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THERMOANALYTICAL AND SINGLE CRYSTAL GROWTH INVESTIGATIONS IN THE SYSTEM $Bi_2O_3-P_2O_5$ AND $Bi_2O_3-Nd_2O_3-P_2O_5$

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ABSTRACT

The melting diagram $Bi_2O_3-P_2O_5$ has been studied by DTA and simultaneous DTA-high temperature microscopy in the composition range 80 to 92.7 mol% Bi_2O_3. A compound is found at the ratio $Bi_{5.80}PO_{11.20}$ melting congruently at 951°C. By the Czochralski technique single crystals were grown of this compound either pure or doped with neodymium.

INTRODUCTION

Single crystals are advantageously grown from a melt of that composition with the melting point maximum. DTA and high temperature microscopy (HTM) are well suited to characterize the melting and freezing behavior in a binary or more complex system, thereby they provide a model of the transformations underlying the crystal growth process.

A compound was reported to exist at the composition Bi_5PO_{10} in the $Bi_2O_3-P_2O_5$ section of the Bi-P-O ternary [1], melting congruently at 977°C, and to be grown as single crystal [1,2]. Our attempts to prepare Bi_5PO_{10} single crystals as new laser host material failed. Independently of the preparation method we obtained a mixture that exhibited partial eutectic melting. Better knowledge of the relevant part of the pseudobinary $Bi_2O_3-P_2O_5$ melting diagram was necessary as prerequisite for single crystal growth.

PHASE DIAGRAM STUDY

DTA and simultaneous DTA-HTM [3] were applied to mixtures of $BiPO_4$ and Bi_2O_3 to cover a concentration range 80 mol% Bi_2O_3, 20 mol% P_2O_5-92.7 mol% Bi_2O_3, 7.3 mol% P_2O_5. $BiPO_4$ was prepared by sintering Bi_2O_3 + 2 $NH_4H_2PO_4$. Heating curves at β = 10 K min^{-1} of samples ≈ 60 mg were evaluated, since the melts crystallized

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after undercooling by 30 to 50 K. The eutectic effect was quantitatively estimated from the ratio of its peak heigth to the peak height of the liquidus effect. A calorimetric evaluation of the eutectic peak area gave worse results due to partial overlapping with the liquidus peak.

RESULTS

Phase diagram results are shown on fig. 1. A liquidus temperature maximum appeared at a concentration 85.3 mol% Bi_2O_3, 14.7 mol% P_2O_5 and 951°C. A eutectic was found at 925°C for < 85.3 % Bi_2O_3 and three peritectic transformations at 932°C for > 85.3, at 918°C for > 86.5 and at 865°C for > 87.3 mol% Bi_2O_3. Disappearance of the eutectic and peritectic effects suggested a narrow phase width corresponding to a formula $Bi_{5.80+\delta}PO_{11.20+3\delta/2}$ $(-0.06 \leq \delta \leq +0.04)$. The DTA diagrams of both a single crystal sample and powder of the composition

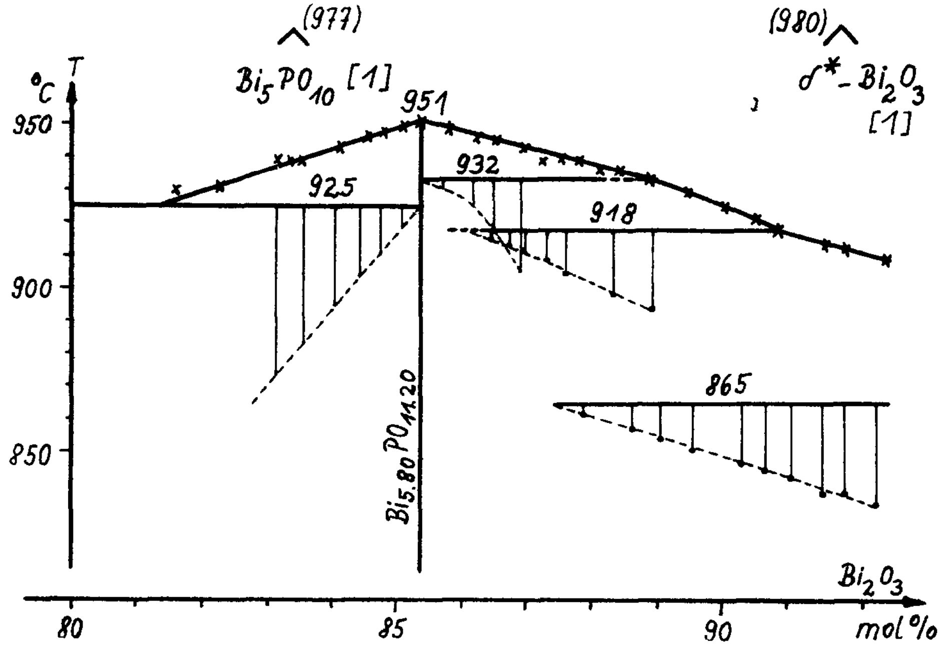

Fig. 1 Melting diagram of the system Bi_2O_3-P_2O_5 between 80 and 92.5 mol% Bi_2O_3. Melting point maxima reported by Volkov et al. [1] are indicated.

$Bi_{5.80}PO_{11.20}$ were identical, only one melting peak is seen. No solid state transformation was detected between room and melting temperature. We assume that the non-stoichiometric compound was erroneously described by previous authors [1,2] as Bi_5PO_{10}. No evidence was found for another congruently melting phase between 91 and 92 mol% Bi_2O_3, assigned [1] to a non-stoichiometric δ^*-Bi_2O_3 phase.

SINGLE CRYSTAL GROWTH

In accordance with the thermoanalytical results single crystals could be easily grown from a melt $Bi_{5.80}PO_{11.20}$ thus confirming this composition. Honey-yellow crystals were obtained by the Czochralski technique (RF heating, platinum crucible and after-heater, ambient atmosphere) with dimensions up to 15 mm diameter, 40 mm length.

NEODYMIUM DOPING

DTA and HTM experiments were performed along the sections $Bi_{5.80}PO_{11.20}$-$Nd_{5.80}PO_{11.20}$ and $Bi_{5.80}PO_{11.20}$-$NdPO_4$ of the Bi_2O_3-Nd_2O_3-P_2O_5 ternary system to get insight into the possibilities for growing neodymium doped $Bi_{5.8}PO_{11.2}$. Even at low Nd:Bi ratio > 0.01 there remained a small undissolved fraction in the melt, indicating a steep increase of the liquidus temperature. An endothermal effect around 925°C may be explained by a ternary eutectic in the Bi_2O_3-Nd_2O_3-P_2O_5 system. At concentrations Nd:Bi $\leq$ 0.01 crystal growth experiments were successful with both $Nd_{5.8}PO_{11.2}$ and $NdPO_4$ as dopants.

CONCLUSIONS

The melting diagram Bi_2O_3-P_2O_5 [1] has to be revised, there exists no compound Bi_5PO_{10}, instead a non-stoichiometric compound $Bi_{5.80}PO_{11.20}$, melting congruently at 951°C, was established. Single crystals of $Bi_{5.80}PO_{11.20}$ can be grown from a melt of this composition, supporting the first conclusion.
$Bi_{5.80}PO_{11.20}$ can be doped with neodymium, probably by crystallochemical substitution $Bi_{5.8(1-x)}Nd_{5.8x}PO_{11.2}$ ($x \leq 0.01$).
DTA and thermomicroscopy are useful techniques to be applied in conjunction with single crystal growth.

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