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Oxidation of Bismuth Tellurite, Bi_2TeO_5

I. Thermoanalytical and Optical Microscopic Studies

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Deatailed thermoanalytical experiments were carried out to reveal the oxidative and reductive processes in the Bi_2TeO_5/Bi_2TeO_6 system. The oxidation of Bi_2TeO_5 starts at about 450°C but completed oxidation can only be achieved in oxygen ambient with a 670°C isothermal treatment. The decomposition of Bi_2TeO_6 stars at 663°C. Above 790°C the loss of TeO_2 is evident. The oxidation rate of Bi_2TeO_5 single crystals is extremly low and develops a very complicated reaction interface changing in the course of reaction. © 2001 Academic Press

Key Words: **bismuth tellurite; Bi_2TeO_5; oxidation; TG; DSC; TG-MS; optical materials.**

INTRODUCTION

Bismuth tellurite, Bi_2TeO_5, is a nonlinear optical material with interesting properties. Its crystals exhibit a long-living photorefractive signal that develops in the four-wave mixing experiments without any fixing process and lasts for years in the dark (1, 2). Homogeneous and high-quality Bi_2TeO_5 single crystals can be grown from the melt by the Czochralski technique (3). Experimental investigations of the crystals have revealed anomalies in the physical properties of the material.

The crystal structure of the bismuth tellurite, Bi_2TeO_5, can be described as a $2 \times 3 \times 1$ multiplication of a perturbed CaF_2 type cell. The required cation charge is $4+$ in this lattice, and the missing positive charge of the Bi^{3+} ions is compensated by a large number (17%) of empty oxygen positions (4).

The oxidation state is an important question in the TeO_2-based binary oxides. In these compounds the Te has $4+$ charge at room temperature as well as at the melting point. Between these temperatures, however, there is a region where the Te^{6+} is the stable charge. For the 1:1 Bi_2O_3–TeO_2 system, the fully oxidized Bi_2TeO_6 composition is thermodynamically stable between 550°C and 700°C. Consequently, the cooling of the Bi_2TeO_5 crystals grown from the melt includes a temperature range where oxidation and respective composition and structural changes may happen before room temperature is reached, deteriorating the quality of the single crystals.

Though the improper oxygen content plays an important role in the physical properties of the actual samples, only a few papers deal with the oxidation of the Bi_2TeO_5. Frit and Jaymes were the first, who studied the oxidation of Bi_2TeO_5 and determined the crystal structure of Bi_2TeO_6 by X-ray diffraction (5). Accordingly, the oxidation does not simply fill the empty oxygen positions, but it results in structural changes in the unit cell. They found that the oxidation starts at 400–500°C and the Bi_2TeO_6 composition is stable up to 730°C. Gospodinov and Gjurova concluded that the oxidation of Bi_2TeO_5 begins at 450–500°C and is completed around 600°C. The decomposition of the bismuth tellurate begins at about 700°C (6).

The actual excess oxygen residue in the room temperature Bi_2TeO_5 crystals can be characterized by Raman spectroscopy (7). The intensity of a specific Raman line at 762 cm^{-1}, with the incident and emitted line directions of [010] and [100] and incident and emitted light polarizations of [100] and [001], respectively, was shown to be sensitive to the oxidation status of Bi_2TeO_5 crystals. Accordingly, in the good-quality Bi_2TeO_5 crystals the amount of the excess oxygen was detectable but not remarkable. The bulk oxidation of the crystals was not efficient under 550°C.

The aim of the present paper is the detailed study of the $Bi_2TeO_5 + O_2 \rightarrow Bi_2TeO_6$ oxidation and the $Bi_2TeO_6 \rightarrow Bi_2TeO_5 + O_2$ decomposition reactions.

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EXPERIMENTAL

Samples. Most of the experiments were carried out on powder samples. Pieces of Bi_2TeO_5 single crystal grown in air by the Czochralski technique from a Pt crucible (3) were ground in an agate mortar and sieved. The fraction with a grain size smaller than 63 μm was used for the investigations.

For microscopic investigations prismatic samples with dimensions of $8 \times 5 \times 2$ mm^3 were prepared from the bulk crystals by cleaving along the (100) plane, cutting and polishing along the (001) and (010) planes.

Equipment. The thermogravimetric (TG) experiments were carried out by using a Mettler TA-1 thermoanalyzer equipped for computerized data acquisition. One charge of the samples was about 100 mg, measured in an alumina crucible of 5 mm height and 8 mm diameter. The powdered samples were compacted by 30-s vibrations before the experiments. The thermobalance was evacuated to 0.1 mbar before each run and filled with the appropriate gas. Air, pure oxygen, argon, and different argon + oxygen mixtures were used at a flow rate of ~ 75 cm^3/min. The measured TG curves were corrected for the buoyancy effect by measuring 100 mg of powdered aluminum oxide under the same experimental conditions. The DTG curves were obtained by a spline smoothing procedure. Heating and cooling rates were varied between 1 and 10°C/min and isothermal sections at various temperatures were also employed. The single crystals studied by thermogravimetry were subjected to prolonged isothermal section. They were heated to 670°C at 4°C/min, and kept isothermally for 51.5 h.

The thermal decomposition of Bi_2TeO_6 was studied by coupling a Balzers QMS 420 quadrupole mass spectrometer to the thermoanalyzer via a GES10 capillary inlet interface heated to about 120°C (TG–MS). The working gas was 6 N helium at a flow rate of 85 cm^3/min. Mass spectral scans were made continuously at a scan rate of 100 ms/amu and the electron impact (EI) mass spectra obtained at 70 eV were recorded.

The Bi_2TeO_6 samples were prepared inside the thermoanalyzer equipment. Bi_2TeO_5 powder was heated in oxygen ambient at a 4°C/min heating rate to 670°C, followed by a 180-min isothermal section.

The DSC measurements were carried out by using a PL Thermal Sciences 1500 differential scanning calorimeter (DSC) equipped with a data acquisition and evaluation system, in a flowing oxygen and argon atmosphere (10 cm^3/min), using 4°C/min heating rates. The sample weight was ~ 50 mg, and the crucible material was platinum. The temperature and heat flow response of the calorimeter were calibrated using 6 N purity metals.

RESULTS

Examinations in Air Atmosphere

The most characteristic features of the $Bi_2TeO_5 + 1/2O_2 \rightleftharpoons Bi_2TeO_6$ reaction in air atmosphere can be seen in Fig. 1. During heating in air flow the oxidation becomes

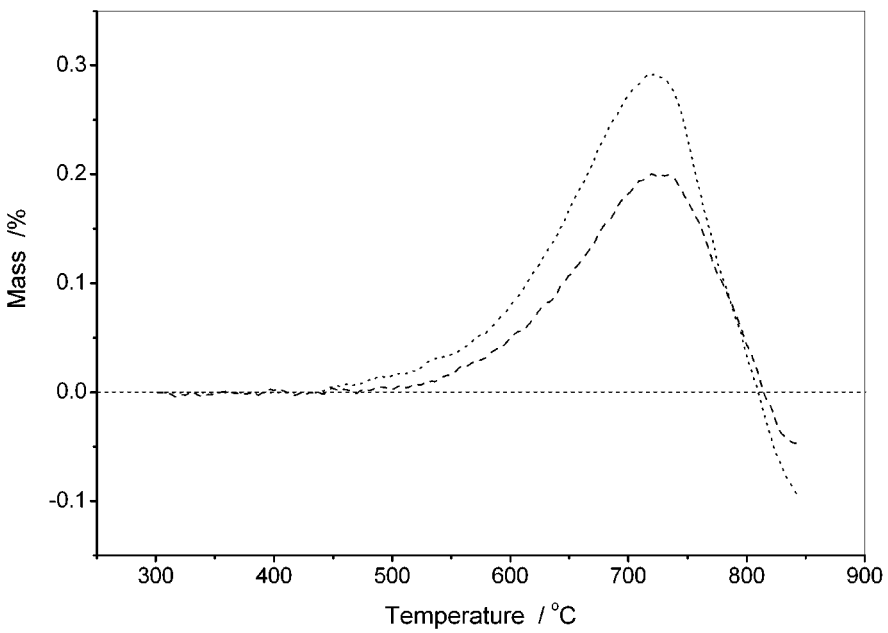


FIG. 1. The change of the sample mass during the thermogravimetric experiments of Bi_2TeO_5 in air atmosphere at 2°C/min (·····) and 4°C/min (– – –) heating rates.

observable around 450°C. The reaction rate is low and it depends strongly on the heating rate. The lower the heating rate, the higher the mass gain. Above ~730°C the decomposition reaction dominates and a mass loss can be observed. Note that the mass decreases below the initial sample mass above 800°C.

The theoretical mass gain for the oxidation reaction is 2.56%. In air flow, however, only 0.2–0.3% mass gain was observed, even at the low heating rate, 2°C/min. For this reason, further experiments have been carried out in a pure oxygen atmosphere.

The Main Features of the Reaction in the Oxygen Atmosphere

Figures 2a and 2b show the thermogravimetric and DSC curves, respectively, at 4°C/min heating and cooling rate. During the heating, the oxidation starts at 456°C and the maximum reaction rate is reached at 674°C. The oxidation process is strongly exothermic. Above 761°C the decomposition of Bi_2TeO_6 dominates, which is an endothermic process. The exothermic oxidation and the endothermic decomposition overlap each other at the

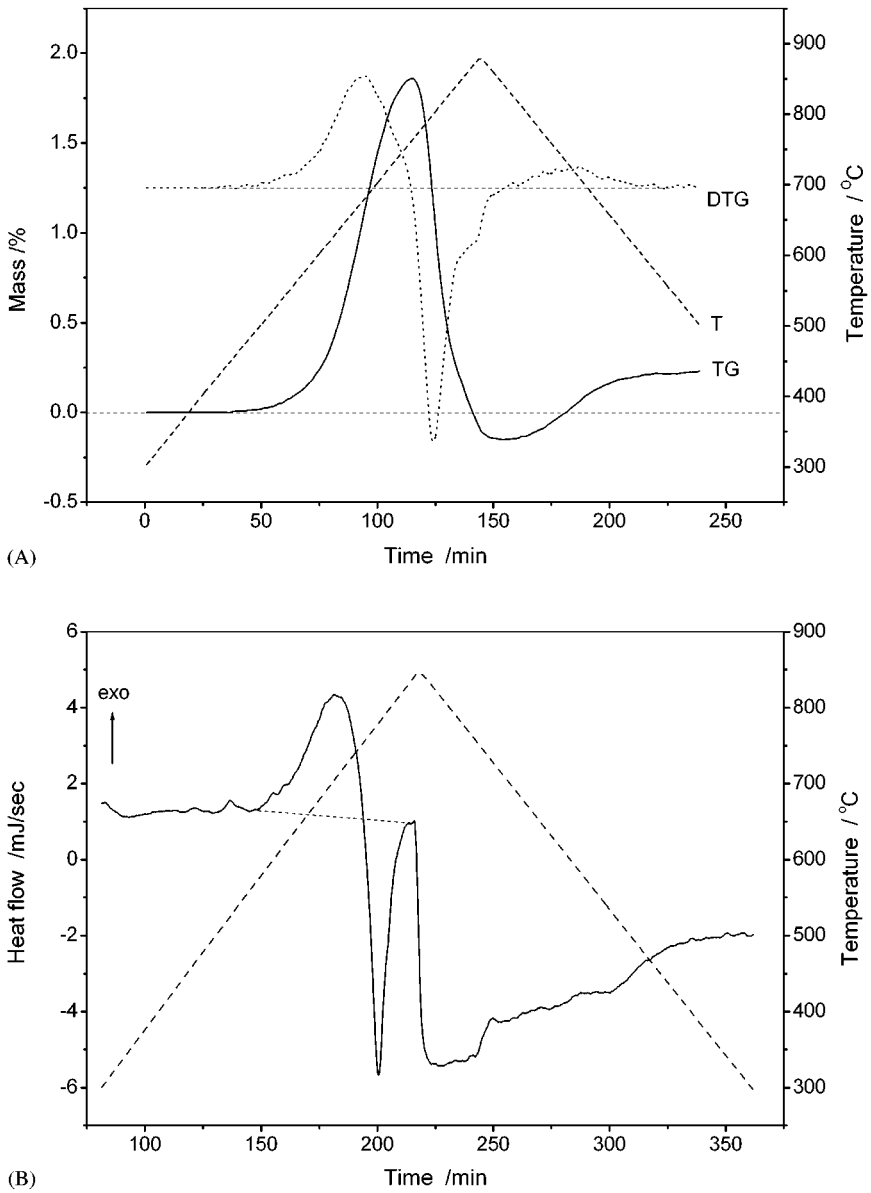


FIG. 2. Investigation of the oxidation and decomposition reactions by TG (A) and DSC (B) applying 4°C/min heating and cooling rates in oxygen ambient. In (B) an approximate baseline (– – –) was drawn to the DSC curve (—) in the heating section to indicate the magnitude of the exothermic and endothermic effects.

TABLE 1
Mass and Heat Changes during Heating and Cooling of Bi_2TeO_5 at 4°C/min in Oxygen and Argon Atmosphere

Ambient	Program	Temp range (°C)	Mass change (%)	DTG_{peak} (°C)	ΔH (mJ/mg)
O_2	Heating	456–761	+ 1.86	674	− 87
	Heating	761–835	− 2.01	798	59
	Cooling	845–578	+ 0.37	710	—
Argon	Heating	790–890	− 0.12	—	—

heating rate used, and reliable enthalpy changes could not be determined.

The thermoanalytical results at 4°C/min are summarized in Table 1. The data show that the measured mass gains with the 4°C/min heating rate are still smaller than the expected 2.56% value for the stoichiometric Bi_2TeO_6 production. The incomplete oxidation is due to the decomposition of the formed Bi_2TeO_6 at higher temperatures before the oxidation is finished. When the Bi_2TeO_6 decomposes at higher temperature, a larger mass loss was observed than the mass gain during the oxidation. The difference may be explained by assuming the sublimation of TeO_2. To check this assumption, a Bi_2TeO_5 sample was heated in an argon atmosphere to 890°C at a rate of 4°C/min, and a mass loss of 0.12% was observed between 790°C and 890°C. This amount corresponds to the difference between the measured mass gain and mass loss within the experimental error (Table 1).

During the cooling period, the Bi_2TeO_5 starts to oxidize again at 845°C, as indicated by mass gain in the TG experiments (Fig. 2a) and the baseline shift of the DSC experiments in the exothermic direction (Fig. 2b). The mass of the sample is practically constant below 500°C and the oxidized form is stable even at room temperature for a long period.

It is worth mentioning that much less oxidation occurs in the cooling section than in the heating section. The corresponding mass gain is about one-fourth of the value measured during the heating. The explanation of this observation requires further investigations. We plan to return to this question in a later paper.

Detailed Investigation of the Oxidation Process

Figure 3a compares the experiments with 670°C isothermal section. The TG curves indicate that the oxidation reaction was not far from completion in the reaction times employed. The reaction rate is acceleratory in the heating section and decelerating in the isothermal section. Note that a greater part of the reaction occurs in the isothermal section at the highest heating rate, 10°C/min, since the fraction reacted during the heating to 670°C was only 0.18 in that case. At low heating rates 1, 2, and 4°C/min the reaction started at 456°C. At 10°C/min, the start of the reaction shifted to 480°C.

Figures 3b and 3c demonstrate the dependence of the reaction rate on the isotherm temperature and on the partial pressure of oxygen, respectively. Increasing the temperature above 670°C, the rate decreases and the completion of the reaction needs a longer time.

The Thermal Stability of Bismuth Tellurate

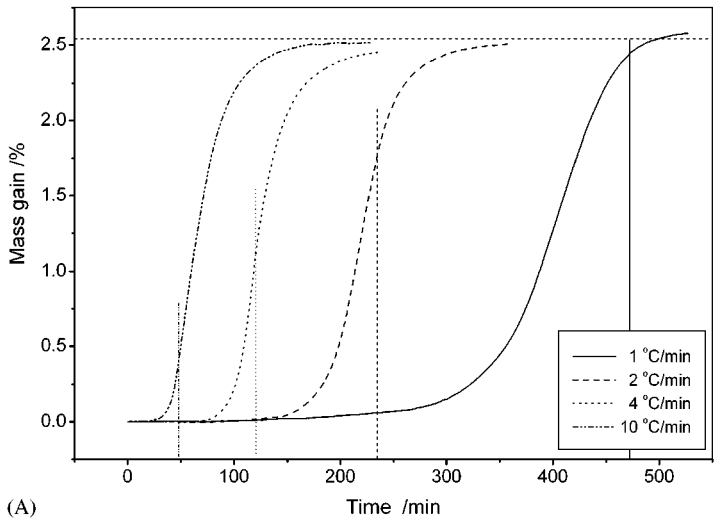
According to the previous section, perfect oxidation of Bi_2TeO_5 (more than 2.5% mass gain) can be achieved by keeping the powdered sample at 670°C for 2–4 h. The thermal properties of the prepared Bi_2TeO_6 are shown in Fig. 4 and Table 2. Heating in Ar ambient with a 4°C/min heating rate, Bi_2TeO_6 is stable up to 663°C. The decomposition has a maximum velocity at 789°C and the process is completed by 860°C. The gaseous reaction products consisted entirely of oxygen ($m/z = 32$ and 16). The measured mass loss is close to the theoretical value within the experimental uncertainty. Note that the mass spectrometer cannot detect sublimation species (TeO_2 and/or Te) since the connection between the MS and the TG and inlet system cannot be heated to properly high temperatures.

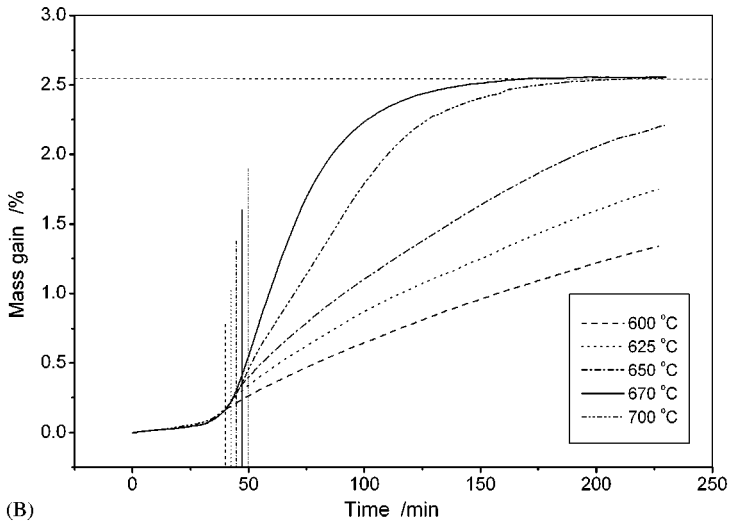
Study of the Oxidation on a Single Crystal

The results outlined in the previous sections suggest that the diffusion of the oxygen has an important effect on the reaction rate. To get a better insight into the factors influencing the diffusion, the reaction was also carried out on a single crystal. The crystal has a prismatic shape with a surface area of 212 mm^2. In that case, the reaction rate was very slow; 51.5 hours were needed to achieve a mass gain of 0.6% (Fig. 5). The shape of the curve is particularly interesting. Though the reaction becomes observable below 670°C, it was so slow that the mass gain could be neglected during the heating period. The reaction rate showed a deceleration in the first 500 min in the isothermal section (magnified part of Fig. 5). However, thereafter an acceleration of the reaction happened that lasted until the end of the experiment. The acceleration suggests the gradual increasing of the reaction surface due to the developing of internal channel structures during the experiment.

Microscopic Observations

Microscopic examinations often provide positive evidence for interpretation of shapes of thermoanalytical curves, especially when microscopic defect structures are formed during the thermal reactions. We studied the topochemistry existing in the course of the $Bi_2TeO_5 + O_2$ reaction by optical microscopy, using reflected (Figs. 6a and 6b) and transmitted illumination (Figs. 6c, 6d, and 6e).





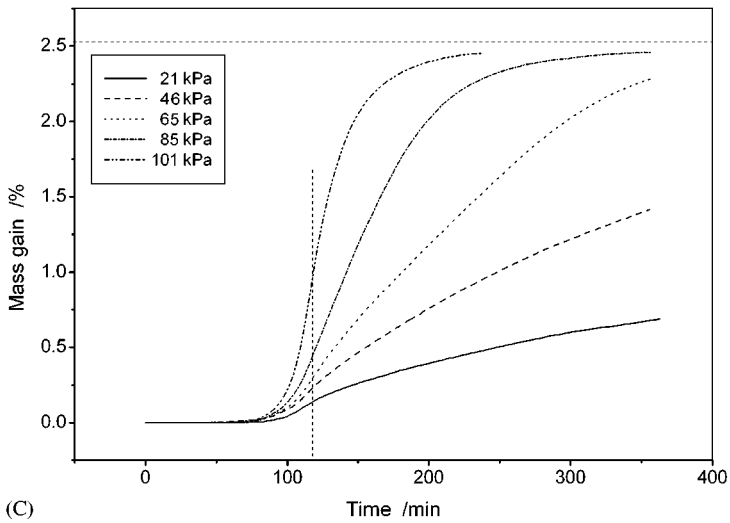


FIG. 3. Detailed thermogravimetic study of the oxidation of Bi_2TeO_5. The temperature program was complemented by an isothermal treatment in each case. The vertical lines represent the starting point of isothermal temperature. (A) Effect of different heating rates at a common isothermal temperature, 670°C. (B) Effect of different isothermal temperatures at a conmmon heating rate, 4°C/min. (C) Effect of different oxygen concentrations in the ambient at a common temperature program (4°C/min and the subsequent isothermal annealing at 670°C).

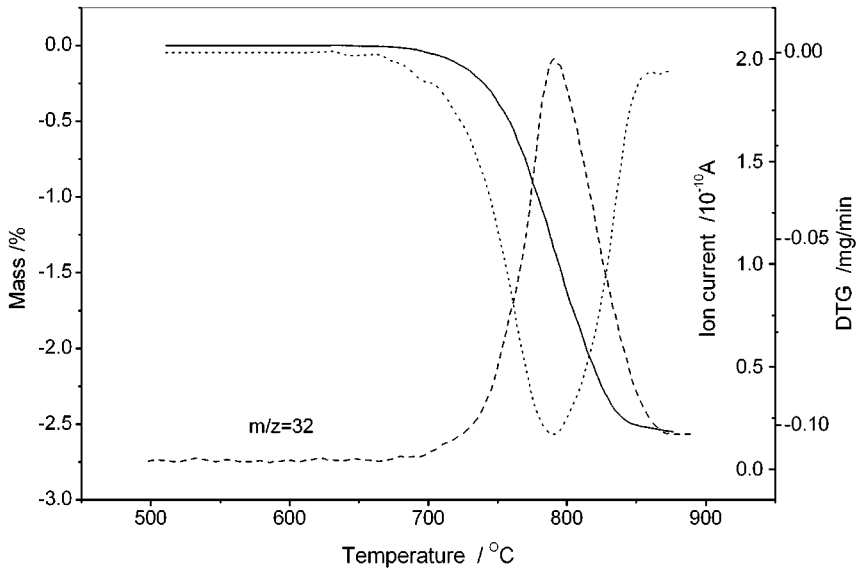


FIG. 4. Thermal decomposition of Bi_2TeO_6 in He ambient, followed by a combined thermoanalytical and mass spectrometric method with 4°C/min heating rate. The mass spectrometric signal (– – –) shows the rate of the oxygen release.

The microscopic pictures have shown that the oxidation strongly depends on the crystallographic orientation of the open surfaces. Only the surfaces (001) and (010) were reacted fully, on which the microcrystalline structure of a product layer could be observed (Fig. 6a). The central part of the (100) plane shows a very complex morphological structure (Fig. 6b). It seems that the reaction starts at selective sites of the surface from which cracks and channels develop. It is revealed from the detailed examinations that microcracks penetrate along the [041] direction, which is the oxygen plane in the Bi_2TeO_5 structure. The other parts of the surface seem to be unreacted, but some dune-like features can be observed. This indicates that the reaction proceeds below the surface and the reactive volume becomes larger, probably due to the microcrystalline structure of the Bi_2TeO_6 already produced. Investigating the crystal in the transmitted light all of these morphological characteristics can be observed. As the reaction proceeds

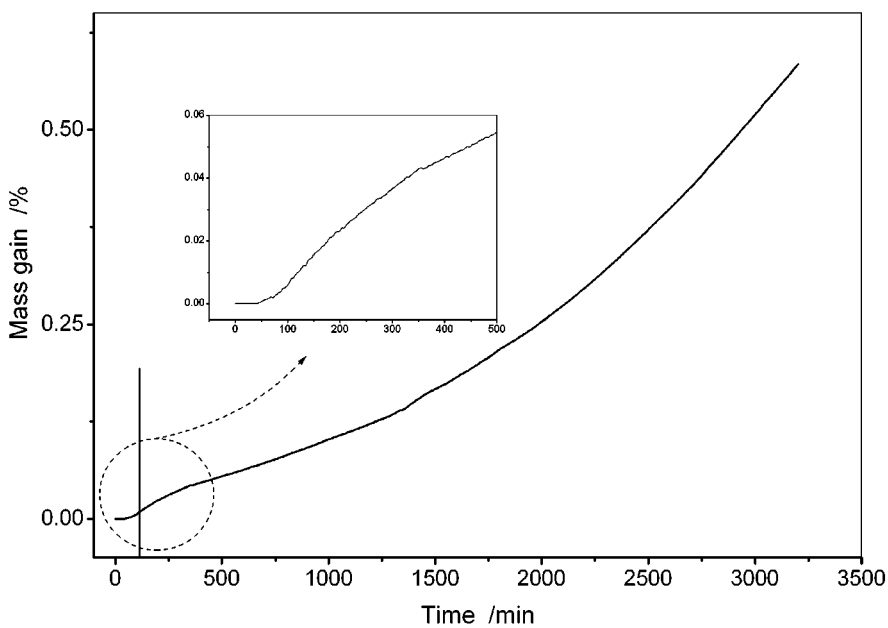


FIG. 5. Oxidation of a Bi_2TeO_5 single-crystal sample in oxygen ambient. The heating period (4°C/min) was followed by an isothermal annealing at 670°C for 51.5 h.

TABLE 2
Decomposition of Bi_2TeO_6 in Argon and Helium Atmosphere

Ambient and heating rate	Temp range (°C)	Mass change (%)	DTGpeak (°C)	ΔH (mJ/mg)
Argon, 4°C/min	663–860	− 2.53	789	190
Helium,10°C/min	677–890	− 2.58	805	—

into the crystal, needle-like cracks and channels develop, which undergo branching and build up fan-shaped product morphology. This generates a very complicated reaction interface growing over the course of the reaction, which is the reason for the acceleratory region of the TG curve.

CONCLUSIONS

The specific oxidative and reductive processes in the Bi_2TeO_5/Bi_2TeO_6 system were studied by detailed thermoanalytical experiments. Using powdered Bi_2TeO_5 samples, the oxidation starts at about 450°C but complete oxidation can be achieved only by long annealing of the samples in oxygen ambient at 670°C. At higher temperatures the Bi_2TeO_6 decomposes. Above 790°C the loss of TeO_2 is also evident. With the regular thermoanalytical heating rates (2–10°C/min) the oxidation and reduction sections overlap each other. Using combined mass spectrometric and thermoanalytical investigations it was shown that starting from pre-prepared Bi_2TeO_6, the decomposition begins at about 670°C and, losing oxygen, the Bi_2TeO_5 composition is restored by 860°C.

The oxidation rate of Bi_2TeO_5 single crystals is extremely low and the thermal treatment destroys only a thin surface layer of the samples. Thus, the oxidation and subsequent reduction do not influence the bulk quality of the single crystals grown from the melt and slowly cooled to room temperature during the growth.

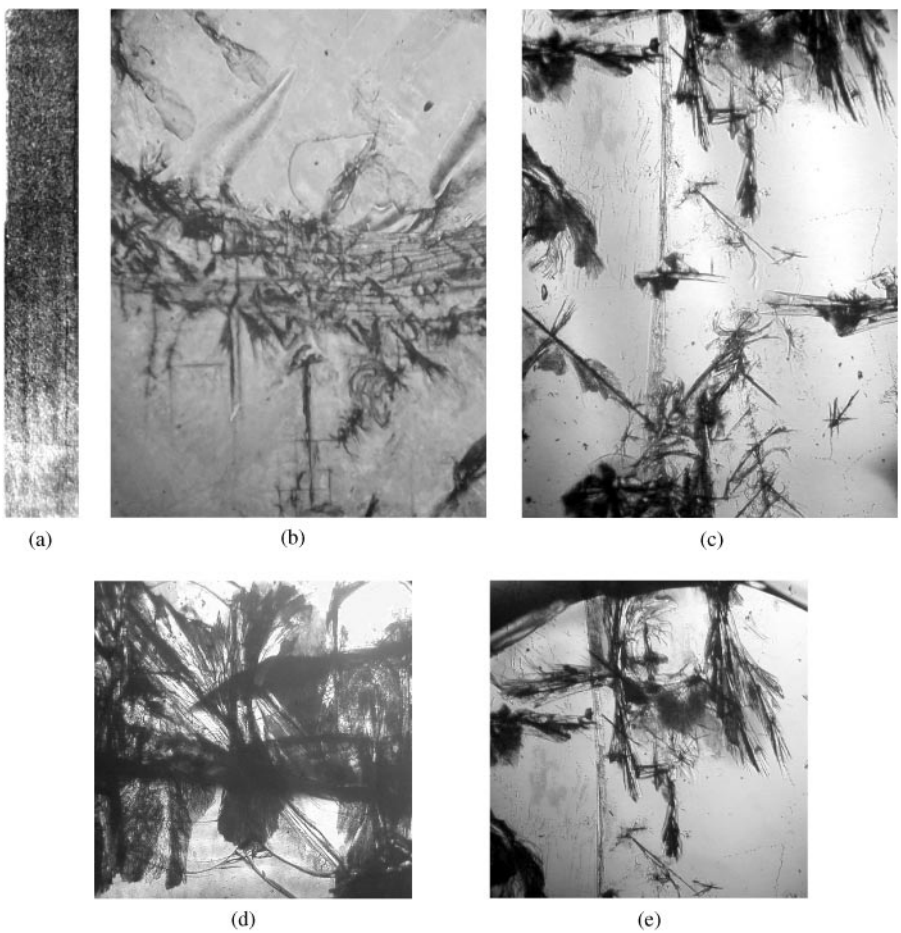


FIG. 6. Optical microscope pictures of the partly reacted ($\alpha = 0.23$) Bi_2TeO_5 single crystal. (a) (010) Plane of the crystal covered by microcrystalline product layer. Magnification: 20×. (b) Selected part of the (100) plane illuminated by reflected light. The picture shows the complicated product structure consisting of cracks and channels. The sand-hill-like formations indicate that the reaction proceeds below the surface. Magnification: 120×. (c–e) Selected parts of the (100) plane illuminated by transmitted light. (Magnifications were 63× and 120× in d and e, respectively.) These pictures prove that the cracks and channels developed during the reaction penetrate into the reactant crystal and generate a very complicated reaction interface.

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