PtTe2: Potential new material for the growth of defect-free TeO2 single crystals

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A R T I C L E   I N F O

Article history:
Received 24 October 2007
Received in revised form 23 February 2008
Accepted 25 February 2008
Communicated by M. Tischler
Available online 6 March 2008

PACS:
81.10.Fq
42.70.-a

Keywords:
A2. Bridgman technique
A2. Single crystal growth
B1. Tellurite
B2. Acousto-optic materials

A B S T R A C T

The dissociation of Te–O bonds is the main drawback, which hampers the yield of large-sized paratellurite single crystals of high optical quality when using platinum crucibles. In this work, it is assumed that a catalytic dissociation process involves the intermediate formation of platinum tellurides, these ones being then responsible for entrapment of gas bubbles and black precipitates when growth proceeds. To alleviate this difficulty, we suggest that platinum ditelluride could be a chemically more appropriate compound instead of pure platinum. First experiments on direct transformation of platinum sheets into PtTe2 under tellurium gas atmosphere are described, as well as the procedure used to elaborate a PtTe2 crucible. First seeded Bridgman growth performed in such container yielded a TeO2 single crystal free of defects, thus confirming the validity of our hypothesis about the dissociation process of Te–O bonds.

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1. Introduction

The growth of large-sized α-TeO2 single crystals free of defects over their whole volume remains a challenging topic. Already well known and extensively used for its attractive acousto-optic properties [1–3], this compound has also found in the last few years strong interest in nuclear physics, where it is used as stacks of massive bolometric detectors in neutrinoless double-beta decay (DBD) experiments [4,5]. Today, both fields of application require a yield of crystals of large dimension, along with a uniform and best level of crystalline perfection. Since the earliest attempts [6], numerous works have been carried out for this purpose, mainly based on using the pulling or so-called Czochralski method [7,8], the Bridgman one being also proposed recently [9,10]. Whatever the technique employed, the growth of crystals is performed from pure TeO2 powder melted in a platinum crucible, despite a clear evidence of a chemical interaction between the liquid phase of TeO2 and the Pt container. As a consequence, this leads to the occurrence of several kinds of defects in grown ingots like striations, black inclusions and entrapment of gas bubbles [11–13].

A detailed description of defects observed in Bridgman grown crystals has been given in a previous paper [9]: SEM and microprobe analysis evidenced the presence of platinum in black inclusions, while micro-Raman spectroscopy allowed assessing oxygen as being the gas content of occluded bubbles. As in the case of Czochralski grown crystals, such drawback may be overcome to some extent through a careful control of the growth parameters like pulling and rotation rates, as well as thermal gradients over the crystal–melt interface [14]. However, obviously, the only way to obtain with a priori most confidence defect-free crystals would be to cancel out efficiently the crucible/melt interaction.

Since metallic platinum was found as small aggregates scattered in the TeO2 matrix, we have suggested that Pt could be regarded as catalyzing the dissociation of Te–O bonds [9]. Originated at the crucible wall, it further generates the formation of oxygen gas bubbles of various sizes in the melt. Already reported, two predictable drawbacks will be induced by such process: on the one hand, dealing with nuclear physics, traces of platinum even at very low concentration, will alter considerably the response of TeO2 bolometers [15]. On the second hand, for application in optics, a high density of oxygen vacancies, as it can be suspected from the observed release of oxygen, will increase the absorption of the material in the UV–blue spectral region, limiting thus its use at short wavelengths [16]. Freezing out the Pt/melt interaction appears indispensable to overcome the...
drawbacks corresponding, respectively, to each one of both fields of interest.

The purpose of this work is to feature the most probable reaction mechanism that could arise in a catalytic type dissociation of Te–O bonds. The analysis suggests selecting a new material, namely PtTe2, as potentially appropriate to prevent from melt reactivity. Manufacturing of a prototype PtTe2 crucible and first result of a Bridgman test growth performed with it are described.

2. Dissociation mechanism of Te–O bonds

Two hypotheses may be drawn, depending on what element of the Te–O bonds is considered to be preferentially attacked by platinum atoms.

2.1. Formation of platinum oxides

Three platinum oxides may exist, namely PtO, PtO2 and Pt3O4. They are unstable at temperatures well below the melting point of TeO2 (733 °C), dissociating into metallic platinum and gaseous oxygen at 325, 450 and 600 °C, respectively [17,18]. However, we cannot exclude completely their formation in a first and short transient step, followed in a second one by their instantaneous dissociation that further leads to O2 gas bubbles and black precipitates in liquid TeO2. In the case of a transient formation of PtO for instance, such process could be formally represented by the following successive reactions:

\[
\begin{align*}
xPt + yTeO_2 & \rightarrow PtO + [TeO_{2x-y}] \\
xPtO & \rightarrow Pt + (x/2)O_2
\end{align*}
\]

\[
\begin{align*}
xPt + yTeO_2 & \rightarrow Pt + [TeO_{2x-y}] + (x/2)O_2
\end{align*}
\]

\[
\begin{align*}
\text{black inclusions}
\end{align*}
\]

\[
\begin{align*}
x & \text{ and } y \text{ standing, respectively, for the number of platinum and paratellurite molecules which are involved in the process.}
\end{align*}
\]

2.2. Formation of platinum tellurides

In this case, the dissociation of Te–O bonds is supposed to be caused by an interaction between platinum and tellurium. Four Pt/Te binary phases may be formed in the temperature range where the growth is performed, which are PtTe, Pt3Te4, Pt2Te3 and PtTe2. The melting or decomposition temperatures are, respectively, 957, 1017, 737 and 1147 °C. Kim has shown that they are thermodynamically stable [19,20], and proposed the phase diagram which is reproduced in Fig. 1. However, chemical analyses of defects observed in grown ingots did not reveal the presence of anyone of them, so that it may be assumed that platinum tellurides react in a subsequent step with gaseous oxygen, which is released during the first one. Such catalytic process would be sketched by the following sequence:

\[
\begin{align*}
xPt + yTeO_2 & \rightarrow Pt_xTe_y + yO_2
\end{align*}
\]

\[
\begin{align*}
Pt_xTe_y + mO_2 & \rightarrow xPt + [TeO_{2x-y}] + (m - n/2)O_2
\end{align*}
\]

\[
\begin{align*}
xPt + yTeO_2 & \rightarrow xPt + [TeO_{2x-y}] + (y - n/2)O_2
\end{align*}
\]

\[
\begin{align*}
\text{black inclusions}
\end{align*}
\]

\[
\begin{align*}
x & \text{ and } y \text{ standing, respectively, for the number of platinum and paratellurite molecules which are involved in the process.}
\end{align*}
\]

Table 1

<table>
<thead>
<tr>
<th>Location</th>
<th>Te (at%)</th>
<th>Pt (at%)</th>
<th>Te/Pt atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strippes</td>
<td>57.08</td>
<td>42.92</td>
<td>1.33 (Pt3Te4)</td>
</tr>
<tr>
<td>Inter stipples areas</td>
<td>65.75</td>
<td>34.25</td>
<td>1.92 (PtTe2)</td>
</tr>
</tbody>
</table>

Fig. 1. Pt–Te phase diagram [20].

Fig. 2. SEM observation of nonstoichiometric PtTe2 samples: (a) large excess of tellurium (10%); (b) tellurium deficiency (10%). White crosses indicate locations where microprobe analyses were performed, along with the corresponding identified Pt/Te phases.
where \((x, y)\) are written according to the chemical formulas of the known platinum tellurides, that is \((x, y) = (1, 1), (3, 4), (2, 3)\) or \((1, 2)\). \(m\) and \(n\) are the number of oxygen molecules which are successively involved in the process by unit of time, with \(n \leq m \leq y\).

In both cases, black inclusions would be composed of a mixture of platinum and tellurium oxides. As a matter of fact, we have already pointed out [9] that coupled SEM and microprobe analysis performed on numerous inclusions exhibited always the coexistence in much diversified proportions of three elements only, namely Pt, Te and O, and no other one. Thus it appears that these defects are not correlated to an eventual presence of some impurities in the starting raw materials, which are high-purity TeO\(_2\) powder (99.9995%) and pure platinum (99.9%). Complementary XRD studies were tentatively performed on several defects, which exhibited a complex mixture of amorphous and micro-sized crystalline phases that we were not able to assign precisely. We notice however that (TeO)-based glasses are easily obtained when impurities are added in melted pure TeO\(_2\) [21,22]; this could be the role played by Pt atoms in the present case, leading to the formation of the above-mentioned [Te\(_y\)O\(_{2y-1}\)] or [Te\(_3\)O\(_n\)] compounds.

Now, since platinum oxides become decomposed at temperatures relatively moderate compared to the melting point of TeO\(_2\), 733 °C, we can suppose that the most probable mechanism of dissociation of Te–O bonds proceeds from the intermediate formation of platinum tellurides. Among them platinum ditelluride corresponds to the highest possible oxidation number of platinum (+IV), and we can assume that this compound should not react with liquid TeO\(_2\) as it could be the case with other Pt/Te alloys.
3. Synthesis of platinum ditelluride

In view of performing a Bridgman growth experiment, we had to first determine a suitable method to elaborate a massive PtTe$_2$ container. This material is not a usual alloy and very few works report on the synthesis of Pt/Te compounds. Phase diagrams were established from several mixtures of elemental platinum and tellurium, loaded in small amounts in evacuated and sealed silica glass capsules, which are then heated at selected temperatures [19,20,23,24]. The single and congruent phase PtTe$_2$ was obtained by heating a stoichiometric mixture at 800 °C, followed by a soak at this temperature during 22 days [20].

Starting from this work, we have examined the possibility of transforming directly massive sheets of pure metallic platinum into the desired compound. Laminated platinum disks of 2 cm diameter and 200 μm thickness are placed in suitably designed silica glass ampoules, where they rest on a circular silica corolla soldered to the wall. The ampoule is previously loaded with high-purity tellurium powder (5 N). The cells are then sealed under a 10$^{-2}$ Torr vacuum, and heated in a vertical furnace at constant and stable 800 °C temperature for 12 h. The vapor pressure of tellurium at this temperature is about 100 Torr.

Taking into account the weight of the sample used, several experiments were carried out varying the initial load of tellurium.

Table 2
Stability of PtTe$_2$: microprobe analyses of a sample at some steps of thermal annealing under ambient atmosphere

<table>
<thead>
<tr>
<th>Thermal process</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Te (at%)</th>
<th>Pt (at%)</th>
<th>Te/Pt atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (initial state)</td>
<td>–</td>
<td>–</td>
<td>66.67</td>
<td>33.33</td>
<td>2.00</td>
</tr>
<tr>
<td>1</td>
<td>500</td>
<td>16</td>
<td>65.31</td>
<td>34.69</td>
<td>1.88</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>2</td>
<td>58.83</td>
<td>41.17</td>
<td>1.43</td>
</tr>
<tr>
<td>3</td>
<td>770</td>
<td>2</td>
<td>58.68</td>
<td>41.32</td>
<td>1.42</td>
</tr>
<tr>
<td>4</td>
<td>770</td>
<td>160</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 6. Stability of PtTe$_2$: SEM pictures at some steps of thermal annealing under ambient atmosphere (same scale). (a) Initial state, stoichiometric PtTe$_2$; (b) Step #2 of Table 1; and (c) last annealing, pure Pt.
within a ±10% interval around the value corresponding to the expected stoichiometric compound. It was found that platinum transforms entirely into the single-phase PtTe₂ only for tellurium loads that match the stoichiometry or that are within 5% higher. In these conditions, XRD spectra did not reveal any other Pt/Te phase. When larger Te loads are used, excess of tellurium collapses on cooling in the form of droplets at the surface of the sample. Lower Te loads lead to the coexistence of two phases, namely PtTe₂ and Pt₃Te₄. SEM pictures in Fig. 2(a and b) illustrate both cases, respectively, while indicating also various locations where electronic microprobe analyses were performed to assign observed Pt/Te phases. The results corresponding to Fig. 2b are summarized in Table 1 and confirmation of identified phases was obtained by recording characteristic X-ray diffractogram, as shown in Fig. 3.

3.1. Swelling and deformation

In all cases, the samples obtained exhibit strong swelling. A perfectly dense Pt sample of 200 μm thickness would give a resulting thickness of around 1 mm, as it can be evaluated from the cell parameters of hexagonal PtTe₂. The measured one is 80% greater, due to a high porosity of the material, as shown for example in Fig. 4, and which renders it relatively friable. We estimated, however, that the cohesion was high enough to later attempt direct transformation of a whole Pt crucible into a PtTe₂ one, by using the same procedure.

A deformation of the samples is also observed: initially flat, the shape becomes slightly curved towards the bottom of the ampoule, as shown in Fig. 5. Subsequent thermal cycling of PtTe₂ disks performed at 800 °C and up to 1000 °C under vacuum did not reveal further deformation, indicating that this phenomenon is not due to intrinsic mechanical properties of the material, but should occur during the synthesis.

3.2. Stability of PtTe₂

The stability of the material was tested by submitting a PtTe₂ sample to four successive thermal annealing under ambient atmosphere; the experimental conditions are given in Table 2, along with the results of microprobe analyses performed at each step. SEM pictures given in Fig. 6 show that progressive deterioration of grains unrolls: an increase in the porosity of the sample is observed, which is actually correlated to the decrease in the Te/Pt atomic ratio. After the last annealing only platinum is detected, so that it might be stated that PtTe₂ decomposes at high temperature and under oxygen atmosphere into pure platinum and vaporized tellurium oxides.

4. Elaboration of a PtTe₂ crucible

A conical-shaped pure (99.9%) platinum crucible of 200 μm wall thickness, 70 mm in length and 25 mm in diameter, is mounted in a silica glass ampoule specifically designed to limit the deformation during the chemical treatment. As depicted in Fig. 7(a and b), the crucible is supported by a complementary and hollow silica cone, which is soldered to a corolla similar to that mentioned in Section 3. The cone and the corolla are provided with numerous holes to ensure flowing of gaseous tellurium all over the crucible. A stoichiometric amount of tellurium is previously loaded in the bottom of the silica container, which is then sealed under vacuum and heated at 800 °C during 12 h [25].

A picture of the PtTe₂ crucible obtained is given in Fig. 8. A deformation of the initial shape is observed, along with a crack that extends from about ‒2 of the height up to the top. The worthless portion was cut, leaving a usable part with final dimension of 40 mm in length and 25 mm in diameter. As shown in Fig. 9, XRD analyses performed on some fragments confirmed that platinum was transformed into the phase PtTe₂ only.
5. Bridgman growth experiment

5.1. Preparation of the crucible

The internal surface of the crucible must be first cleaned up from an eventual layer of nonadherent material. The crucible is filled up with pure TeO$_2$ powder and inserted in a silica container where it is maintained between two silica corollas. The ampoule is then sealed under vacuum and heated at 800°C; after cooling down to room temperature at a rate of 100°C/h, it is turned upside down and reheated up to 800°C to drain liquid TeO$_2$ along with nonadherent PtTe$_2$ grains out of the crucible. After this operation the internal wall looked glassy, covered by a thin layer of solidified TeO$_2$.

5.2. Crystal growth

A (110)-oriented TeO$_2$ seed of 10 mm$^2$ cross-section and 20 mm in length is placed at the bottom of the crucible before filling it up with high-purity (5N) TeO$_2$ powder. An appropriate quartz ampoule is used as a holding container, which is then sealed under vacuum and mounted on a vertical Bridgman furnace that we described previously [9]. The thermal gradient over a length of 6 cm around the melting temperature of TeO$_2$, 733°C, was 10.5°C/cm; the initial elevation of the fused silica/PtTe$_2$ crucible assembly was set to allow melting of the seed over half of its length. The growth was then performed by translating the ampoule at a constant rate of 10 mm h$^{-1}$.

5.3. Results

A (110)-oriented single crystal of 25 mm in diameter and about 10 mm thickness was extracted from the crucible without any difficulty. In contrast to those obtained with pure platinum it did not stick to the wall [10], and, after polishing, the examination under the microscope ($\times$ 40) did not reveal any black inclusion or gas bubble. However, as shown in Fig. 10, two cracks are observed, which may be attributed to an inadequate procedure during cooling down to room temperature. The first one is oriented along the (100) cleavage plane, the second one being conchoidal and without any assignable preferential direction.

As a first characterization, we have examined the transparency of several samples cut in various regions of the crystal. Spectra were performed under polarized light on 5 mm thick (110)-oriented slices on a Lambda 900 Perkin Elmer spectrometer and compared to those given by similar samples cut in a boule grown in a conventional Pt crucible, as described in our previous work [9]. Fig. 11 displays results obtained in the UV–visible spectral region, where a broad absorption band is observed around 375 nm with a sample exhibiting a relatively high density of defects (Pt crucible), while being absent for all samples resulting from the growth procedure described in the present work.

Calvert et al. [16] has shown that oxygen vacancies created by reducing TeO$_2$ single crystals under hydrogen atmosphere generate such characteristic absorption, the intensity of which depends on their density level. Thus, along with removal of dark inclusions we observed, it may be concluded that TeO$_2$ does not dissociate in PtTe$_2$ crucible, which confirms that the catalytic dissociation of Te–O bonds in pure platinum containers is actually due to the intermediate formation of platinum tellurides.

6. Conclusion

The yield of TeO$_2$ single crystals free of defects is known to be hampered by an unavoidable interaction between the melt and platinum, which is usually employed as a material container. Assuming that the catalytic dissociation of Te–O bonds is primarily due to the intermediate formation of platinum tellurides,
we have identified and synthesized PtTe$_2$ as being a potentially suitable material to overcome these drawbacks. The elaboration of a PtTe$_2$ crucible by direct transformation of pure platinum under tellurium atmosphere was successful, and allowed performing first seeded Bridgman growth of a TeO$_2$ single crystal in this material. The obtained boule was free of gas bubble or black inclusion over the whole volume, and transmission spectra performed in the UV–visible wavelength range led to the conclusion that TeO$_2$ does not dissociate in PtTe$_2$ container. Further progress in the elaboration procedure of such crucible should lead to a breakthrough in the yield of large TeO$_2$ single crystals of highest optical and crystalline perfection, whatever the growth technique employed.

Acknowledgment

The authors would like to thank Eric Lebraud from the Institut de Chimie de la Matière Condensée de Bordeaux–UPR CNRS no. 9048 for kindly performing XRD analysis of PtTe$_2$ samples obtained with tellurium deficient-load.

References


Fig. 11. Transmission spectra of 5 mm thick TeO$_2$ plates in the UV–visible spectral range. The full curve corresponds to a sample cut in the boule shown in Fig. 10 of the present work (PtTe$_2$ crucible), and the dashed line to an imperfect sample obtained from a growth performed in pure Pt crucible. Polarization of light: (a) extraordinary and (b) ordinary.