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DETERMINATION OF THE PHASE DIAGRAMS, PbO—$Pb(Fe_{1/2}Nb_{1/2})O_3$ AND PbO—$Pb(Mn_{1/2}Nb_{1/2})O_3$

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ABSTRACT

The phase diagrams of the pseudo-binary systems PbO—$Pb(Fe_{1/2}Nb_{1/2})O_3$ and PbO—$Pb(Mn_{1/2}Nb_{1/2})O_3$ have been determined by means of differential thermal analysis in connection with a project to grow the respective perovskite single crystals by high temperature solution techniques.

INTRODUCTION

According to the literature [1,2], $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) and $Pb(Mn_{1/2}Nb_{1/2})O_3$ (PMN) undergo structural and ferroelectric phase transitions and, at lower temperatures, exhibit several changes in magnetic ordering.

Up to now, all physical characterization has been made on ceramics or on very small single crystals (<1 mm cube edge) without any optical control of the ferroelectric and/or magnetic domain structure. With a view to studying optical properties, which are so sensitive to changes in magnetic and crystallographic structure, a program has been launched to grow good quality PFN and PMN single crystals of sufficient size to make such measurements.

Previous workers have synthesized these perovskites from high temperature solutions using fluxes of PbO, $PbCl_2$, PbO—$PbCl_2$, or PbO—PbF_2 [1—4] but without knowledge of the relevant phase diagrams. To minimise the complexity of the solvent—solute system, we have preferred a flux of PbO and have studied the pseudo-binary phase diagrams of PbO—PFN and PbO—PMN using differential thermal analysis (DTA). The results indicate the optimal conditions for crystal growth and so allow a saving of project time and expense, especially important factors in slow-cooling flux growth experiments, which can easily take up to 3 months.

EXPERIMENTAL

To produce ceramic PFN, stoichiometric ratios of PbO p.a. *, Fe_2O_3 p.a. *, and Nb_2O_5 p.a. * were thoroughly mixed and pellets of 5 mm diame-

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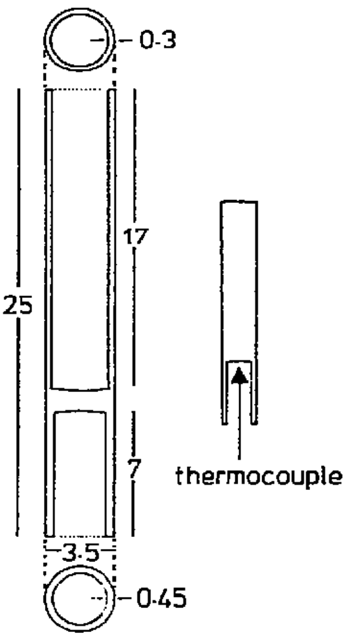

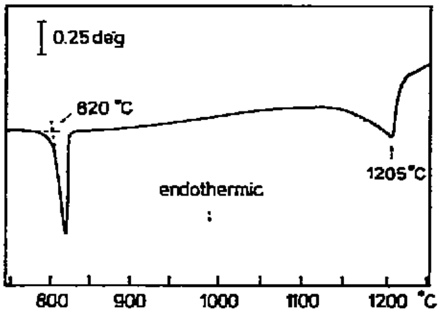

Fig. 1. The platinum sample crucible. The dimensions are in mm.

Fig. 2. A typical DTA measurement with 30 wt. % PbO—70 wt. % PFN. Sample weight 99.64 mg; heating rate 4 deg min^{-1}.

ter and about 3 mm thickness prepared. These were fired in air for about 5 h at around 840°C in a platinum crucible with lid, after which they were ground and the process repeated. For the PMN compound, MnO_2 p.a. * was heated in air at 700°C for several hours to form Mn_2O_3 [5], confirmed by X-ray diffraction, and the correct ratios of PbO, Mn_2O_3, and Nb_2O_5 (all p.a. *) were then mixed. The same procedure was followed as with PFN but firing was performed at 920°C. A monophase perovskite structure was verified for both compounds using Guinier powder photographs.

DTA measurements were recorded on a Mettler TA1 apparatus. The sample and reference (Al_2O_3) weight was typically about 80 mg. All experiments were performed with a heating/cooling rate of 4 deg min^{-1} and under a nitrogen flow of 5 l h^{-1}.

The first type of crucible used was simply a sealed platinum tube which sat in a bed of fine Al_2O_3 powder in an open crucible in contact with the thermocouple; however, the sensitivity of this system was too low to observe the liquidus peaks. To solve this problem, we adopted another crucible design, shown in Fig. 1. It was machined from an annealed platinum rod and its form allows it to sit directly in contact with the thermocouple. In order to prevent weight loss and decomposition of the oxides, the full sample crucibles were sealed by an argon arc or a propane—oxygen flame. Preliminary tests were made with PbO alone to make sure that no decomposition was occurring as lead readily forms an alloy with platinum [6] at the temperatures of the study. Great care was taken to avoid contamination of the crucible with traces of organic material or water during the sample loading.

An example of a typical measurement is displayed in Fig. 2. Temperature calibration was effected by measurements on the following standard substances (with their melting points): Na_2SO_4 (884°C), $SrCO_3$ (925°C), K_2SO_4 (1069°C), and CaF_2 (1418°C). In addition, the phase transition at 585°C in K_2SO_4 was used.

RESULTS AND DISCUSSION

The phase diagrams of PbO—PFN and PbO—PMN systems are shown in Figs. 3 and 4. A eutectic temperature of 820 ± 5°C was found for PFN and 830 ± 5°C for PMN with the eutectic compositions located at 15 wt.% PbO—85 wt.% PFN (±3%) and 10 wt.% PbO—90 wt.% PMN (±3%). Additionally, a hysteresis between the liquidus temperature recorded for heating and that for cooling was observed and amounted to 10—20 degrees in both systems. This quantity is a measure of the width of the Ostwald—Miers or metastable region in the phase diagrams and is important for high temperature solution crystal growth experiments [7].

After the DTA run, the capsule was opened and small micro-crystals could be observed under the microscope. X-Ray analysis showed that the perovskite structure stands in equilibrium with PbO. After melting, the nominal PFN and PMN compositions yielded the perovskite phase only. This latter result strongly indicates congruent melting for these compounds and so suggests the interesting possibility to synthesize crystals adopting the Czochralski technique.

Recent successful crystal growth experiments [8] using the phase diagrams have produced good quality single crystals of dimensions superior to those reported previously and several are shown in Fig. 5. Preliminary optical studies on PFN polished platelets have revealed a previously unreported phase transition below the ferroelectric Curie point [9].

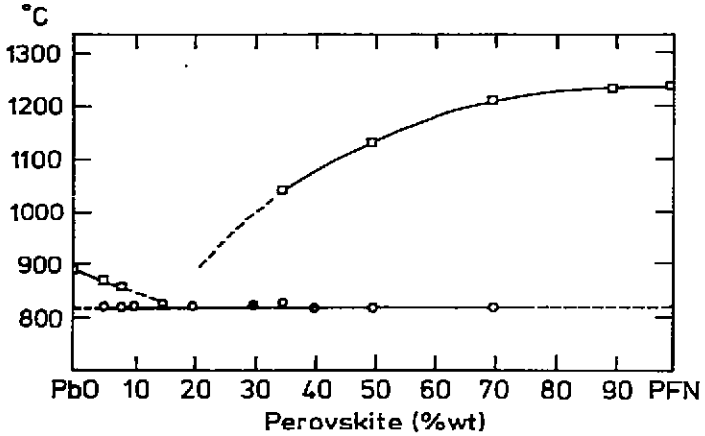

Fig. 3. The PbO—PFN phase diagram. The filled circles indicate the measurements made with the less sensitive platinum tube crucible form.

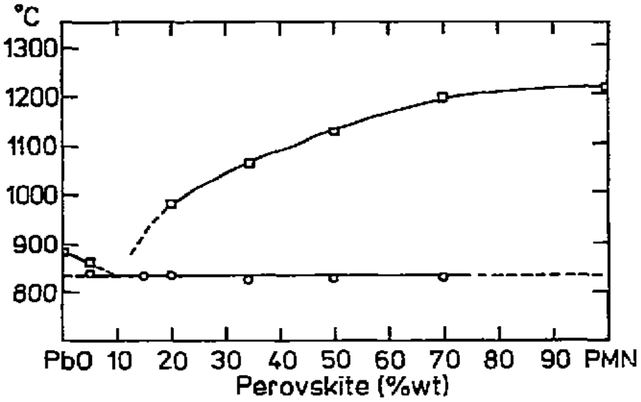

Fig. 4. The PbO—PMN phase diagram.

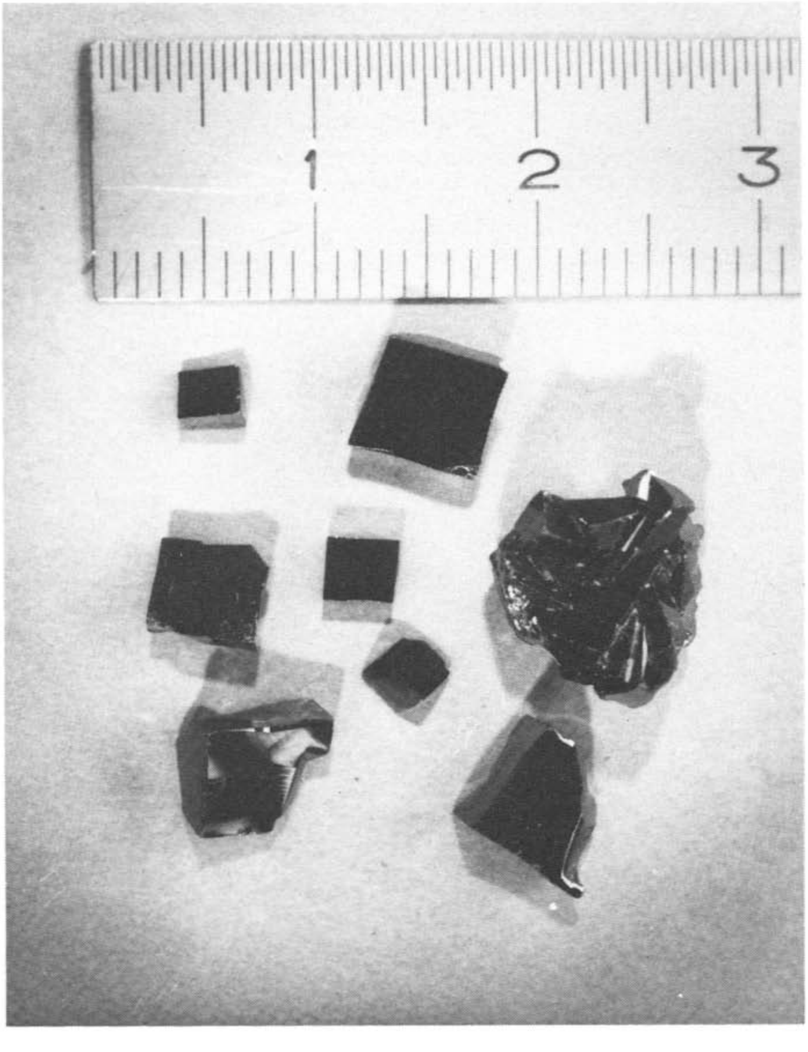

Fig. 5. A selection of some of the perovskite crystals, $Pb(Fe_{1/2}Nb_{1/2})O_3$, grown [8] using the phase diagram reported in this paper.

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