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Study of the Liquidus in the System Bi_2O_3–TiO_2

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The liquidus in the system Bi_2O_3–TiO_2 has been determined in the range 2 to 22 mole % TiO_2 by a thermobalance technique and by DTA. It has been confirmed that $Bi_{12}TiO_{20}$ melts incongruently at 875°C and that the eutectic composition between $Bi_{12}TiO_{20}$ and Bi_2O_3 melts at 795°C.

Introduction

There is much interest in the system Bi_2O_3–TiO_2 for the growth of single crystals of $Bi_{12}TiO_{20}$ (*1*) and $Bi_4Ti_3O_{12}$ (*2*) from solution using excess Bi_2O_3 as solvent. $Bi_{12}TiO_{20}$ is a noncentrosymmetric material of cubic symmetry (*3*) with interesting piezo electric (*4*), magneto-optic (*5*) and electro-optic properties (*6*). $Bi_4Ti_3O_{12}$ is a ferroelectric material with a very low switching voltage in the *C* direction and has received much study as a FERPIC device material (*7*). In order to grow single crystals of these materials by the top-seeded solution growth technique (*8*), a determination of the liquidus in the system relevant to the growth of these materials has been carried out.

The system Bi_2O_3–TiO_2 has been the subject of some study and recent work (*9*) has shown that three compounds exist, namely: $Bi_{12}TiO_{20}$, $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$. Two phase diagrams have been published. In 1965, Speranskaya et al. (*10*) using the DTA technique, identified three compounds: Bi_8TiO_{14}, $Bi_4Ti_3O_{12}$ and $Bi_2Ti_4O_{11}$ which were all incongruently melting. In 1964, work by Levin and Roth (*3*) identified the bismuth rich compound as $Bi_{12}TiO_{20}$ by hot stage X-ray diffraction and suggested that it is congruently melting. This work was extended by Morrison (*1*) who used a horizontal temperature gradient freeze technique and proposed two alternative phase diagrams with $Bi_{12}TiO_{20}$ melting either congruently or incongruently. Morrison concluded that the experimental evidence favored congruent melting but that the departure from congruent melting was small (less than 1 wt % TiO_2).

In this investigation a thermobalance technique (*11–13*) was used for the determination of solubility. Additional information was obtained by DTA and hot stage microscopy. Using these results single crystals of $Bi_4Ti_3O_{12}$ and $Bi_{12}TiO_{20}$ were grown from solution and more measurements of solubility could be made from these experiments.

Experimental Methods

The thermobalance technique has been reported as a tool in the investigation of solubility in high temperature solutions which does not suffer from the disadvantages of DTA and quenching experiments where there are uncertainties in interpretation and in the exact temperatures that are measured. The apparatus used was essentially as described in the literature (*11–13*) except that the balance was a Beckman LM600 electronic microbalance. The technique was to immerse a platinum wire, suspended from the balance, into a given composition of solution which had been heated until no solid was visible on the solution surface. The solution was slowly cooled at 20°C hr^{-1}. At the liquidus temperature an increase was observed in the weight of the wire. The wire could then be removed and the grown crystals were identified by X-ray diffraction. The temperature was recorded by two Pt–Pt 13% Rh thermocouples welded one to the side and one to the base of the crucible containing the solution. The exact temperature of the solution was different from that recorded by the welded thermocouples. The correlation between solution temperature and the welded thermocouples was

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determined separately by measuring the solution temperature above the liquidus with a Pt–Pt 13% Rh thermocouple sheathed in a platinum rhodium alloy (supplied by Johnson Matthey Metals Ltd.). The reagents used in the determination were grade 1 bismuth oxide and titanium oxide supplied by Johnson Matthey Chemicals Ltd.

In determining the liquidus by growth onto a platinum wire there was a systematic error due to the additional driving supersaturation required to nucleate growth onto platinum. Usually a period of rapid growth followed the initiation of nucleation. To determine the liquidus more exactly an approximate determination was made using the platinum wire. The solution was heated up by 20°C and a seed crystal of the appropriate phase was immersed in place of the platinum wire and weighed. The solution was then cooled at 20°C hr^{-1} and, the weight of the seed crystal decreased (dissolution), remained constant and then increased with decreasing temperature. The liquidus temperature was taken as that temperature for which the seed crystal was constant, i.e., the temperature at which the solid phase was in equilibrium with the liquid. This liquidus was used for the results shown in Fig. 1. The determination was repeated three times at each composition. The difference between the liquidus temperature as determined by using a platinum wire and a seed crystal was typically 4°C in the region where $Bi_4Ti_3O_{12}$ crystallized but was much greater in the $Bi_{12}TiO_{12}$ region where differences as great as 20°C could be observed but 8°C was more typical at 10 mole % TiO_2.

DTA using a Dupont 990 instrument was carried out on samples of ground crystals of $Bi_{12}TiO_{20}$ and on samples of ground crystals of $Bi_{12}TiO_{20}$ mixed with Bi_2O_3 to give compositions of 2 and 10 mole % TiO_2. The latter samples were repeatedly fired at 900°C and reground prior to the DTA determination. A hot stage microscope was used to measure the melting point of $Bi_{12}TiO_{20}$.

Crystal growth experiments were carried out by seeding solutions of which liquidus temperature had previously been determined and slowly cooling at 1°C hr^{-1}. The grown crystal was left in the solution for several hours when the slow cooling program had stopped so that equilibrium between solid and liquid could be attained. The grown crystal was then weighed and knowing the initial composition of the solution its final composition was then calculated assuming that the grown crystal was all $Bi_4Ti_3O_{12}$ or $Bi_{12}TiO_{20}$ as appropriate. As the solution was in equilibrium with the solid, the final temperature of the solution is the liquidus temperature for the final composition. In this way crystal growth experiments were used to verify the findings of the thermobalance determinations. This procedure was used with three different melts and agreement with the thermobalance determination was found to within ±3°C.

Results and Discussion

The liquidus in the system Bi_2O_3–TiO_2 has been measured in the range 2 to 22 mole % TiO_2 and the results are shown in Fig. 1. The form of

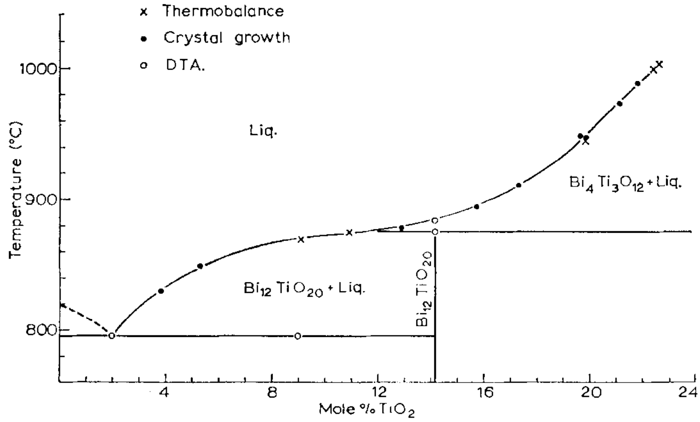

FIG. 1. The liquidus of the system Bi_2O_3–TiO_2 in the range 2 to 22 mole % TiO_2 as measured by thermobalance, DTA and crystal growth experiments.

the results is similar to that given by Speranskaya et al. (*9*) except the bismuth-rich compound is identified as $Bi_{12}TiO_{20}$. The bismuth:titanium ratio was measured by X-ray fluorescence for bismuth and a colorimetric method for titanium on single crystals grown from solution and was found to be 12:1 in agreement with the most recent work (*1*, *9*). The eutectic composition between Bi_2O_3 and $Bi_{12}TiO_{20}$ is 2 mole % TiO_2 and the melting point of this composition is 795°C as measured by DTA.

Figure 1 shows $Bi_{12}TiO_{20}$ melting incongruently. This conclusion was reached on the evidence that $Bi_4Ti_3O_{12}$ single crystals could be grown from solutions by the seeded growth technique in the composition range 14 to 12 mole % TiO_2, i.e., on the Bi_2O_3-rich side of the $Bi_{12}TiO_{20}$ composition; that when crystals were grown by the Czochralski technique from the stoichiometric $Bi_{12}TiO_{20}$ melt the grown boule invariably contained only Bi_2O_3 and $Bi_4Ti_3O_{12}$ (*14*); that the DTA curve for the composition $Bi_{12}TiO_{20}$ showed a broad peak corresponding to the peritectic at 875°C and a smaller peak at 884°C corresponding to the observed liquidus determined by the thermobalance measurements. Hot stage microscopy gave the melting point of $Bi_{12}TiO_{20}$ as 873°C.

The conclusion that $Bi_{12}TiO_{20}$ is incongruently melting is apparently inconsistent with the reports that it may be grown by the Czochralski technique (*4*, *5*). No details were given of the growth procedure but it may be seen from Fig. 1 that only slight excess Bi_2O_3 (to change the composition of the melt by 0.4 wt % TiO_2) needs to be added to grow single phase $Bi_{12}TiO_{20}$. The fact that the Czochralski growth technique has been used for this material is not sufficient evidence to establish congruent melting. It is well known that the technique can be used to grow materials from nonstoichiometric melts, e.g., in this laboratory single crystals of $Bi_{40}Ga_2O_{63}$ which is very similar to $Bi_{12}TiO_{20}$, have been grown from such a melt (*15*).

Morrison (*1*) noted that $Bi_{12}TiO_{20}$ was precipitated from solutions more Bi_2O_3 rich than 97.2 wt % Bi_2O_3. The results of this study are in agreement, the transition growth of $Bi_4Ti_3O_{12}$ to $Bi_{12}TiO_{20}$ occurs at 12 mole % TiO_2 (97.2 wt % Bi_2O_3). The peritectic melting of $Bi_{12}TiO_{20}$ was found to be lower (875°C) than that given by Morrison (920°C) but was close to that given by Speranskaya et al. (865°C). Morrison's high figure was probably due to errors in assigning exact temperatures to different regions of the boat.

Conclusion

The liquidus of the system Bi_2O_3–TiO_2 has been determined for the range 2 to 22 mole % TiO_2 with sufficient precision for single crystals of $Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$ to be grown by the top-seeded solution growth technique. It has been confirmed that $Bi_{12}TiO_{20}$ is incongruently melting and this observation is consistent with previous published work.

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