

REACTIONS AND PHASES WITHIN THE TeO₂-RICH PART OF THE Bi₂O₃–TeO₂ SYSTEM

The non-equilibrium phase diagram

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Abstract

The chemical reactions between Bi₂O₃ and TeO₂ oxide powder and pellets have been investigated by differential scanning calorimetry (DSC) and electron microprobe analyses applying 10°C min⁻¹ heating and cooling rate, as well as isothermal heat treatment, respectively. The reaction pathway was identified in which the Bi₂O₃ is the stationary phase and the TeO₂ is the moving phase. The reaction starts by grain boundary diffusion. But at the same time, from 450°C the TeO₂ evaporates onto the Bi₂O₃ grains producing TeO₂ layer. Melts participation in the mechanism was proved. The reaction sequence is independent of the sample composition, always the TeO₂-rich phases form first. Bi₂TeO₅ could not be detected until the TeO₂ is fully reacted. The 10°C min⁻¹ cooling rate applied is relatively high and permits the formation of metastable phases (β-Bi₂Te₄O₁₁, Bi₂Te₇O₁₇) with cubic symmetry between 54 and 100% composition range. Though stable phases form during the subsequent heating the phase diagram has been determined under non-equilibrium conditions. In the contrast with the literature data the 54% composition is considered as the border of solid solution, from which the homogeneous and high-quality single crystal can be grown.

Keywords: bismuth oxide, Bi₂O₃, bismuth tellurites, DSC, phase diagram, reaction mechanism

Introduction

As a non-linear optical material with remarkable photorefractive properties, bismuth tellurite, Bi₂TeO₅, has been investigated for several decades. Homogeneous and high quality Bi₂TeO₅ single crystals can be grown from the melt of the oxide components mixed and preheated to appropriate temperature supporting the completion of the solid-state reactions [1].

However, applying the conventional ‘mixing and heating’ method, the solid-state reaction between powdered precursors rarely yields the pure product. The chemical transformation is frequently partial, the product may be inhomogeneous, metastable

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phases and solid solutions can be formed. This is particularly true in the case of the Bi₂O₃–TeO₂ system.

The chemical reaction between Bi₂O₃ and TeO₂ can be described by the following equation:



Three stable compositions were identified within the TeO₂-rich region of the phase diagram, namely Bi₂TeO₅ ($x=0.333$), Bi₂Te₂O₇ ($x=0.50$) and Bi₂Te₄O₁₁ ($x=0.667$). Investigations based on the diffraction methods were mainly directed to determine the crystal structure of the above compounds and the phase relationships between them [2–9]. Orthorhombic solid solution region between 50 and 66.7% was detected by Mercurio *et al.* [5, 6]. They suggested that this solid solution was composed of a homologous series of microphases with a superstructure consisting of ordered intergrowths of Bi₂TeO₅ and Bi₂Te₂O₇-like units.

There are some contradictions in the published phase diagrams. Jakhkind and Martishhenko found two eutectic compositions at 70.5 and 88% of TeO₂ [10]. Demina *et al.* reported on a solid solution range between 50 and 65% in the phase diagram [11, 12]. Bi₂Te₂O₇ was found to be a stable compound at room temperature [12], Bi₂Te₄O₁₁ as a congruently [12, 13] or peritectically melting phase [13].

Szaller *et al.* studied the formation of Bi₂Te₄O₁₁ in detail [14]. Phases of 8Bi₂Te₄O₁₁+23TeO₂ (eutectic), Bi₂Te₄O₁₁ and Bi₂Te₂O₇ have been identified by electron microprobe analysis applying isotherm heat treatment.

It follows from the above results that it is desirable to study the solid-state reactions between Bi₂O₃ and TeO₂ precursors and to revise the phase diagram. From the point of view of crystal growth it is important to know the border of the solid solution range and the range of compositions suitable for homogeneous crystallization, because the TeO₂ component has a relatively high vapor pressure at the melting point of Bi₂TeO₅ even after the solid state reaction. Hence the present investigation was undertaken.

Experimental

Materials

Starting materials were Bi₂O₃ (Johnson Matthey Grade 1) and TeO₂ prepared from tellurium metal (99.999%) by oxidation with double distilled HNO₃ (Carlo Erba for analysis). The Bi₂O₃ powder was annealed in air at 450°C for 4 h to complete the decomposition of the carbonate traces. The oxides were ground and sieved. The fraction with a grain size smaller than 63 μm was used for the synthesis and for the DSC measurements, but the effect of the grain size (<5, <63 and >63 μm) was also investigated.

Sample preparation

The oxide powders mixed in the desired ratio were carefully homogenized in an agate mortar using a few drops of methanol. After the first DSC run the solidified sample

removed from the crucible, ground and weighed in for the second run in order to identify the phases formed.

For electron microprobe analysis pellets were prepared from Bi₂O₃ and TeO₂ powders, respectively; and they were slightly compressed to each other. The heat treatment was carried out by using a Mettler TA-1 thermoanalyzer in argon atmosphere to avoid disturbing oxidative effects [15]. The samples were heated to 608°C isotherm temperature at 10°C min⁻¹ heating rate and annealed for different times (0.5, 1, 2, 5, 15 and 30 h) with subsequent quenching. The cooled samples were broken perpendicular to the reaction layer and the broken area was polished. This cross-section was subjected to analysis.

Methods

The DSC measurements were carried out by a PL Thermal Sciences 1500 differential scanning calorimeter in flowing argon atmosphere (50 cm³ min⁻¹), using 10°C min⁻¹ heating and cooling rates. The sample mass was ~50 mg, the crucible material was platinum. Highly sintered α -Al₂O₃ was the thermally inert reference material. In the first run the samples were heated by 50°C higher than the appropriate melting temperature. The temperature and heat flow response of the calorimeter was calibrated using 6N purity metals.

The cross-section of the prepared samples was analyzed with a Jeol Microprobe 733 instrument using an accelerating voltage of 20 kV and a beam current of 20 mA. Bi₂O₃ and TeO₂ were used as standards and ZAF correction was applied.

X-ray powder diffraction experiments were carried out for selected samples applying Cu-radiation ($\lambda(\text{CuK}_\alpha) = 0.154178$ nm) on a Siemens D5000 powder diffractometer system using theta-theta geometry. The system was equipped with a pyrolytic graphite curved crystal secondary monochromator. Data collection and all subsequent calculations were performed on the integrated computing facilities of the D5000 system. The intensity data were collected with the step-scan technique in the 5–65° and 22–110° 2 θ ranges, using 0.02° 2 θ step width.

Results and discussion

Reactions between powdered oxide mixture applying linear heating rate

The most characteristic features of the solid-state reaction of the Bi₂O₃+TeO₂ 1:1 mole ratio mixture investigated by DSC can be seen in Fig. 1a. While heating up the sample the base line remains stable up to 450°C, but above this temperature an exothermic shift can be observed. Then an endothermic process takes place at 607°C peak maximum, upon which an exothermic one is superimposed at 613°C. These processes are taking place again at 654°C endotherm and 659°C exotherm peak maximum (the magnified part of Fig. 1a). On heating the sample further, only a slight exothermic baseline shift can be detected, then the sample melts at 909°C onset temperature, which is the melting temperature of Bi₂TeO₅.

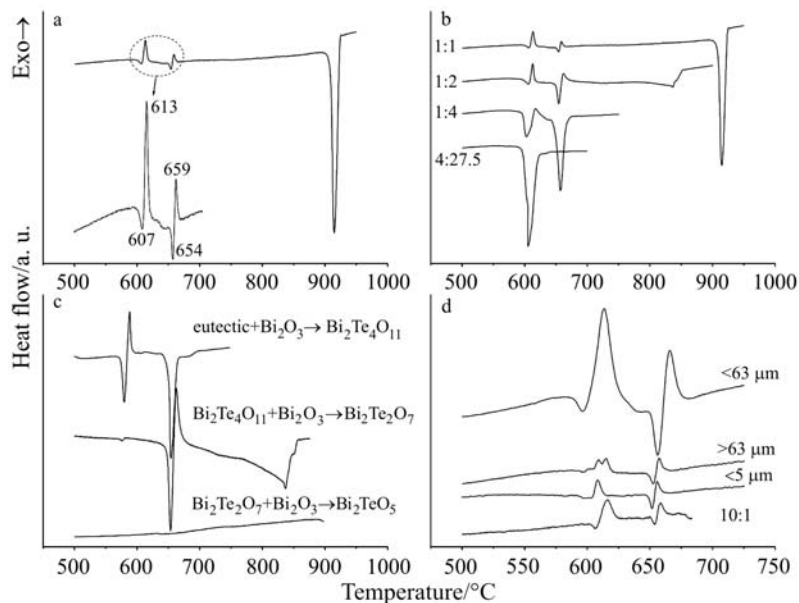


Fig. 1 Solid-state reactions between powdered oxides studied by DSC. a – DSC curve of the 1:1 mole ratio mixture. The magnified part shows the consecutive reactions, b – Reactions in the representative compositions, c – Identification of the origin of the peaks and d – Effect of the particle size and high bismuth oxide concentration

The first three peaks measured between 600 and 700°C temperature range were identified and discussed in our earlier publication [14]. Accordingly, based on the X-ray powder diffraction, electron microprobe analyses and DSC results, it was proved, that the reaction between the two oxides starts near 450°C and $\text{Bi}_2\text{Te}_4\text{O}_{11}$ forms in diffusion controlled reaction. When the amount of $\text{Bi}_2\text{Te}_4\text{O}_{11}$ is sufficient the eutectic is formed and it melts (first endotherm peak). According to the phase diagram of the Bi_2O_3 – TeO_2 system the eutectic composition corresponds to the lowest melting point [12]. (The accurate value of the eutectic composition was found to be $8\text{Bi}_2\text{Te}_4\text{O}_{11}+23\text{TeO}_2$ or $4\text{Bi}_2\text{O}_3+27.5\text{TeO}_2$). The formation of $\text{Bi}_2\text{Te}_4\text{O}_{11}$ is completed in the molten phase and this phase solidifies (first exotherm peak). The $\text{Bi}_2\text{Te}_4\text{O}_{11}$ content of the mixture melts (the second endotherm peak) as the temperature increases.

These processes are clearly demonstrated by the DSC curves in Figs 1b and c. In the course of heating the $4\text{Bi}_2\text{O}_3+27.5\text{TeO}_2$ mixture the eutectic was formed and melted at 606°C peak maximum (Fig. 1b, curve 4:27.5). If already present the melting point of the eutectic is at 580°C peak temperature (the upper curve of Fig. 1c). It was consistent with the experimental work that the melting temperature of the eutectic depends on the nature of the reactants. If the starting materials were pure oxides the melting temperature of the eutectic was always higher. The explanation is that the chemical (i.e. oxide) composition of the eutectic is $4\text{Bi}_2\text{O}_3+27.5\text{TeO}_2$, but $\text{Bi}_2\text{Te}_4\text{O}_{11}$ and TeO_2 are the compounds, which form an eutectic. Namely, if $\text{Bi}_2\text{Te}_4\text{O}_{11}$ is not present as reactant it has to be formed

and the melting temperature will be higher. But if Bi₂Te₄O₁₁ is already present the real melting temperature of the eutectic can be measured.

In order to show that the origin of the first exothermic peak is due to the reaction of unreacted Bi₂O₃ with TeO₂ component of eutectic and/or to the solidification of the Bi₂Te₄O₁₁ we added stoichiometric quantity of Bi₂O₃, needed for the formation of Bi₂Te₄O₁₁, to the eutectic. The obtained DSC curve (Fig. 1c) is similar to that of the Bi₂O₃+4TeO₂ mixture (Fig. 1b curve 1:4); and they also prove the origin of second endotherm peak (i.e. the melting of Bi₂Te₄O₁₁).

Considering the Bi₂Te₄O₁₁ (1:4) composition the second exotherm peak could not be detected. But if we add a stoichiometric quantity of Bi₂O₃ needed for the formation of Bi₂Te₂O₇ (Fig. 1c), or if the excess Bi₂O₃ is already present as reactant (curve 1:2 in Fig. 1b) this peak appears. The only explanation is that Bi₂O₃ reacts with the molten phase forming Bi₂Te₂O₇, which solidifies, because while increasing the temperature the incongruent melting process of Bi₂Te₂O₇ can be measured.

Coming back to the formation of Bi₂TeO₅ no thermal event could be detected between 700°C and the melting point, except a small exotherm baseline shift (Figs. 1a and c). This proves that the Bi₂TeO₅ should be formed by diffusion controlled reaction.

The grain size has not a significant effect on the reaction sequence (Fig. 1d), but the peak temperatures increase with increasing particle size. It can be assumed, that the reaction rate decreases because of the smaller specific surface, since these heterogeneous processes are taking place at the grain boundaries. The result of the 10Bi₂O₃+1TeO₂ oxide composition proves that even when bismuth oxide is in excess always the TeO₂ rich phase forms first.

Figure 2 shows the DSC curves obtained in the 50–95 mol% TeO₂ composition range. In conformity with the above results the first endotherm-exotherm peaks can be

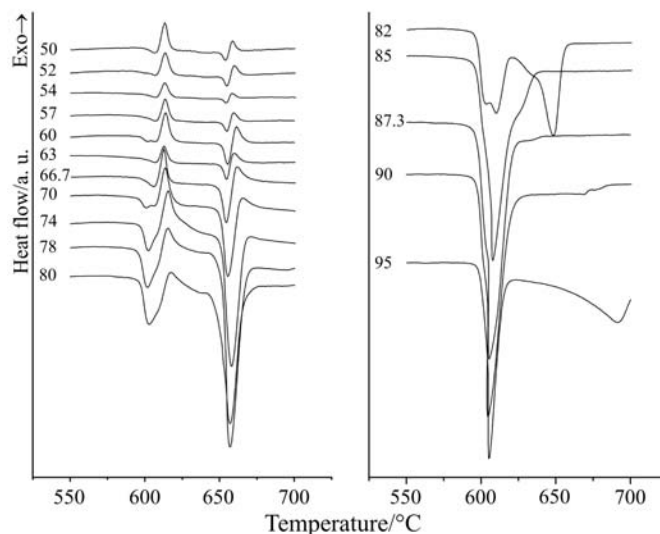


Fig. 2 DSC curve as a function of the sample composition

detected in the 50–80 TeO_2 mol% concentration, the second ones in the 50–79 mol% composition. Above 80% TeO_2 content the melting of eutectic and the appropriate $\text{Bi}_2\text{Te}_4\text{O}_{11} + \text{TeO}_2$ composition can be measured. The latter will determine the liquidus curve of the phase diagram discussed later.

Figure 3 summarizes the quantitative results obtained from the evaluation of the DSC curves.

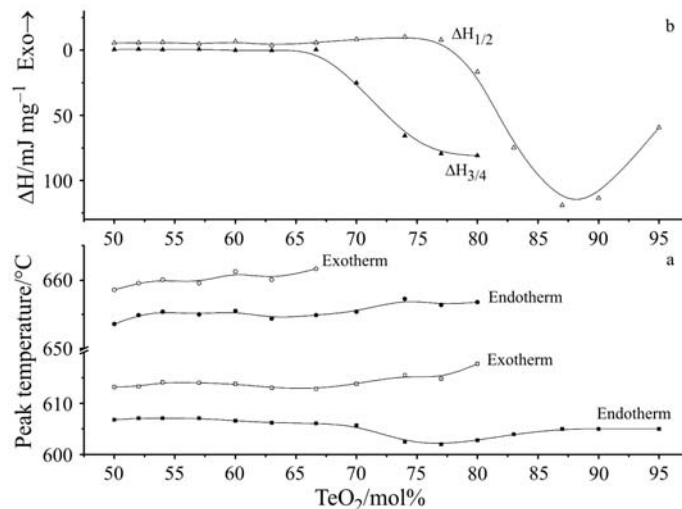


Fig. 3 a – Peak temperatures and b – the arising heat of reactions as a function of the sample composition

Because the exothermic peaks are superimposed to the endothermic ones, neither the onset temperatures nor the enthalpy changes could be evaluated separately and precisely. Thus the peak temperatures and the resultant enthalpy changes are measured. The peak temperature does not change significantly, indicating that the same processes are taking place independently of the tellurium oxide content. Another important result is that the resultant enthalpy of the corresponding peaks is constant in the 50–77% and 50–66.7% range, respectively. Above these concentrations the amount of both the eutectic and $\text{Bi}_2\text{Te}_4\text{O}_{11}$ increases.

Reactions between oxide pellets at 608°C isothermal temperature

Electron microprobe analyses were performed to identify the different phases existing in the course of $\text{Bi}_2\text{O}_3 + \text{TeO}_2$ reaction. The back scattered electron pictures were taken from the cross-section of the reaction interface. Results of these measurements cannot be strictly correlated with the powdered mixture samples, because the reaction could only take place within the contact surface layer and the mole ratio varies locally. This relatively low temperature was chosen to avoid the melting of the $\text{Bi}_2\text{Te}_4\text{O}_{11}$ phase.

Figure 4a shows the phases in the sample treated for 30 min. The dark gray phase on the bottom of the picture is the unreacted TeO_2 . In contact with this reactant

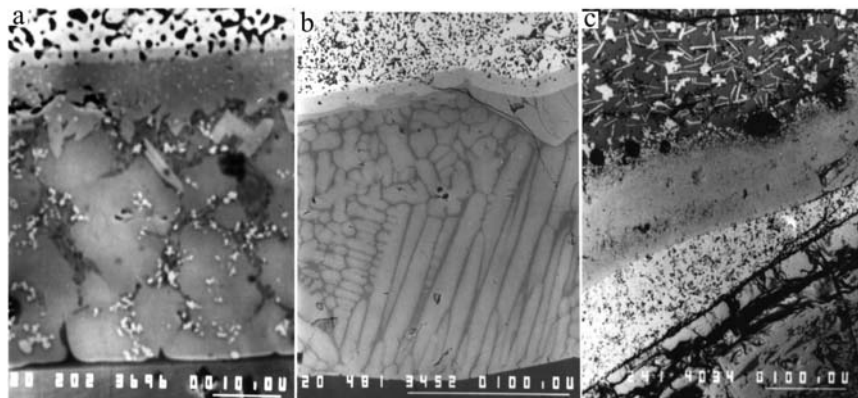


Fig. 4 The back scattered electron pictures taken from the cross-section of the sample annealed for a – 30 min, b – 2 h and c – 30 h, at 605°C

there is a heterogeneous phase, which is 30–35 μm thick. It consists of three well distinguishable compounds. The composition of the light gray dendrite like crystals with rounded outline boundary is close to $\text{Bi}_2\text{Te}_4\text{O}_{11}$, but the concentration of Bi_2O_3 is a little lower (84% TeO_2). Between them, the dark background is a solidified melt phase consisting of the eutectic composition. The composition of the small white particles is 67 mol% ($\text{Bi}_2\text{Te}_2\text{O}_7$).

The heterogeneous phase intergrowths with the next layer, the interface is very irregular and complicated. This phase is identified as $\text{Bi}_2\text{O}_3 + 4\text{TeO}_2$ ($\text{Bi}_2\text{Te}_4\text{O}_{11}$, 80 mol%) and its thickness is about 5–10 μm . The composition of the next homogeneous layer is $\text{Bi}_2\text{Te}_2\text{O}_7$ and it is 3–4 μm thick. The unreacted Bi_2O_3 can be seen on the top of the picture showing the morphology of the compressed powder. This morphology can be found in the $\text{Bi}_2\text{Te}_2\text{O}_7$ layer, too. On increasing the reaction time to one hour the structure of the reaction zone does not change remarkably, only a small increase in the layer thickness can be measured.

Reaction time: 2 h (Fig. 4b)

The heterogeneous phase has changed. The small white particles cannot be seen any more. The structure of the phase is a little ordered, the size of a fraction of the dendrites has increased and parallel oriented. The thickness of the reaction zone and the $\text{Bi}_2\text{Te}_2\text{O}_7$ phase increased to 180 μm and 10 μm , respectively.

No remarkable changes can be observed on samples reacted for 5 and 15 h. The order of the structure of the dendrites as well as the thickness of the phases has increased.

Reaction time: 30 h (Fig. 4c)

The unreacted TeO_2 could not be identified, it was fully consumed. The analyses confirmed that the composition of the layer contacting with the Bi_2O_3 reactant is Bi_2TeO_5 , which is 5–10 μm thick. The next phase is the 100 μm thick $\text{Bi}_2\text{Te}_2\text{O}_7$. This

phase is in contact with a dark gray, solidified melt phase; which has the eutectic composition. There are white prismatic and needle-like crystals identified as $\text{Bi}_2\text{Te}_2\text{O}_7$ in the eutectic. The $\text{Bi}_2\text{Te}_4\text{O}_{11}$ phase could not be detected. The dark gray phase in the right bottom corner is the Pt container.

Tellurium compounds are well known as glass forming materials at high TeO_2 content. Thus dendrites, containing 84 mol% tellurium oxide, should be considered as the non-equilibrium (metastable) phase; and the stability will be determined by the kinetic (i.e. the cooling rate) parameters. As mentioned in the experimental, these samples were quenched after the isothermal treatment.

The new phenomenon is the formation of Bi_2TeO_5 in the sample annealed at 30 h, while TeO_2 reactant could not be detected. This indicates that Bi_2TeO_5 could not be formed until the TeO_2 is fully reacted. It also should be pointed out that the $\text{Bi}_2\text{Te}_2\text{O}_7$ phase, even the $\text{Bi}_2\text{Te}_4\text{O}_{11}$ phase too, shows the morphology of the Bi_2O_3 pellet. If the diffusion mechanism is supposed, the only explanation is that the tellurium oxide moves to the Bi_2O_3 reactant. The order of the identified homogeneous phases are $\text{Bi}_2\text{Te}_4\text{O}_{11}$, $\text{Bi}_2\text{Te}_2\text{O}_7$ and Bi_2TeO_5 advancing from the TeO_2 reactant. The following reaction mechanism is suggested on the base of the above results: the reaction interface moves from the tellurium oxide to the bismuth oxide controlled by the diffusion of the tellurium oxide.

Phases in the TeO_2 rich part of the $\text{Bi}_2\text{O}_3 - \text{TeO}_2$ system. The non-equilibrium phase diagram

For studying the reactions of powdered oxides the samples were heated by 50°C higher than the appropriate melting temperature and cooled down to 400 at $10^\circ\text{C min}^{-1}$ temperature program. The measurements were repeated in order to study the phases formed. Figure 5 summarizes the results. Selected compositions were subjected to X-ray diffraction, too.

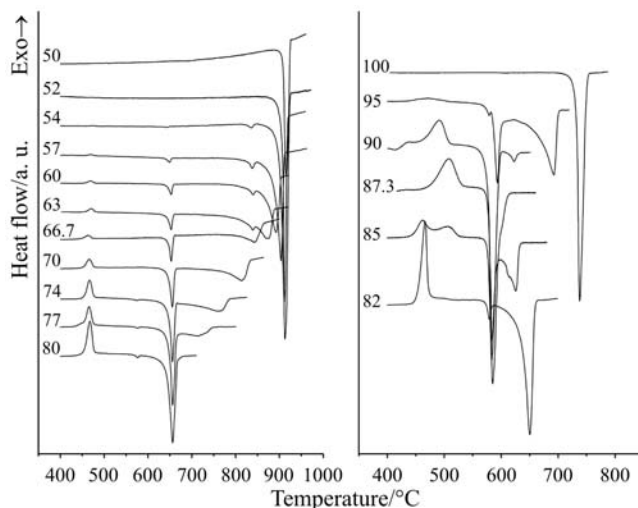


Fig. 5 DSC curves of reacted samples of different compositions (second run). The labels indicate the TeO_2 content in mol%

50–54 TeO₂ mol% region

50–52 % samples consist of congruently melting Bi₂TeO₅ compound. The 54% composition was identified as Bi₂TeO₅ too, though on the heating curve the trace of one exotherm and two small endothermic peaks can be seen before melting at 472, 650 and 838°C, respectively. The onset temperature of the melting decreases slightly with the composition (50% 908°C; 52% 904°C; 54% 900°C). The TeO₂ component has a relatively high vapor pressure at the melting point of Bi₂TeO₅ even after the solid state reactions. This means that the vaporization results in a continuous shifting of the melt composition during growth and the starting composition with excess TeO₂ resulted in the best quality crystals [1]. In the contrast with the literature data the 54% composition is considered to be the border of solid solution, from which the homogeneous and high-quality single crystal can be grown.

54–66.7 TeO₂ mol% region

From 54% concentration the common feature of heating curves is the existence of an exothermic peak at about 470°C, which is the consequence of the cubic(β)–monoclinic(α) phase transition of Bi₂Te₄O₁₁. This transformation has been investigated by Szaller *et al.* [14] and Lovas *et al.* [16] in detail. Increasing the temperature, Bi₂Te₄O₁₁ melts peritectically at 646.7°C onset temperature [14].

The endotherm peak temperature about 838°C can be identified as the melting of Bi₂Te₂O₇, because the reacted 1:2 oxide composition melts incongruently at 843.5°C peak temperature (the melting process starts at 753°C). This sample was subjected to X-ray powder diffraction analyses. A small amount of β-Bi₂Te₄O₁₁ was identified. The main phase is very similar to Bi₂Te₂O₇, but the powder diffraction pattern does not agree with that found in the current ICDD-JCPDS database. The detailed structural analysis is in progress using Selected Area Electron Diffraction method.

The peak temperature of the melting decreases with the increasing TeO₂ content determining the liquidus curve of the phase diagram. The end members of this concentration range are Bi₂TeO₅ and Bi₂Te₂O₇, respectively. Between them, Bi₂TeO₅ and Bi₂Te₂O₇ phases coexist and/or Bi₂TeO₅–Bi₂Te₂O₇ solid solution exists [9]. The presence of Bi₂Te₄O₁₁ indicates that at this relatively high cooling rate a phase separation is taking place at 646°C.

66.7–80% TeO₂ mol% region

The amount of Bi₂Te₄O₁₁ phase increases with increasing TeO₂ content. The end member of this region is the pure β-Bi₂Te₄O₁₁. A small sharp endothermic peak can be detected at about 573°C onset temperature before the melting point of Bi₂Te₄O₁₁, which is attributed to the ordering of oxygen vacancy [16]. Investigating the reacted 74 TeO₂ mol% composition by XRD, a mixture of monoclinic Bi₂Te₄O₁₁ and a structure very similar to Bi₂Te₂O₇ phase could be identified.

80–100% TeO_2 mol% region

Characteristic features of this range are the undercooling and tendency of glass formation [1, 12]. The higher is the TeO_2 content in the sample, the more significant is the non-equilibrium effect. It follows from this fact that this part of the system is metastable under the experimental conditions applied. Eutectic composition is found at 87.87%. This sample is identified by XRD as a regular cubic $\text{Bi}_2\text{Te}_7\text{O}_{17}$ monophas, which separates into monoclinic $\text{Bi}_2\text{Te}_4\text{O}_{11}$ and TeO_2 (paratellurite) annealing below the melting point. The amount of paratellurite significantly increases at higher TeO_2 content. The end members of this region are $\text{Bi}_2\text{Te}_4\text{O}_{11}$ and TeO_2 , respectively.

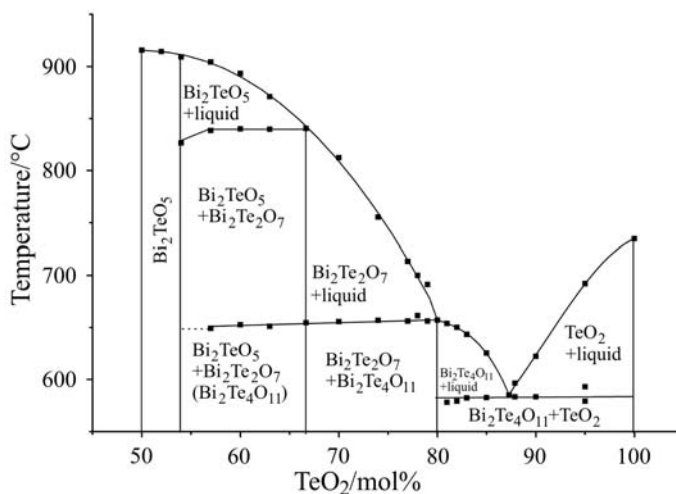


Fig. 6 The non-equilibrium phase diagram of the TeO_2 -rich part of the Bi_2O_3 - TeO_2 system

The phase diagram (Fig. 6) was constructed on the base of the above results. The peak temperatures were used, because the onset temperature could not be determined precisely and reproducibly in most cases.

Conclusions

Rasrogi *et al.* have investigated the solid state reaction between Bi_2O_3 and MoO_3 at 580°C [17]. They stated that MoO_3 diffuses into bismuth oxide grains and this grain boundary diffusion is followed by bulk diffusion during which the MoO_3 rich phases form. These results are very important from the point of view of the present reactions because some physical properties of MoO_3 are very close to the ones of TeO_2 (ionic radius, volatility and melting point). The phase diagrams of the two oxide systems are very similar, too.

The $\text{Bi}_2\text{O}_3 + \text{MO}_2$ ($M = \text{Si, Ge and Ti}$) reactions were studied by Fu and Ozoe [18]. It was established that the reactions were controlled by the diffusion, where the reac-

tion rate is determined by the diffusion of MO₂. Bi₂O₃ rich phases were detected as reaction products.

In both cases the Bi₂O₃ is the stationary phase and the other reactant oxide (MO_x) is the moving phase. The composition of the product depends on the volatility of MO_x. If it is very low, the Bi₂O₃ rich phases arise. But if the volatility of MO_x is sufficiently high, the MO_x-rich phases are the products. The vapor pressure of solid TeO₂ is 0.438 Pa at 605°C and 3.62 Pa at 650°C, respectively [19].

Applying linear heating rate the following reaction pathways can be established on the base of DSC and electron microprobe analyses results. The reaction starts by grain boundary diffusion. But at the same time, from 450°C the TeO₂ evaporates onto the Bi₂O₃ grains producing TeO₂ layer. This TeO₂ layer reacts with the Bi₂O₃ by bulk diffusion forming Bi₂Te₄O₁₁. When the amount of Bi₂Te₄O₁₁ is sufficient, the eutectic forms and melts. The reaction rate increases in the liquid phase. The conversion of Bi₂Te₄O₁₁ completes and the melt is solidified. When increasing the temperature the Bi₂Te₄O₁₁ melts and reacts with Bi₂O₃ forming Bi₂Te₂O₇, which is solidified. The Bi₂O₃+Bi₂Te₂O₇ reaction is taking place by bulk diffusion at higher temperature.

The formation of structures of samples cooled down from melt is controlled by cation-ordering processes. Ions have to move from one site to another through strong potential walls of other ions. This ‘kinetic hindrance’ can be strong and require long annealing time [20]. The 10°C min⁻¹ cooling rate applied is relatively high and permits the formation of metastable phases (β-Bi₂Te₄O₁₁, Bi₂Te₇O₁₇) with cubic symmetry between 54–100% composition range. Though stable phases form during the subsequent heating, the phase diagram has been determined under non-equilibrium conditions.

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