Synthesis and Characterization of Bismuth Telluride by Bridgeman Technique

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Abstract: This article tells us about the Bridgman Method for single crystal growth of Bismuth Telluride. Ittells us about the working principal and components of the Bridgman method. It also tells us about the limitations and the advantages of material synthesis from this route. The temperature profile for growth of single crystal of Bismuth Telluride have been stated down in this article as observed from various literatures and later characterization of powder Bismuth Telluride has been done in order to determine the phase purity of the crystal.

IndexTerms – **Topological Insulator, ARPES, Spin orbit coupling, Bismuth Telluride**

Introduction

A topological insulator is a material which is insulating in the bulk and conducting at the surface. This non-trivial nature of the material stems from the spin orbit coupling (SOC) and time-reversal symmetry. These materials were first predicted by theoretical basis and later further observed by experiments which include Angle Resolved Photoemission Spectroscopy (ARPES).The ARPES diagram of these materials clearly shows a band inversion in the energy band diagram and thus confirms the material to be a topological insulator. In this paper, I will basically focus on the literature survey of synthesis of a single crystal of Bismuth Telluride through Bridgman Furnace technique. I will tell in detail about the Bridgman furnace, its working, its advantages and disadvantages. Then I will discuss about the temperature profiling to grow single crystal of Bismuth Telluride as reported in various literature. In the end I will characterize powder of Bismuth Telluride and compare it to the reported literature to check any unusual phase which can be arising from a defect or a impurity whatsoever be the case.

Bridgman technique

This technique was developed in 1925 by Bridgman to grow single crystals of certain metals.The growth systems typically consist of a single- or dual zone furnace. A single-zone furnace has thehighest temperature at the center of the furnace where as in a dual zone furnace; specific temperature gradient can be established between different zones. This method can be applied to grow nearly all of the single crystals of any element or compound, if we know the melting point of the compound and there is no phase transition near the melting point of the temperature. This method works on the principle ofdirectional solidification by translating a melt or the molten substance from hot zone to cold zone ofthe furnace. The temperature of two zones is kept near the melting point of the substance i.e.- hot zone temperature is kept above the melting point of the substance in order to make the molten material and cold zone temperature is kept lower than melting point of a substance in order to grow a single crystal by nucleation process of a molten material. Fig 1 represents a two zone Bridgman furnace.

The Bridgman setup consists of three principal components which are – a furnace, a crucible and asystem for movement of ampoule from hot zone of furnace to cold zone of furnace. Fig 2 shows us in detail components of Bridgman Furnace. The crucible material should not react with the molten state of the compound and should have a low thermal expansion coefficient than the crystal which is to be grown. To favour single nucleus growth the crucible must have smooth inner walls.

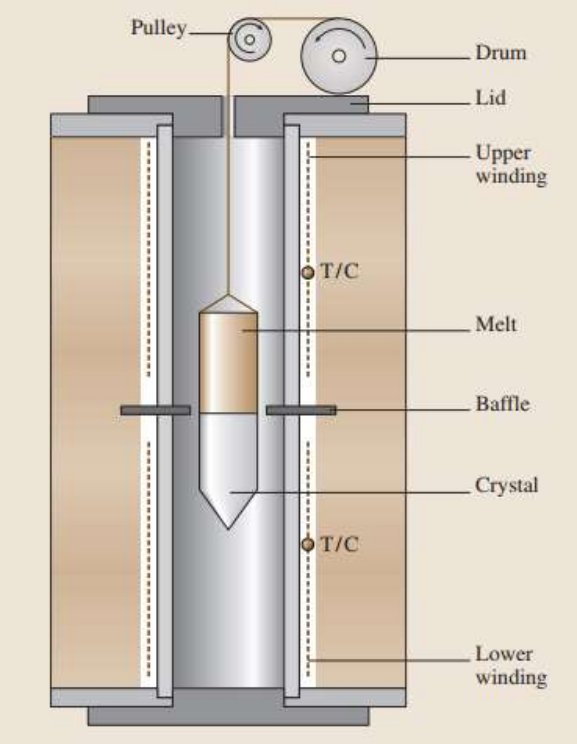

Fig1 -Bridgman Furnace setup [6]

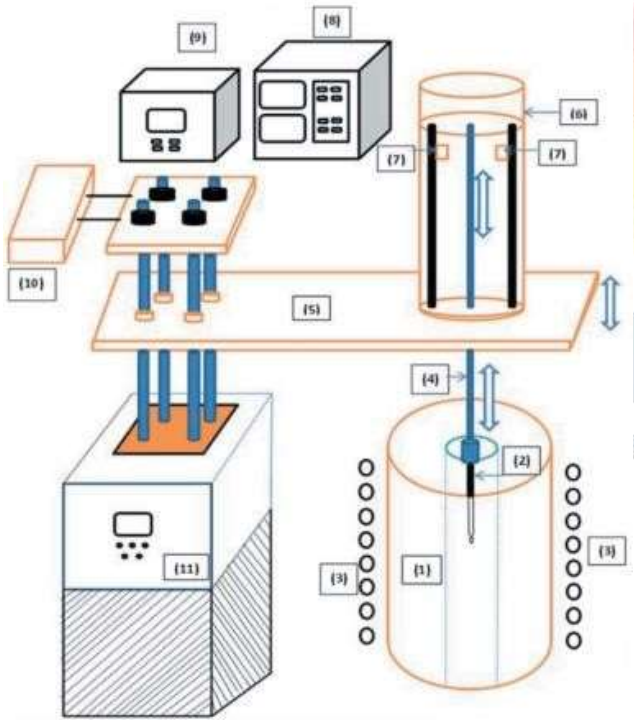

Fig 2 - Schematic diagram of Bridgman furnace. (1) furnace, (2) ampoule holder, (3) coils, (4) moving rod for translation of ampoule, (5) vertical movable mechanical stand, (6) cylinder containing stepper motor, (7) stepper motor, (8) nanotranslation controller, (9) furnace temperature controller, (10) motor for mechanical stand, (11) controller for mechanical stand.[7]

In the vertical configuration, the material whose single crystal is to be formed is kept in a cylindrical crucible, which is lowered through the temperature gradient with the help of a pulley .The rate at which the crucible is lowered from hot zone to cold zone is generally in the range of millimeter per hour. The exact rate depends on the type of crystal which is grown and to which group the constituent elements of the compound belong to. If we don't want to move the crucible from hot zone to cold zone then other way around this is to move the furnace which is set to a fixed temperature with a particular temperature gradient and to hold the crucible

stationary. Initially, the entire material in the crucible is melted and homogenized at a temperature above its melting point. After this the molten material is translated down to the second zone whose temperature is lower than the melting point of the substance in order to grow a single crystal by nucleation process. If the ampoule containing the melt has a flat bottom then during solidification then there would be multi nucleation rather than single nucleation and thus a single crystal will not be formed. However, we can prevent this by modifying the bottom of crucible and making it in such a way that multi nucleation does not occur and only a single crystal grows. Thetypes of modified crucibles which can be used in order to prevent multi nucleation and only proceed with the single crystal growth are shown in Figure3. Among them, the ampoule in Figure 3.1a is most widely used design to prevent multi nucleation at the tip. The conical tip of the ampoule allows the melt to solidify only in a small volume so that less number of nuclei is formed andmulti nucleation is restricted. If we want to avoid using different shapes of ampoule than we can usea seed crystal of the compound whose single crystal is being synthesized and then use a simple ampoule with a seed crystal situated at the bottom of the ampoule which starts the single crystal growth. However we do not use a seed crystal because it is very hard to control the temperature inthe furnace and prevent the seed crystal from melting. Moreover as we know the ampoule that we use are opaque so it is very difficult to find out the melt solid interface and therefore separate the single crystal from seed crystal. However, if the crystal growth occurs at relatively low temperature then we can use silica or glass ampoules which are transparent and therefore easy to determine the melt solid interface.

As we can see this setup of crystal growth is very advantageous over other methods as very little human interference is required and large quantity of single crystal can be grown by this method but still there are some limitations to this setup. As we know crystal grows from melt by nucleation so there is difficulty in order to find the crystallographic orientation but if the crystal has an easy growth axis, than this axis can coincide with the axis of the ampoule or crucible in which the crystal is being grown. One major problem is crystal adhesion with the crucible and thereforehard to extract the crystal from the .The materials which expand on solidification cannot be grown bythis method.

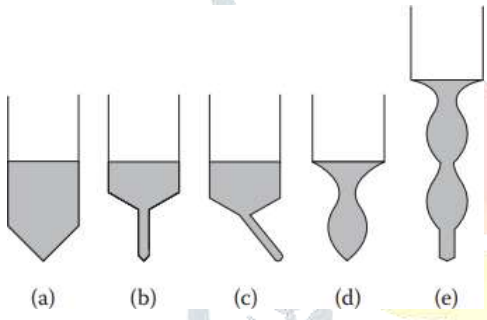

Fig 3- Various types of ampoules used in Bridgman single crystal growth [1]

Bismuth Telluride

Bismuth Telluride (Bi_2Te_3) is one of the first discovered topological insulator and a champion thermoelectric material. Research has shown that there can be many usages of single crystal of this compound such as device fabrication etc. As we know the principal requirement of growth of a single crystal through Bridgman method is the knowledge of melting point of the compound. As reported in literature melting point of Bismuth Telluride is 585^0-587^0 Celsius. A 160 mm long quartz ampoule with outer and inner diameter 16 mm and 13 mm was used for crystallization. A special ampoule with a sharp tip at the end was used in order to form a single crystal rather than polycrystal of the compound. To remove impurities ampoule was rinsed with distilled water and by acetone afterwards and later, the ampoule was kept for 5 hours in an oven. 19 gm of Bi_2Te_3 (Alfa Aesar) was poured in the ampoule up to 50 mm height. After this the ampoule was subjectedto high vacuum and sealed. After this the ampoule was hanged inside furnace at a 580 mm depth fromthe top. Then the temperature of furnace was fixed at 620ºC and for homogenization of the crystal thistemperature was kept for a period of 12 hours. Then the ampoule was translated down in the furnace at 1.5mm/hr and later on at different cooling rates till room temperature is reached as depicted in fig 4 b. The pictorial representation of the complete process is shown in fig 4a.

Possible Characterization Techniques

After synthesizing materials by various process,we need some techniques by which a structure's properties are found out. These techniques can be broadly divided into microscopy and spectroscopy. Microscopy techniques are used to find out the surface and sub-surface structure of a material. Some of the techniques involved are SEM, TEM, STM, SPM, AFM, etc. On the other hand spectroscopy techniques are used to determine the chemical composition, the structure of the crystal, composition variation and the photoelectric properties of materials. Some of the techniques involved in spectroscopy are Raman spectroscopy, XRD, XPS, TL,

PL, etc. In this article we have done powder XRD on commercially available Bismuth Telluride and compare it with the data reported in literature. Data were collected at room temperature during routine scans between 2θ ranges from 10^0 to 80^0 with a step size of 0.02^0.The phase purity was established by this process. Rietveld refinement of the X –Ray patterns were performed using FULLPROOF software as shown in figure 5.

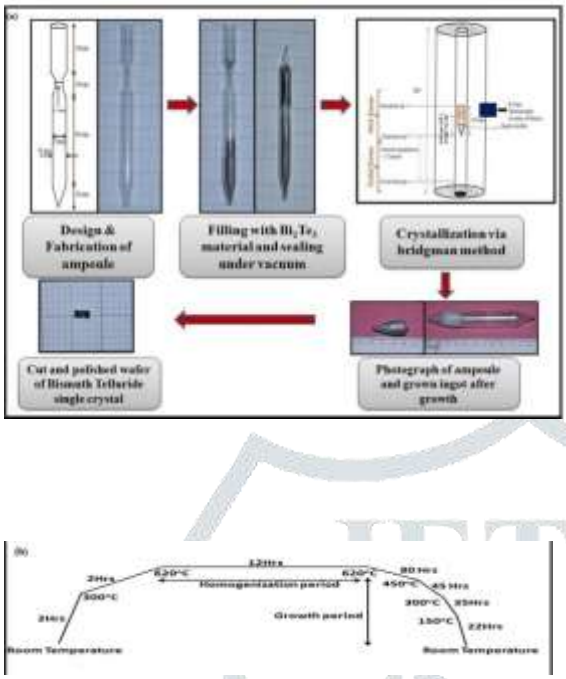

Fig 4- (a) Procedure to grow single crystal of Bismuth Telluride [4]. (b) Temperature profile of the furnace.

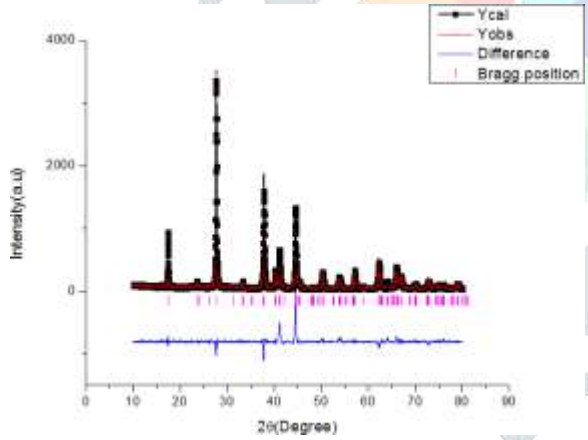

Fig 5 - Rietveld refinement of XRD data of Bismuth Telluride using FULLPROOF software.

Results

Bismuth Telluride has a rhombohedral crystal structure with refined lattice parameters a=b=4.38342 A^0 and c=30.492201 A^0 and the space group is $D^5$3d(R3M) with five atoms in trigonal unit cell. Fig 3 shows the refined XRD pattern of Bismuth Telluride. We can observe the rhombohedral phase purity from the compound.No new peaks in the XRD plot were found and thus the Bismuth Telluride is highly phase pure. The new peaks tell us about the impurities presentin the compound.

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