystal can be further ground into particles for use in devices and each such particle is a mono-crystal. A grinding technique is selected so as not to introduce many defects and dislocations into the crystal. However, because of the weakness of the van der Waals attractive force, the crystal cleaves readily along the length of the channel without much danger of lattice distortion.

Once formed, the material is tested by introducing it as the cathode-active material into a galvanic cell. The use of highly intercalated crystalline materials in an energy storage cell is disclosed in a co-pending U.S. application entitled "Energy Storage System" which is being filed this date. A standard battery is constructed using a lithium anode, a non-aqueous LiClO_4 electrolyte solution and the test material as the cathode. The amount of lithium that can be introduced into the van der Waals layer is determined by monitoring the moles of Faraday electrons passed through an external circuit during intercalation. A typical discharge curve 50 using a bismuth chalcogenide cathode prepared according to the invention is shown in Fig. 3. An acceptable crystalline material is capable of intercalating at

least three mole of lithium per mole of bismuth chalcogenide and has discharge curve that is essentially flat, that is, a change of no more than 0.1-0.3 V is observed over an intercalation capacity range of 0.4 to 8 moles lithium. The flatness of the curve is an indication of the
5 substantial independence of Gibbs free energy change on guest concentration.

Condensation of a lattice gas to a quasi-liquid manifests itself in the discharge curve as a sudden change in the discharge voltage. The actual change in voltage is quite small, however, and is not significant
10 to operation of the cell. Fig. 3 illustrates the smooth, flat discharge curve. In an enlarged portion 52 of the curve at approximately a guest load of three it is possible to observe a "blip" in the curve. This is observable under carefully controlled conditions.

Once a highly defect free crystalline material is prepared as
15 described above, it can be intercalated to obtain the highly intercalated crystalline material of the present invention. Intercalation can be carried out using conventional methods, such as exposing the crystalline material to the vapor phase of the intercalant or placing the crystalline material in a liquid that contains the intercalant or passing a current
20 through an electrochemical cell where the crystalline material is an electroactive material in one of the electrodes. The preferred method for achieving high load of intercalant is the electrochemical method.

What is claimed is:

1. A layered mono-crystalline material, wherein said material has a sufficiently low defect density and an appropriate impurity distribution, together sufficient to permit intercalation of at least 3 moles of lithium within van der Waals channels per one mole of said material without significant distortion of the lattice, said material further characterized in that ΔG is substantially independent of the lithium intercalation concentration.

2. A layered mono-crystalline material having the formula, Me_yCh_z , where Me is selected from the group consisting of Bi and Sb, Ch is selected from the group consisting of Te, Se and S, y is 1 or 2 and z is 1, 2, 3, wherein said material has a sufficiently low defect density and an appropriate impurity distribution, together sufficient to permit intercalation of at least 3 moles of lithium within van der Waals channels per one mole of said material without significant distortion of the lattice, said material further characterized in that ΔG is substantially independent of the lithium intercalation concentration.

3. A layered mono-crystalline material having the formula, Me_yCh_z , where Me is selected from the group consisting of Bi and Sb, Ch is selected from the group consisting of Te, Se and S, y is 1 or 2 and z is 1 to 3, wherein said material has a sufficiently low defect density and an appropriate impurity distribution, together sufficient to permit intercalation of at least 3 moles of lithium within van der Waals channels per one mole of said material without significant distortion of the lattice, and wherein a discharge curve from an electrochemical cell in which said material is the cathode has a voltage change of no more than 0.3 volts over an intercalation capacity range of 0.4 to 8.

4. The mono-crystalline material of claim 1, 2 or 3, wherein said material has a hexagonal lattice structure, defect density less than $10^{12}/\text{cm}^3$ and a gradient of impurity distribution in the van der Waals channel inversely proportional to the direction of lithium intercalation.

5. The mono-crystalline material of claim 1, 2 or 3, said material further characterized in that a condensation of lithium lattice gas occurs at approximately a loading capacity of three.

6. The mono-crystalline material of claim 2 or 3, wherein said material comprises a solid solution of Me_yCh_z , where Me is selected from the group consisting of Bi and Sb, Ch is selected from the group consisting of Te, Se and S, y is 1 or 2 and z is 1, 2, 3.

7. The mono-crystalline material of claim 1, 2 or 3, wherein said material is ground into a powder, such that each powder particle comprises a mono-crystal.

8. The crystalline material of claim 4 wherein said condensation is from a lithium lattice gas to a quasi-liquid.

9. A battery comprising the crystalline material of claim 1, 2 or 3.

10. A capacitor comprising the crystalline material of claim 1, 2 or 3.

11. A thermoelectric device comprising the crystalline material of claim 1, 2 or 3.

12. A method of preparing a highly purified bismuth chalcogenide, comprising the steps of:

charging an ampoule with stoichiometric quantities of a chalcogenide element and bismuth;

providing the ampoule with an atmosphere selected to prevent oxidation;

sealing the ampoule;

heating the sealed ampoule at a temperature in the range of 5°C to 10°C above T_{liq} of the bismuth chalcogenide, said temperature controlled to within a range of ± 0.5 along the length of the ampoule and for a time sufficient to melt the component materials and react to form the desired bismuth chalcogenide, whereby the ampoule is agitated during heating to ensure homogeneous mixing of the component materials;

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cooling the material to room temperature at a controlled rate to form a homogeneous polycrystalline bismuth chalcogenide;

placing the polycrystalline bismuth chalcogenide in surface contact with a seed crystal of a specific crystal lattice structure;

5 heating the seed crystal and polycrystalline bismuth chalcogenide to a temperature which is in the range of 30°C to 40°C below T_{liq} of the bismuth chalcogenide;

heating a zone of the polycrystalline bismuth chalcogenide adjacent to the seed crystal to a temperature which is in the range of 5°C to 15°C above T_{liq} of the bismuth chalcogenide;

10 moving said zone along the length of the polycrystalline chalcogenide at rate in the range of 2 to 10 mm/hr, whereby a single crystal highly defect-free bismuth chalcogenide is formed; and

cooling the single crystal bismuth chalcogenide to room temperature at said controlled cooling rate.

15 13. The method of claim 12, wherein said single crystal bismuth chalcogenide has a hexagonal lattice structure, a defect density of less than $10^{12}/cm^3$ and a gradient of impurity defect distribution in the van der Waals channel inversely proportional to the direction of

20 lithium intercalation.

14. The method of claim 12, wherein said selected atmosphere is argon.

15. The method of claim 12, wherein said selected atmosphere is hydrogen.

25 16. The method of claim 12, wherein said bismuth and chalcogenide element are of 99.9999% purity.

17. The method of claim 12, wherein said zone is in the range of 2-5 cm wide.

18. The method of claim 12, wherein said agitation comprises

30 vibration.

19. The method of claim 12, wherein said agitation comprises oscillation from a fixed point.

20. The method of claim 19, wherein said oscillation has a frequency in the range of 25 to 100 Hz.

21. The method of claim 12, wherein the agitation occurs in the last hour of heating.

5 22. The method of claim 12, wherein controlled cooling has a rate in the range of 30 to 50°C/hr.

23. The method of claim 12, wherein said heating temperature is 10°C above T_{liq} of the bismuth chalcogenide.

10 24. The method of claim 12, wherein the chalcogenide is tellurium and the heating of said sealed ampoule occurs for 10 hours, said controlled cooling rate is 50°C/h, and said zone travel rate is 8 mm/h.

15 25. The method of claim 12, wherein the chalcogenide is selenium and said heating of said sealed ampoule occurs for 15 h, said controlled cooling rate is 40°C/h, and said zone travel rate is 6 mm/h.

26. The method of claim 12, wherein the chalcogenide is sulfur and said heating of said sealed ampoule occurs for 20 hours, said controlled cooling rate is 35°C/h, and said zone travel rate is 3 mm/h.

20 27. The method of claim 12, wherein said heating of said seed crystal and said polycrystalline bismuth chalcogenide is 35 °C below T_{liq} and said zone temperature is 10°C above T_{liq} for a hexagonal structure.

28. The method of claim 12, wherein said heating of said seed crystal and said polycrystalline bismuth chalcogenide is 30°C below T_{liq} and said zone temperature is at T_{liq} for a rhombohedral structure.

25 29. A capacitor comprising the bismuth chalcogenide prepared according to the method of claim 12.

30. A thermoelectric device comprising the bismuth chalcogenide prepared according to the method of claim 12.

30 31. A highly defect-free mono-crystalline material prepared according to the method of claim 12.

32. An intercalated crystalline material comprising a guest in the range of three to ten moles within van der Waals channels per one

mole of said intercalated material without significant distortion of the lattice, said guest selected from the group consisting of Group IA and Group IIA metals, said intercalated material further characterized in that ΔG is substantially independent of the guest concentration.

5 33. An intercalated crystalline material having the formula, $G_xBi_yCh_z$, where G is selected from the group consisting of Group IA and Group IIA metals, Ch is selected from the group consisting of Te, Se and S, x is in the range of 3 to 10, y is 1, 2 or 3 and z is in the range of 1 to 3, such that there is no significant lattice distortion, said
10 material further characterized in that ΔG is substantially independent upon the lithium intercalation concentration.

34. The intercalated crystalline material of claim 32 or 33, wherein said intercalant is lithium.

15 35. An energy storage system comprising the intercalated crystalline material of claim 32 or 33.

36. A capacitor comprising the intercalated crystalline material of claim 32 or 33.

20 37. A thermoelectric device comprising the intercalated crystalline material of claim 32 or 33.

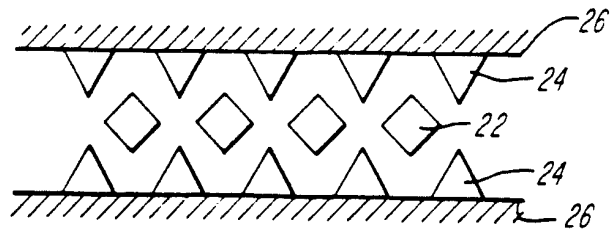


FIG. 1

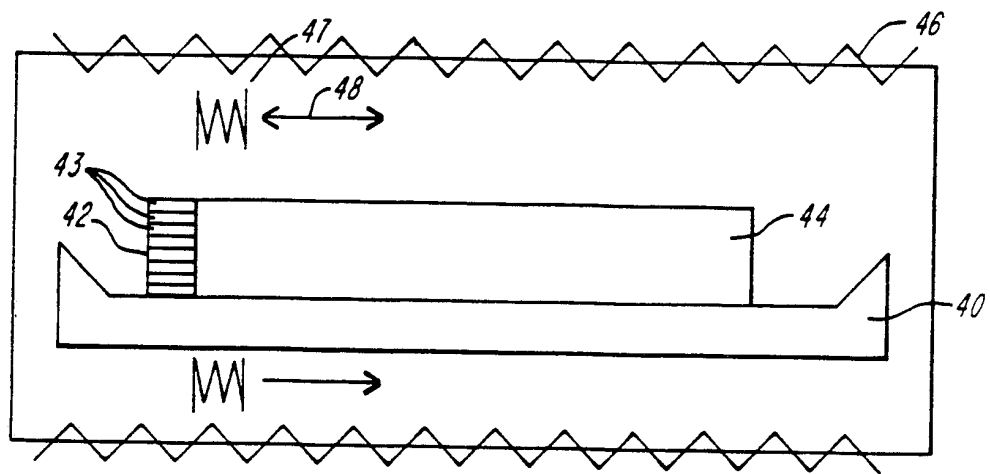


FIG. 2

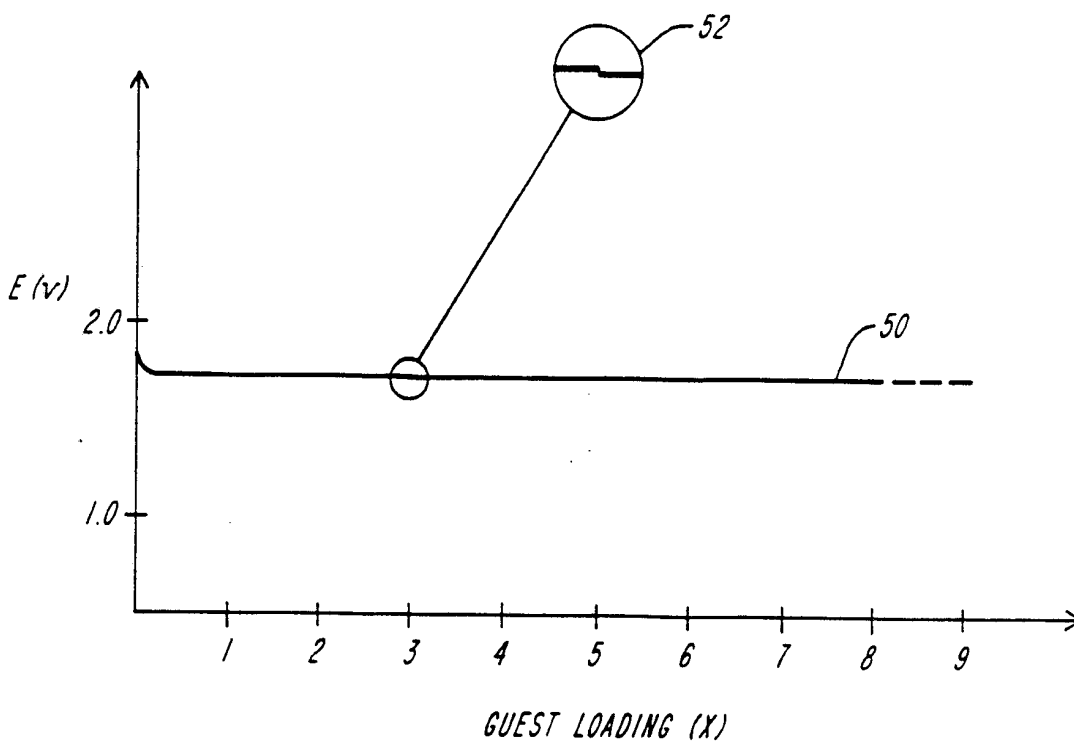


FIG. 3