Diagram of the PbF$_2$–SnF$_2$ System

P. P. Fedorov$^a$, V. K. Goncharuk$^b$, I. G. Maslennikova$^b$, I. A. Telin$^b$, and T. Yu. Glazunova$^c$

$^a$Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, Moscow, 119991 Russia
$^b$Institute of Chemistry, Far-East Branch, Russian Academy of Sciences, pr. Stoletiya Vladivostoka 159, Vladivostok, Russia
$^c$Moscow State University, Moscow, 119991 Russia

e-mail: ppf@lst.gpi.ru

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Abstract—A phase diagram of the PbF$_2$–SnF$_2$ system has been studied by differential thermal analysis and X-ray powder diffraction. The system forms Pb$_{1-x}$Sn$_x$F$_2$ ($x \leq 0.33$) solid solution and three compounds. Pb$_2$SnF$_6$ decomposes in solid state by a peritectoid reaction at 350°C; Pb$_3$Sn$_2$F$_{10}$ and PbSnF$_4$ melt by peritectic reactions at 565 and 380°C, respectively. The eutectic coordinates are 180°C, 90 mol % SnF$_2$.

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The compound PbSnF$_4$ has a maximal anionic conductivity among the fluoride-ion conductors [1]. These properties of PbSnF$_4$ were discovered at the Laboratory of Solid State Chemistry (Bordeaux, France), headed by Hagenmuller [2–4]. Abundant documentation concerns electrochemical properties, polymorphism, and preparation of PbSnF$_4$ (see, e.g., [3–14]). Many lead fluoride-based [1, 15–18] and tin-based [1, 19, 20] compounds and solid solutions have been studied for finding fluoride-conductive solid electrolytes and for recognizing the trends of high anionic conductivity.

Phase equilibria in the PbF$_2$–SnF$_2$ system have been studied incompletely. Some data were obtained in the synthesis and characterization of solid electrolytes. PbSnF$_4$ is a compound having complex polymorphism [3, 5] (Fig. 1). All of its polymorphs have fluorite-like structures. The lattice symmetry increases, as temperature rises, from orthorhombic (monoclinic) (α) through tetragonal (β) to cubic (γ).

Studies of the title system in solid state showed the formation of fluorite solid solutions Pb$_{1-x}$Sn$_x$F$_2$, where $x \leq 0.3$, with the saturation boundary being $x = 0.25$ at 350°C [6]. Two fluorite-like phases were found to exist, β" and β", whose compositions approximately correspond to compounds Pb$_2$SnF$_6$ and Pb$_3$SnF$_{10}$, respectively. These phases have tetragonally distorted fluorite lattice, just as β-PbSnF$_4$, but with differing superstructures.

Tin(II) fluoride compounds have unusual crystal chemistry due to the stereochemically active lone pair of Sn$^{2+}$ [21]. This specific feature facilitates the formation of SnF$_2$-containing fluoride glasses [22–23].

Our goal in this study was to construct a PbF$_2$–SnF$_2$ phase diagram and elucidate the melting characters of phases and the specifics of their equilibration with melt. Preliminary data pertaining to the 50–100% SnF$_2$ region can be found in the survey [26]. Here we continue our studies into phase diagrams in PbF$_2$–MF$_2$, where M = Mg [27], Ca, Sr [28], Ba [29], and Cd [30] systems.

EXPERIMENTAL

We tested two protocols. In the region where compositions are rich in lead fluoride, we used the protocol similar to that we used earlier to study the PbF$_2$–ZrF$_4$ phase diagram [31]. A lead difluoride sample (high purity grade) was vacuum dried at 300–350°C for 1 h. Tin difluoride was prepared by fluoriding metallic tin (a pure for analysis grade sample) with ammonium hydrodifluoride [32]. After the ammonium fluoride was removed almost completely, the thus-prepared SnF$_2$ containing minor NH$_4$Sn$_2$F$_5$ was recrystallized from hydrofluoric acid over metallic tin.

![Fig. 1. Scheme of polymorphic transformations in PbSnF$_4$ according to Perez et al. [5].](image-url)
The resulting tin difluoride was dried for 24 h in air, then pounded in a mortar for 5 min, and vacuum dried at 100°C. A sample with a total weight of 5 g was stirred at room temperature in a Pulverisette 7 premium line (FRITSCH) planetary micromill at 800 rpm for 60 min (six 10-min cycles). Reverse was up; the working body was made of zirconia. Samples to be milled were charged in and discharged from milling beakers inside a drybox. Milled samples were stored inside a drybox filled with argon and cells with P₂O₅. Differential thermal analysis (DTA) was performed on an MOM Q-1000 instrument interfaced with a computer. Samples were transferred to DTA crucibles inside a drybox. A crucible was mounted in a special designed construct for heating a sample in a covered crucible under the vapor pressure of the sample with an access of air being precluded to the maximal possible degree. Platinum crucibles were used; the heating rate was 5 K/min. The measurement accuracy was ±5 K/min; sample sizes were 0.90–0.95 g.

Fig. 2. PbF₂–SnF₂ phase diagram. Notations: L = melt, F = Pb₁₋ₓSnₓF₂ fluorite solid solution, S₁ = Pb₂SnF₆, S₂ = Pb₃Sn₂F₁₀. (1) platinum crucibles, (2) graphite crucibles, and (3) borrowed from [2, 4].