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Formation and decomposition of the Bi_2TeO_6 compound

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Abstract

XRD and SEM studies of the formation of Bi_2TeO_6 confirmed that the Bi_2TeO_6 compound forms in an oxygen atmosphere and also during prolonged calcination in air. At elevated temperatures the compound decomposes with the degree of the decomposition being dependent on the oxygen partial pressure. The decomposition products were identified as $Bi_6Te_2O_{15}$ and the high-temperature phase $2Bi_2O_3 \cdot 3TeO_{2+x}$. The sublimation of TeO_2 was proved not to be the main reason for the appearance of the $Bi_6Te_2O_{15}$ phase during the decomposition of Bi_2TeO_6.

Keywords: Bismuth tellurates; Calcination; X-ray methods and electron microscopy; Bi_2TeO_5; Bi_2TeO_6

1. Introduction

In the Bi_2O_3–TeO_2 system several compounds were reported to exist. In addition to phases reported to appear in a nitrogen atmosphere[1] a few studies of the phase relations in vacuum[2–6] were reported so far. The only phase relations investigated in an atmosphere that contains oxygen are the phase relations analyzed in air, which were published by Kikuchi et al.[7] They observed an oxidation of Te^{+4} to Te^{+6}, which causes a different phase formation in the Bi_2O_3–TeO_2 system compared to a synthesis in a vacuum.

The literature data about the existence and stoichiometry of phases from the Bi_2O_3–TeO_2 system is rather contradictory,[2–4] however, authors agree on the existence of a Bi_2TeO_5 compound, which is an end member of the $Bi_2Te_2O_7$–Bi_2TeO_5 solid solution.[8] The Bi_2TeO_5 compound was already recognized as a material that exhibits interesting nonlinear optical and photo-refractive properties and might be utilized as a holographic memory substrate.[9] The crystal structure was determined by Mercurio et al.[10] to be an anion-deficient fluorite with an orthorhombic unit cell and cell parameters $a = 11.602$ Å, $b = 16.461$ Å and $c = 5.523$ Å. It was further revealed that the cations' lone-electron pairs are stereoactive. The Bi_2TeO_5 compound is stable up to 900 °C, above this temperature it melts congruently.[11] Hartmann et al.,[12] using electrical conductivity measurements at high temperatures, revealed that the firing atmosphere is one of the main factors affecting the electrical properties of Bi_2TeO_5 single crystals.

By firing Bi_2TeO_5 at 680 °C in an oxygen atmosphere it oxidizes to form Bi_2TeO_6.[13,14] The crystal structure of the orthorhombic Bi_2TeO_6 compound was resolved[13] and an orthorhombic unit cell was proposed (space group Cmca) with the unit-cell parameters $a = 5.319$ Å, $b = 16.599$ Å and $c = 5.318$ Å. At elevated temperatures Bi_2TeO_6 decomposes with the release of oxygen and a consequent loss of weight. The decomposition temperature is in the range 720–730 °C[13,15] Pöppl et al.[14] suggested that oxidation/reduction reactions are, in the case of Bi_2TeO_5/Bi_2TeO_6, competitive, and that their equilibrium depends on the oxygen partial pressure. The reduction of Bi_2TeO_6 starts at 670 °C in an argon atmosphere, at 730 °C in air and at 760 °C in an oxygen atmosphere. In general, the final weight loss does not deviate from the theoretical loss, calculated for a full reduction of Te^{+6} to Te^{+4}, which strongly suggests that Bi_2TeO_6 decomposes to Bi_2TeO_5 and oxygen.[14] Recently, the synthesis, processing and dielectric properties of Bi_2TeO_6 were analyzed.[16] Due to the decomposition process that begins before the sintering occurs the solid-state sintering did not result in single-phase, dense Bi_2TeO_6 ceramics. To avoid the decomposition a reaction-sintering technique was applied and, as a result of sintering at 720 °C for 15 h, a dense ceramic body was obtained with only traces of secondary phases present.

With regard to the formation and decomposition of the Bi_2TeO_6 compound it has mainly been thermo-

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gravimetric studies that were reported so far. A study of Bi_2TeO_6 formation in an air atmosphere has not been published yet and, in addition, no XRD and microstructural studies of the decomposition process have been perfomed so far. Therefore, the aim of our study was to analyze the influence of oxygen partial pressure on the synthesis of the Bi_2TeO_6 compound. In addition, using XRD and microstructural studies we analyzed the Bi_2TeO_6 decomposition as a function of oxygen partial pressure.

2. Experimental

The samples were prepared using solid-state synthesis. Bi_2O_3 (Alfa, 99.975%, lot I09J22) and TeO_2 (Alfa, 99.999%, lot I15J04) were weighed out, homogenized in alcohol and dried. The firing was performed in the temperature range from 670 to 800 °C in air and oxygen atmospheres. The mass gain was measured by weighing the mixture before and after the calcination process. For the phase-composition determination an X-ray diffraction (XRD) analysis using a Bruker Endeavor D4 X-ray diffractometer was applied. Powdered samples were stepscanned in the 2θ range 20–70° (step 0.02/s, 2s per step, V12 receiving slit) using CuK_α radiation. Additional information on the phase composition and microstructural characteristics was obtained by a microstructural analysis of the polished ceramics using a Jeol 5800 scanning electron microscope, equipped with a LINK ISIS system for EDS analysis.

3. Results and discussion

3.1. Formation of the Bi_2TeO_6 compound

Our XRD analysis of the sample with the composition Bi_2O_3:TeO_2, fired for 40 h at 670 °C in an oxygen atmosphere, confirmed the formation of the Bi_2TeO_6 compound. In the diffraction pattern only the Bi_2TeO_6 lines were observed, there were no secondary phases present. Additional evidence for the oxidation of Te^{+4} to Te^{+6} was obtained during the mass-gain measurements, which showed a mass gain of 2.43 wt.%. These findings are in good agreement with Pöppl et al.,[14] who showed that by firing the Bi_2O_3:TeO_2 composition for only 170 min in oxygen it is possible to achieve a 2.54 mass% gain, which matches the theoretical mass gain (2.55 wt.%) for the complete oxidation of Te^{+4} to Te^{+6}, according to the reaction scheme:

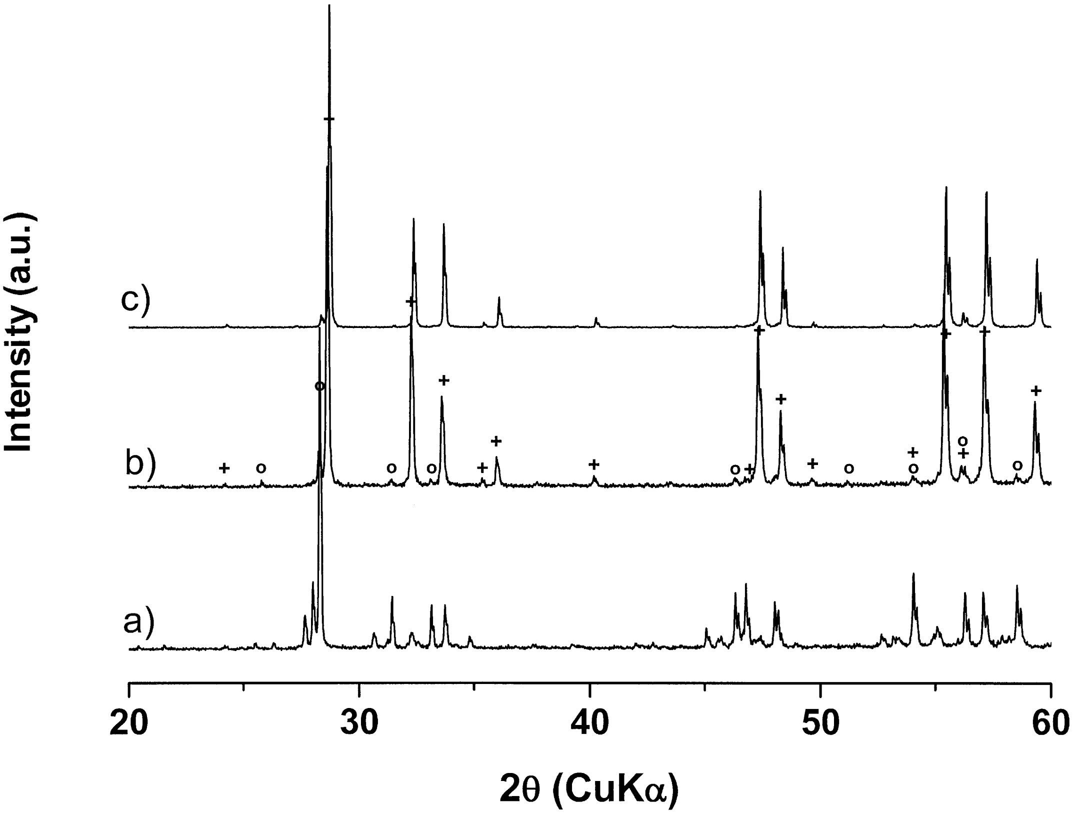

Fig. 1. XRD patterns of the composition Bi_2O_3:TeO_2 fired at 670 °C in air: (a) for 20 h; (b) for 40 h; (c) for 60 h. Peaks marked with + represent Bi_2TeO_6 lines while o denotes the presence of secondary phases.

$$Bi_2TeO_5 + 1/2O_2 \rightarrow Bi_2TeO_6 \quad (1)$$

Pöppl et al.,[14] in their thermoanalytical study of Bi_2TeO_6 formation, showed that as a result of decreasing the oxygen partial pressure the mass gain decreases, which in an air atmosphere is as low as a 0.7 mass% gain after firing for 350 min at 670 °C. For the composition Bi_2O_3:TeO_2, Kikuchi et al.,[7] in their phase diagram investigated in air, did not report the formation of the Bi_2TeO_6 compound or any phase with the composition Bi_2O_3:TeO_2. At this composition a two-phase area was determined with the phases identified as "$Bi_2O_3{\cdot}2TeO_2$", later shown to be $Bi_2Te_2O_8$, and $Bi_6Te_2O_{15}$.[16–18] Such literature data raise further questions regarding the formation of the Bi_2TeO_6 compound. Does the observed mass gain in air[14] mean oxidation to the phases reported by Kikuchi[7] or that the lower oxygen partial pressure hinders the rapid oxidation to equilibrium Bi_2TeO_6?

Our XRD analysis of the samples with the nominal composition Bi_2O_3:TeO_2, calcined in an air atmosphere, revealed that after prolonged firing (20 h at 670 °C) a yellowish powder is obtained, with the main phases being $Bi_2Te_2O_8$ and $Bi_6Te_2O_{15}$, as shown in Fig. 1. However, during the next 20 h of firing both these phases reacted to form the Bi_2TeO_6 compound and the color changed to brown. The main phase was identified as Bi_2TeO_6, and a small concentration of the $Bi_6Te_2O_{15}$ phase could still be detected. After a further 20 h of firing (a total calcination time of 60 h) only traces of secondary phases could be detected in the XRD pattern. This result confirms that the Bi_2TeO_6 compound is thermodynamically stable in air, and so contradicts the phase diagram published by Kikuchi et al.;[7] however, the kinetics of the oxidation and the Bi_2TeO_6 formation is obviously influenced by the oxygen partial pressure.

3.2. Decomposition of Bi_2TeO_6

Based on thermogravimetric studies several authors[13–15] have suggested that in an oxygen atmosphere Bi_2TeO_6 decomposes according to the reaction:

$$Bi_2TeO_6 \rightarrow Bi_2TeO_5 + 1/2\ O_2 \quad (2)$$

In contrast, Kikuchi et al.,[7] in the phase diagram prepared in air, observed that in the temperature range between ~660 and ~830 °C a two-phase area exists for the composition Bi_2O_3:TeO_2. The phases were identified as $3Bi_2O_3$:$2TeO_2$ and $2Bi_2O_3$:$3TeO_2$. Using such an expression the exact definition of the oxidation number of the tellurium is avoided. The "$3Bi_2O_3.2TeO_2$" phase was already identified as the $Bi_6Te_2O_{15}$ compound with the tellurium exclusively in +6 oxidation state. This phase around 830 °C decomposes with the release of oxygen.[13,15,18] There are no other literature data on the high-temperature phase with the composition $2Bi_2O_3$:$3TeO_2$.

Our SEM analysis of the sintered ceramics, prepared from Bi_2TeO_6 powder and fired for 10 h at 760 °C in air, confirmed the decomposition of Bi_2TeO_6. The microstructural analysis of the so-prepared sample showed the presence of three phases (Fig. 2a). Using the EDS analysis we observed that the phases exhibited the approximate Bi/Te ratios 3/1, 2/1 and 4/3. Phases with the same Bi/Te ratio were also observed when the sample was fired in an oxygen atmosphere; only the amounts of the corresponding phases were significantly different (Fig. 2b). Such a result confirms that the level of decomposition depends on the oxygen partial pressure as suggested by Pöppl et al.[14] and further implies that the decomposition according to the reaction scheme (2) does not occur. Instead, a two-phase area with the $Bi_6Te_2O_{15}$ and "$2Bi_2O_3{\cdot}3TeO_{2+x}$" phases was confirmed, in agreement with the report of Kikuchi[7] for experiments carried out in air. According to our results at

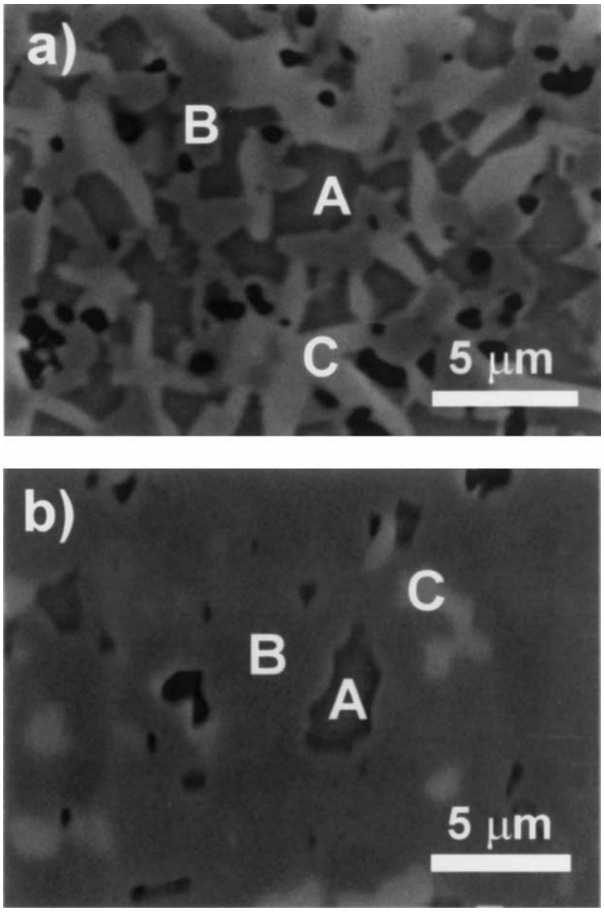

Fig. 2. Scanning-electron image of the calcined Bi_2TeO_6 powder, sintered for 20 hours at 760 °C: (a) air atmosphere and (b) oxygen atmosphere. Approximate Bi/Te ratio ($A = 4/3$, $B = 2/1$, $C = 3/1$).

800 °C in oxygen atmosphere the Bi_2TeO_6 decomposes according to the reaction scheme:

$$\begin{aligned} &5\ Bi_2TeO_6 \rightarrow Bi_6Te_2O_{15} + 2Bi_2O_3 \cdot 3TeO_{2+x} + yO_2 \\ &\quad 0<x<1, \\ &\quad 3/2<y<0 \end{aligned} \tag{3}$$

In the "$2Bi_2O_3{\cdot}3TeO_{2+x}$" phase the value of x depends on the unknown oxidation state of the tellurium and ranges from 0 for Te^{+4} to 1 for Te^{+6}. Except for Kikuchi's phase diagram there are no literature data about the $2Bi_2O_3{\cdot}3TeO_{2+x}$ phase; however, based on the previously published thermogravimetric studies[14,15] there are indications that it includes Te^{+4}, thus giving an x value of 0.

Some authors have suggested that TeO_2 sublimates from the Bi_2TeO_6 sample.[19,14] If the decomposition mechanism (2) occurred in combination with the TeO_2 sublimation this would result in the presence of $Bi_6Te_2O_{15}$ lines in the high-temperature quenched Bi_2TeO_6 pattern. In addition, the XRD pattern of the $2Bi_2O_3{\cdot}3TeO_{2+x}$ phase is similar to the Bi_2TeO_5 patterns, so one could easily confuse the XRD patterns and conclude that the presence of the $Bi_6Te_2O_{15}$ lines in the quenched Bi_2TeO_6 pattern is due to the sublimation of TeO_2, which would confirm reaction scheme (2). To exclude such a possibility several compositions between $2Bi_2O_3{:}3TeO_2$ and $3Bi_2O_3{:}2TeO_2$ were weighed out, calcined for 40 h at 700 °C, annealed for 24 h at 800 °C in oxygen and subsequently quenched. In all the samples only the XRD lines of two phases were present: these phases were identified as $Bi_6Te_2O_{15}$ and $2Bi_2O_3{\cdot}3TeO_{2+x}$. The XRD lines (Fig. 3) of only these two phases were also found in the samples that were slightly shifted from the Bi_2TeO_6 composition towards $Bi_2Te_2O_8$. Mass-loss measurements performed by Pöppl et al.[14] in the temperature range between 790 and 890 °C revealed a weight loss of only 0.12 wt.% and, in addition, in our quenched sample the $Bi_6Te_2O_{15}$ phase was present throughout the whole of the pellet's cross-section and not only near the pellet's surface. These facts confirm the decomposition scheme (3) and disprove the occurrence of any intensive evaporation of TeO_2 from the pellet.

3.3. The $2Bi_2O_3{\cdot}3TeO_{2+x}$ phase

The phase with the composition $2Bi_2O_3{:}3TeO_2$ is not stable at room temperature. After the calcination of a starting composition $2Bi_2O_3{:}3TeO_2$ at 700 °C for 40 h in an oxygen atmosphere only the $Bi_2Te_2O_8$ and Bi_2TeO_6 phases can be detected (Fig. 4). However,

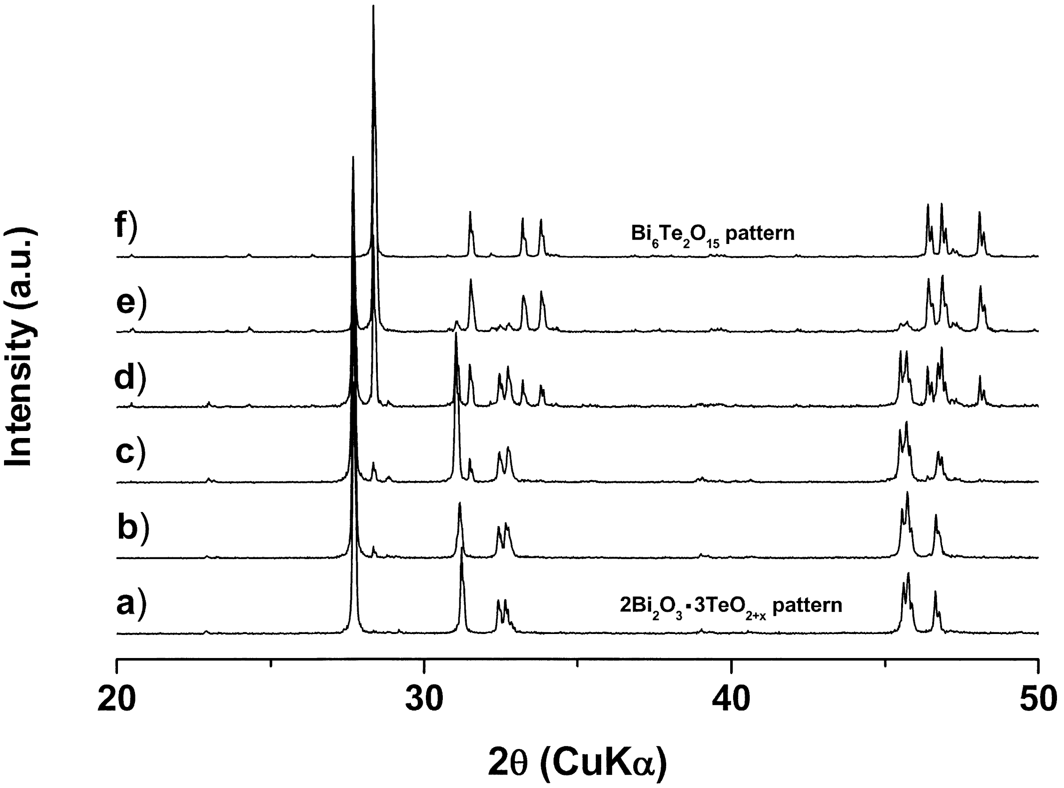

Fig. 3. XRD patterns of the compositions from the Bi_2O_3–TeO_2 system fired in an oxygen atmosphere and quenched from 800 °C: (a) 60 mol% TeO_2 (the $Bi_6Te_2O_{15}$ pattern) ; (b) 59.1 mol% TeO_2; (c) 54.8 mol% TeO_2; (d) 50 mol% TeO_2; (e) 42.8 mol% TeO_2; (f) 40.0 mol% TeO_2 (the $2Bi_2O_3{\cdot}3TeO_{2+x}$ pattern). Across the whole composition range only the XRD lines of the $Bi_6Te_2O_{15}$ and $2Bi_2O_3{\cdot}3TeO_{2+x}$ phases can be observed.

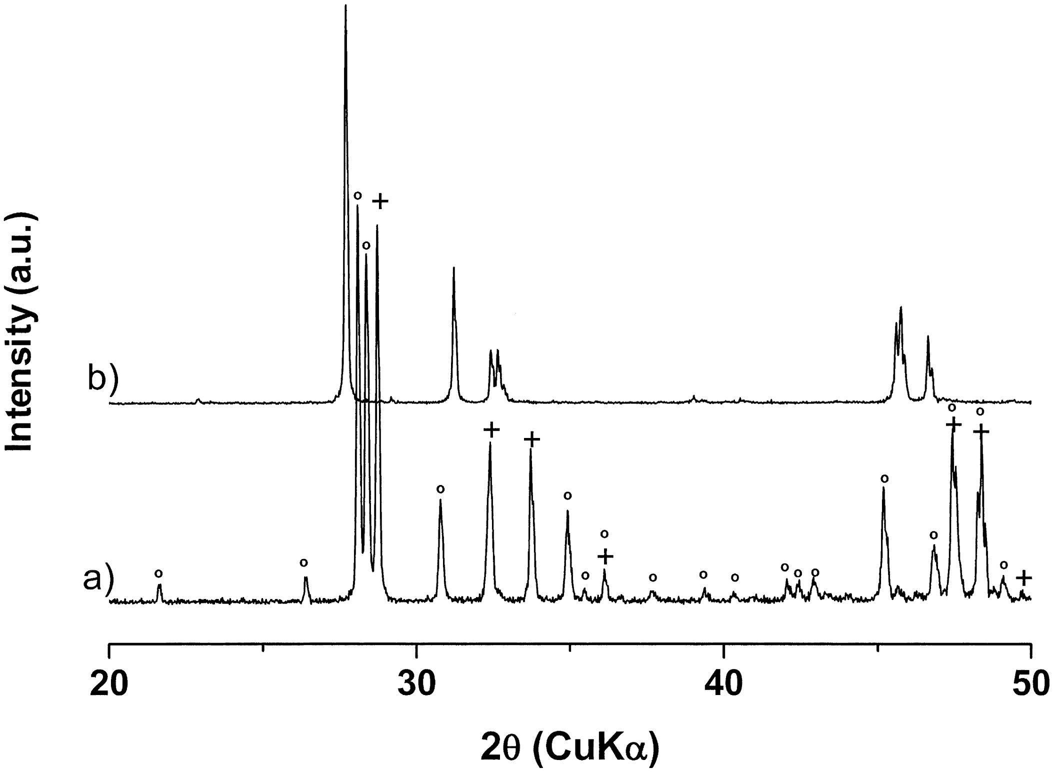

Fig. 4. XRD patterns of the nominal composition $2Bi_2O_3$:$3TeO_2$ fired in an oxygen atmosphere: (a) for 40 h at 700 °C and (b) followed by 24 h annealing at 800 °C and quenching. ○ represents the $Bi_2Te_2O_8$ lines while Bi_2TeO_6 lines are marked with +.

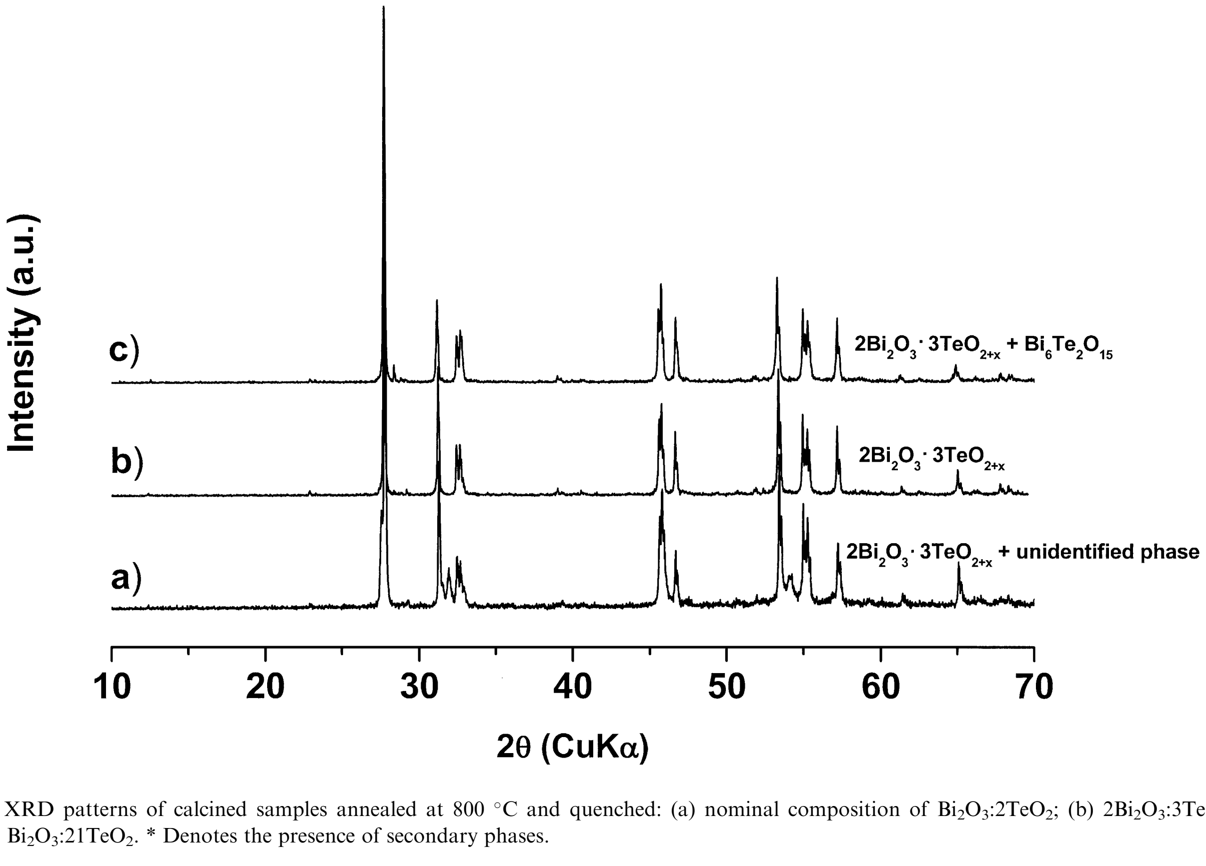

Fig. 5. XRD patterns of calcined samples annealed at 800 °C and quenched: (a) nominal composition of Bi_2O_3:$2TeO_2$; (b) $2Bi_2O_3$:$3TeO_2$ and (c) 14.5 Bi_2O_3:$21TeO_2$. * Denotes the presence of secondary phases.

annealing experiments, performed at 800 °C with consequent quenching into ice-cooled water, resulted in changes to the XRD patterns suggesting the phase transformation.

When the composition was shifted from $2Bi_2O_3$:3-TeO_2, either towards Bi_2O_3 or TeO_2, and then quenched, additional lines appeared while the diffraction pattern of the high-temperature phase remained (Fig. 5.). When the $Bi_2Te_2O_8$ compound, which is shifted towards TeO_2, was fired at 800 °C some pellet deformation was observed, which indicates the appearence of the liquid phase and the phase with an X-ray pattern that corresponds to the pattern of $2Bi_2O_3{\cdot}3TeO_{2+x}$. Such a result agrees with the determined phase relations of Kikuchi,[7] investigated in air, which proposes that above ~720 °C the $Bi_2Te_2O_8$ compound decomposes peritectically to the liquid phase and the phase $2Bi_2O_3{\cdot}3TeO_{2+x}$.

4. Conclusions

The Bi_2TeO_6 compound forms during prolonged firing (60 h) at 670 °C in air. Initially, $Bi_2Te_2O_8$ and $Bi_6Te_2O_{15}$ are formed, which then further react to form Bi_2TeO_6. After 60 h of firing at 670 °C only traces of secondary phases can be detected. At 800 °C the Bi_2TeO_6 decomposes into $Bi_6Te_2O_{15}$ and $2Bi_2O_3{\cdot}3$-TeO_{2+x}, last one probably with tellurium in the +4 oxidation state. An analysis of quenched compositions between $Bi_6Te_2O_{15}$ and $2Bi_2O_3{\cdot}3TeO_{2+x}$ revealed the existence of a two-phase area, thus confirming the proposed decompositional mechanism.

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