Phase Identification in the Tl_2O_3–BaO System: $Ba_2Tl_2O_5$ and $Ba_4Tl_6O_{13}$

WUZONG ZHOU, RU-SHI LIU, AND PETER P. EDWARDS

Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom

$Ba_2Tl_2O_5$ has been reinvestigated by a combination of X-ray diffraction, electron diffraction, and energy dispersive X-ray spectroscopy. A new monoclinic unit cell was observed with $a = 5.836$, $b = 6.226$, $c = 17.342$ Å, and $\gamma = 91.34°$. The impurity phase coexisting with $Ba_2Tl_2O_5$ was determined to be $Ba_4Tl_6O_{13}$, having an orthorhombic unit cell with $a = 5.748$, $b = 7.221$, and $c = 9.361$ Å. The possible mechanism of solid–solid reaction of Ba, Tl oxides is discussed. © 1990 Academic Press, Inc.

Introduction

Since the $Tl_2Ba_2Ca_nCu_{n+1}O_{2n+6}$ phases were discovered to be high T_c superconductors, Tl-containing compounds have been widely investigated. In our previous work, the ternary oxide system Tl_2O_3–CuO has been studied and no compounds were observed except Tl_2O_3-related solid–solution phases, $Tl_{2-x}Cu_xO_3$ (*1*).

To date, few compounds in the Tl_2O_3–BaO system have been reported, the exception being $Ba_2Tl_2O_5$, which was first prepared and studied by X-ray powder diffraction (XRD) methods in 1974 (*2*). The structure of $Ba_2Tl_2O_5$ was determined to be orthorhombic with $a = 6.264$, $b = 17.258$, and $c = 6.05$ Å, and was isotopic with $Ca_2Fe_2O_5$ (*3–5*). The compound has recently been reinvestigated using the same techniques (*6*). The reported unit cell parameters were almost identical to those determined previously, with $a = 6.257$, $b = 6.038$, and $c = 17.232$ Å. It was further proposed (*6*) that these cell dimensions were related to a monoclinic perovskite cell with the dimensions of $a_p = b_p = 4.347$

± 0.001, $c_p = 4.308 \pm 0.001$ Å, and $\gamma = 87.96°$. The superstructure and the perovskite subcell have a relation of $a = 2a_p \cos(\gamma/2)$, $b = 2a_p \sin(\gamma/2)$, and $c = 4c_p$. The oxygen content, x, in $Ba_2Tl_2O_x$ was determined to be close to 5. Therefore the valence of Tl cations was determined to be $3+$. We noted that, although almost all XRD peaks have been indexed into the determined unit cell, there were still some extra peaks unindexed and were marked to be an unknown phase with a higher Tl content as compared to the main phase, $Ba_2Tl_2O_5$. There are obvious difficulties in indexing a single phase from the XRD pattern of a (bulk) multiphasic material. For distinguishing individual phases in a composite material, we have found that electron diffraction is a particularly powerful technique since it can examine individual microcrystals and determine their compositions as well as their unit cell dimensions. Moreover, there are instances where electron diffraction studies yield a different structure from that determined from an XRD refinement. A recent example is the investigation of $Sr_{1-x}Cu_2O_3$ by high resolution elec-
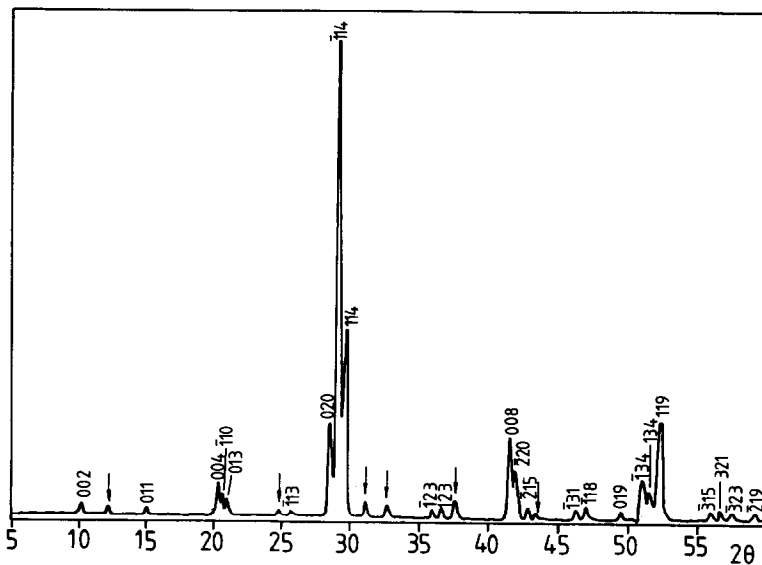
FIG. 1. XRD spectrum of the initially prepared $Ba_2Tl_2O_5$, indexed onto an SAED-revealed monoclinic unit cell with $a = 5.836$, $b = 6.226$, $c = 17.342$ Å, and $\gamma = 91.34°$. Those unindexed peaks marked by arrows belong to the $Ba_4Tl_6O_{13}$ phase (see Fig. 5).

tron microscopy (7). In our view, the relationship between the superstructure and the subunit cell in the $Ba_2Tl_2O_5$ phase in the previous study (6) was problematic. For example, if the perovskite lattice dimensions were correct, the superstructure should have dimensions of $a = 6.1978$ and $b = 6.097$ Å.

In this present work, although we can repeat the previously described preparation of $Ba_2Tl_2O_5$ and obtain a similar X-ray diffraction pattern, selected area electron diffraction (SAED) studies reveal a different unit cell for $Ba_2Tl_2O_5$ and some diffraction peaks indexed to the $Ba_2Tl_2O_5$ lattice in the previous reports (6) were found to belong to the second phase, $Ba_4Tl_6O_{13}$. The unit cell for the later phase has also been determined by SAED studies and confirmed by XRD studies on a freshly prepared sample of nominal composition of $Ba_4Tl_6O_{13}$.

Experimental

$Ba_2Tl_2O_5$ was prepared by a conventional solid state reaction from stoichiometric mixtures of high purity Tl_2O_3 and BaO_2 powders following the same preparation method as used previously (6). The mixed powders were ground and pressed into a pellet, 10 mm in diameter and 2 mm in thickness, under a pressure of 5 tons/cm². To alleviate loss of thallium in the form of Tl_2O during heating, the pellet was wrapped in a gold foil and the reaction was performed under oxygen atmosphere. The pellet was then heated at 650°C for 20 hr and cooled down at a rate of 5°C/min to room temperature. The yellow reacted sample was ground again, pressed into a pellet, wrapped in a gold foil, and heated at 720–730°C for 15–20 hr, followed by cooling to room temperature. After this process, the black sample was obtained and had a semiconducting behavior. After revealing two phases in the first preparation, new specimens of $Ba_2Tl_2O_5$ and $Ba_4Tl_6O_{13}$ were prepared by changing the preparation temperature and time described later.

Initial characterization of specimen was by XRD using $CuK\alpha$ radiation with the use
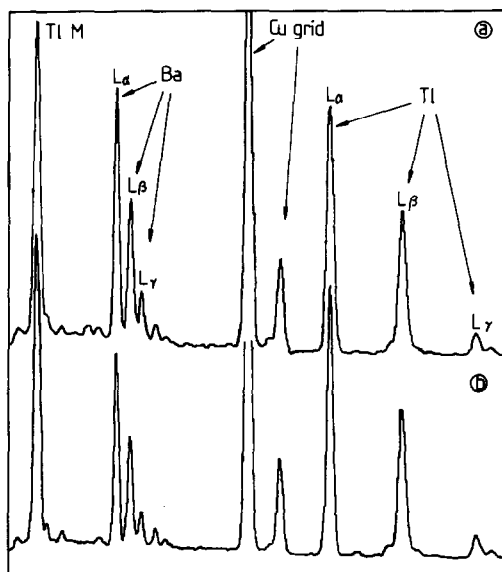
FIG. 2. EDS spectra of (a) $Ba_2Tl_2O_5$ and (b) $Ba_4Tl_6O_{13}$ from the initial prepared nominal composition $Ba_2Tl_2O_5$.

of a Spectrolab CPS-120 diffractometer. Compositions of individual phases were examined by energy dispersive X-ray spectrometry (EDS) in a Jeol EM-200CX electron microscope. $TlL\alpha$ and $BaL\alpha$ emission lines were collected and used in calculation of cation ratio in the materials. Twenty-five particles were randomly chosen from each specimen. Selected area electron diffraction (SAED) patterns were obtained from the same electron microscope. A $\pm$ 45° double tilt specimen stage was used which enabled us to record series SAED patterns from one single microcrystal through a tilting specimen grid. Camera length was calibrated using a standard Au film.

Results and Discussion

The XRD pattern from as-prepared $Ba_2Tl_2O_5$ is identical to that previously reported (6) (Fig. 1). Most of the diffraction lines can be indexed onto the orthorhombic

unit cell of $Ba_2Tl_2O_5$ with $a = 6.26$, $b = 6.04$, and $c = 17.2$ Å. Several unmarked weak peaks reported previously to belong to a Tl-richer phase (6) were also observed in our work. To understand the compositions of the ternary oxides, we examined 25 randomly chosen particles. An average value for the $TlL\alpha/BaL\alpha$ emission line ratio was 1.4(1) from 20 particles and 2.1(1) from 5 particles. Since we have no good monophasic Tl–Ba–O ternary oxide standard sample, $Tl_2Ba_2CaCu_2O_8$ (in which an average $TlL\alpha/BaL\alpha$ was 1.29(9)) was used as an initial reference in the calibration of the EDS results. We then obtained a Tl/Ba cation ratio from the majority phase to be 1.08(8):1. The phase was confirmed to be $Ba_2Tl_2O_5$ and the EDS data from this phase was used as a new reference. We then obtained a cation ratio (Tl/Ba) from the minority phase, 1.50(7):1. This is a Tl-rich phase as compared to $Ba_2Tl_2O_5$, in agreement with the previous report (6). The typical EDS spectra of these two phases are shown in Fig. 2. Consequently, the main phase in the specimen was confirmed to be $Ba_2Tl_2O_5$ and the remaining phase was $Ba_4Tl_6O_{13}$, with the oxygen content appropriate for the proposed valences of Tl^{3+} and Ba^{2+} in the material.

We took advantage of the SAED technique for examining individual crystals. One set of SAED patterns obtained from a single crystal of the $Ba_2Tl_2O_5$ phase through tilting the specimen grid around the c axis is shown in Fig. 3. Since we can read the tilting angles corresponding to the relative orientations between each two SAED patterns, we then can determine the orientations within certain of these patterns to be [1-10], [1-20], and [1-30] in Fig. 3. Surprisingly, we obtained monoclinic unit cell parameters from the SAED patterns, $a = 5.8$, $b = 6.3$, $c = 17.4$ Å, and $\gamma = 91°$, instead of the previously reported XRD determined orthorhombic unit cell dimensions, $a = 6.257$, $b = 6.038$, and $c = 17.232$ Å (6). Using this new unit
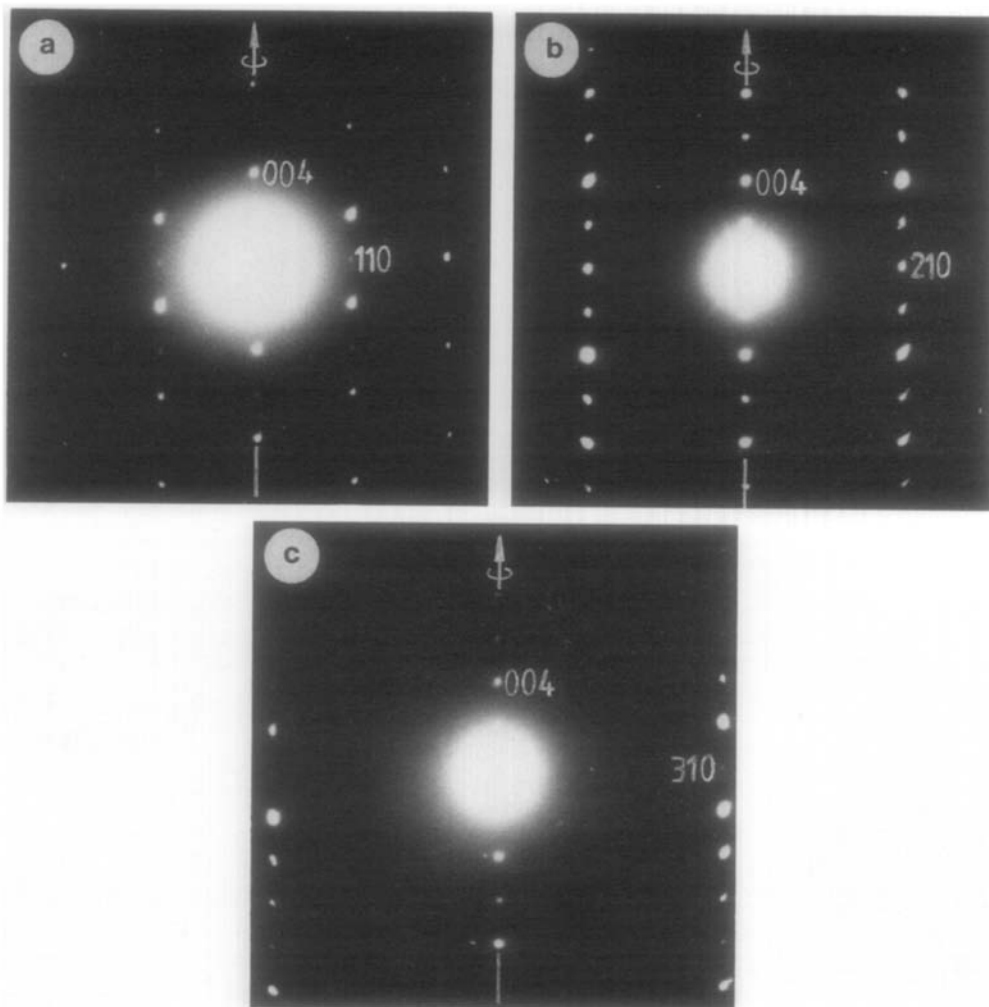
FIG. 3. One set of SAED patterns from same crystal of the $Ba_2Tl_2O_5$ phase through tilting the specimen grid, viewed down the (a) [1-10], (b) [1-20], and (c) [1-30] directions.

cell, we can also index most observed diffraction lines in the XRD spectrum in Fig. 1 and the unit cell has been refined as monoclinic with $a = 5.836$, $b = 6.226$, $c = 17.342$ Å, and $\gamma = 91.34°$ according to the XRD data (see Table 1).

It is believed that the structure is related to $Ca_2Fe_2O_5$, in which Fe cations are coordinated by oxygen alternatively in octahedra and tetrahedra along the c axis. All these polyhedra are distorted and the chain of Fe–O is in a zigzag arrangement (4). There-

fore, monoclinic symmetry for the $Ba_2Tl_2O_5$ phase (where Ba replaces Ca and Tl replaces Fe) can be expected.

We have also varied the preparation conditions in an attempt to produce monophasic material. When the preparation temperature was relatively lower, say 650°C, the produced yellow phase has an XRD pattern matching the impurity phase in Fig. 1. As the reaction temperature was increased, the concentration of this impurity phase decreased and that of $Ba_2Tl_2O_5$

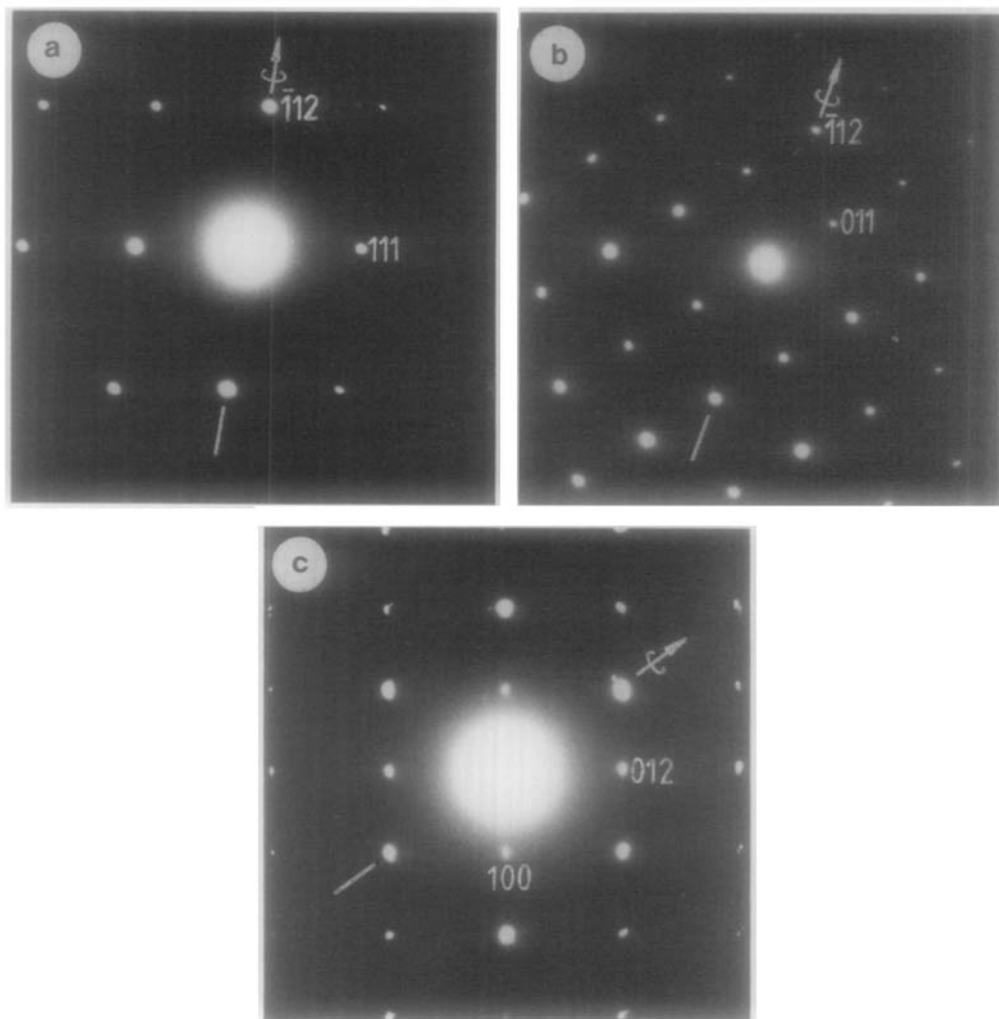FIG. 4. SAED patterns from one single microcrystal of $Ba_4Tl_6O_{13}$ through tilting the specimen grid, viewed down the (a) [1-32], (b) [1-11], and (c) [0-21] directions.

increased. Unfortunately, pure $Ba_2Tl_2O_5$ phase could never be successfully synthesized. For the second phase, $Ba_4Tl_6O_{13}$, we have also recorded several sets of SAED patterns. One of them is shown in Fig. 4. Through tilting the specimen grid around one zone axis, we observed three SAED patterns and then obtained a three-dimensional reciprocal lattice. Therefore, we can deduce the unit cell of this phase as orthorhombic with $a = 5.748$, $b = 7.221$, $c =$ 9.361 Å, after understanding the orientations of the SAED patterns in Fig. 4.

The $Ba_4Tl_6O_{13}$ specimen was prepared by similar methods to those for the $Ba_2Tl_2O_5$ phase. As seen in Fig. 5, when the stoichiometric mixture of oxides was heated at 700°C for 12 hr, the resulting material contained $Ba_4Tl_6O_{13}$ coexisting with an impurity phase (Fig. 5a), which has a composition close to $BaTl_2O_4$ as indicated by our EDS studies. When the specimen was reheated at

TABLE I

XRD Data from Previous Report (6), Presently Observed on the Initially Prepared Nominal Composition $Ba_2Tl_2O_5$, and Calculated from the New Monoclinic Unit Cell for $Ba_2Tl_2O_5$ with $a = 5.836$, $b = 6.226$, $c = 17.342$ Å, and $\gamma = 91.34°$

Ref. (6) d_{obsd}	Presently observed data		$Ba_2Tl_2O_5$			
	d_{obsd}	I_{obsd}	h	k	l	d_{calcd}
8.61	8.66	1	0	0	2	8.67
Tl-rich*	7.237	1	—	—	—	—
—	5.860	1	0	1	1	5.858
4.349	4.341	4	0	0	4	4.336
4.312	4.305	3	−1	1	0	4.307
4.235	4.226	2	0	1	3	4.236
BaCO₃*	3.580	<1	—	—	—	—
3.460	3.458	<1	−1	1	3	3.454
3.133	3.126	18	0	2	0	3.112
3.061	3.057	100	−1	1	4	3.056
3.022	3.020	39	1	1	4	3.020
Tl-rich*	2.867	2	—	—	—	—
2.744*	2.734	1	—	—	—	—
2.503	2.498	<1	−1	2	3	2.500
2.458	2.455	1	1	2	3	2.461
2.396*	2.390	3	—	—	—	—
2.174	2.171	19	0	0	8	2.168
2.154	2.153	10	−2	2	0	2.153
2.114	2.110	2	−2	1	5	2.113
2.081*	2.081	1	—	—	—	—
1.956	1.957	1	−1	3	1	1.957
1.941	—	—	1	3	0	1.941
1.930	1.931	1	3	0	1	1.933
1.903*	—	—	—	—	—	—
1.843	1.840	1	0	1	9	1.841
1.818	—	—	−2	1	7	1.815
1.793	1.790	11	−1	3	4	1.793
1.774	1.772	3	1	3	4	1.771
1.752**	1.751	23	1	1	9	1.752
1.723	—	—	−3	1	4	1.716
1.708	—	—	−2	3	1	1.701
1.685*	—	—	—	—	—	—
1.644**	1.643	2	−3	1	5	1.645
1.632**	—	—	3	1	5	1.628
1.625	1.624	2	3	2	1	1.625
1.602	1.601	1	−3	2	3	1.602
1.594**	—	—	0	3	7	1.591
1.564	1.563	1	−2	1	9	1.562
1.530	1.529	7	0	1	11	1.528
1.509	1.509	2	2	2	8	1.510
1.436	—	—	−3	3	0	1.436
1.432	—	—	−3	3	1	1.431
1.428	—	—	—	—	—	—
1.395	—	—	−3	3	3	1.393
1.389	1.388	1	−2	4	0	1.386
1.373	1.372	3	4	1	3	1.372
1.363	1.362	3	3	3	3	1.363
1.360	—	—	2	4	0	1.360
1.351	—	—	−2	2	10	1.350
—**	1.263	1	3	1	10	1.263
—**	1.237	1	−4	1	7	1.237
—**	1.197	1	−3	3	8	1.197
—**	1.166	<1	−1	3	12	1.165
—	1.150	2	−5	1	1	1.149
—	1.144	1	5	0	3	1.144
—	1.030	1	0	6	2	1.030

The data marked by * belong to $Ba_4Tl_6O_{13}$ and those marked by ** could be overlapped by the two phases, confirmed by XRD spectrum of Fig. 5c.
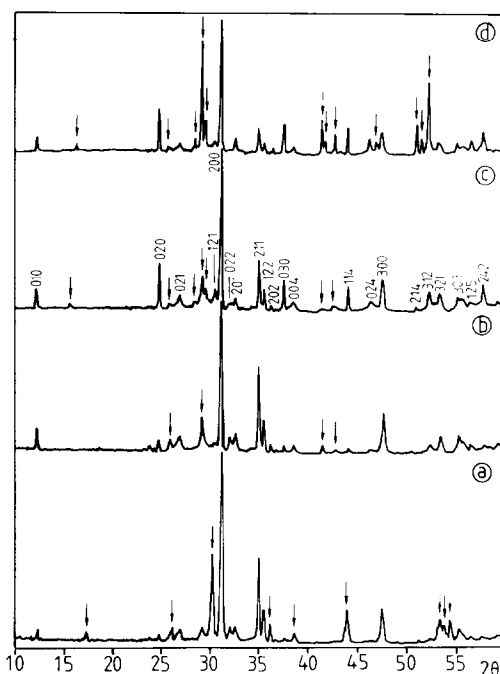

FIG. 5. XRD spectra from the nominal composition of $Ba_4Tl_6O_{13}$ with different preparation conditions, (a) 700°C for 12 hr, (b) 715°C for 20 hr, (c) 775°C for 12 hr and (d) 800°C for 12 hr. Most lines in c are indexed onto an orthorhombic unit cell of $Ba_4Tl_6O_{13}$. Extra peaks marked by arrows are from $BaTl_2O_4$ (a) and from $Ba_2Tl_2O_5$ (b,c,d).

715°C for another 20 hr, this impurity phase disappeared. However, $Ba_2Tl_2O_5$ became a minority phase in the sample (Fig. 5b). The sample which contained the smallest concentration of impurity phase was produced by heating at 775°C for 12 hr. Almost all peaks in the XRD spectrum (Fig. 5c) can be indexed onto the orthorhombic unit cell with $a = 5.748$, $b = 7.221$, and $c = 9.361$ Å deduced from the SAED analysis. It is obvious that the concentration of $Ba_2Tl_2O_5$ increases when the preparation temperature increases from 715 to 800°C. The XRD pattern of $Ba_4Tl_6O_{13}$ can fit that of the impurity phase in $Ba_2Tl_2O_5$ (Fig. 1) very well. Bear in mind that the $Ba_2Tl_2O_5$ structure can be regarded approximately as a $\sqrt{2} \times \sqrt{2} \times 4$ superstructure based on a distorted perov-

skite lattice; we assume that $Ba_4Tl_6O_{13}$ is still perovskite-related. Extra Tl cations replace Ba cations to form some Tl_2O_3-like blocks.

From these studies, we propose that in the process of solid state reaction of Ba and Tl oxides, Ba cations defuse into the Tl oxide lattice to form $BaTl_2O_4$, then $Ba_4Tl_6O_{13}$, and finally $Ba_2Tl_2O_5$, as the temperature and time increase. Clearly, the formation of these thallium-deficient phases may also be correlated with increasing thallium loss during the preparation. Although a single pure phase is difficult to prepare, most of the composite phases can be identified by a combination of SAED and EDS methods in conjunction with XRD studies. The structure of $Ba_2Tl_2O_5$ is still $Ca_2Fe_2O_5$-like; however, the unit cell dimensions determined previously (6) might not be correct. Further investigations of new phases in the Ba–Tl–O system are currently underway.

Acknowledgment

References

1. W. ZHOU, R. S. LIU, R. JANES, AND P. P. ED-WARDS, *Mater. Lett.* 9(4), 169 (1990).
2. VON. R.V. SCHENCK AND HK. MULLER-BUSCH-BAUM, *Z. Anorg. Allg. Chem.* **405**, 197 (1974).
3. E. F. BERTAUT, P. BLUM, AND A. SAGNIERES, *Acta Crystallogr. Copenhagen* **12**, 149 (1959).
4. J. BERGGREN, *Acta. Chem. Scand.* **25**, 3616 (1971).
5. A. COLVILLE, *Acta. Crystallogr. Sect. B* **26**, 1469 (1970).
6. M. ITOH, R. LIANG, AND T. NAKAMURA, *J. Solid State Chem.* **82**, 172 (1989).
7. W. ZHOU, R. JONES, D. TANG, D. A. JEFFERSON, AND P. P. EDWARDS, *J. Solid State Chem.*, in press (1990).