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Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

NUCLEATION AND CRYSTALLIZATION OF WO_3 FROM PURE AND Pb^{2+} DOPED NaF FLUXES

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Abstract

DTA runs and flux growth experiments have shown that the crystallization temperatures of WO_3 from NaF flux are in the range of 1020–1090°C. Addition of Pb^{2+} influences the crystal growth and the crystallization temperatures are altered (within this range). A thermal effect giving rise to an exothermal DTA peak was observed above the crystallization temperature. This peak occurs at a higher temperature when lead ions are present. We propose an explanation based on pre-crystallization clustering and on the number of nucleation sites on the surface of the platinum crucible.

Keywords: nucleation and crystallization of WO_3, WO_3

Introduction

WO_3 was used as a model solute in flux growth experiments because of its relatively low melting point for an oxide (1470°C), its high solubility (in fluxes) below 1250°C (which result in high growth rates and in the possibility of the growth of a few, large crystals) and because of the relatively large, easily observed DTA peaks.

In the past, several aspects were studied: i) the effect of increasing the concentration of Pb^{2+} on WO_3/NaF/Na_2O flux growth systems [1]. Increasing Pb^{2+} concentration resulted (after 10 h soak between 1140–1250°C) in fewer, larger crystals instead of many small ones. X-ray diffraction showed the crystals to be WO_3. Electron microprobe analysis showed that the crystals contained no detectable amounts of Na^+, Pb^{2+} or F^- (less than 100 ppm). The authors suggested

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that lead ions could act as nucleation centers in the liquid, similar to what has been described previously for aqueous solutions of alkali halides containing Pb^{2+} [2–4], the prenuclei being responsible for the exceptional growth of a few large crystals; ii) induction times. In the WO_3/NaF flux growth system, induction times became longer after higher soak temperatures [5]. Induction times in the system $Pb_2V_2O_7/V_2O_5$ became longer when the melt was successively cooled to above the eutectic and then reheated [6]. When cooled below the eutectic and reheated the original induction time was restored. The longer induction times were explained as being due to dissolution of nucleation centers on the platinum surface. The same authors conclude in a later article [5] that "At that time (1984) the idea of clusters in fluxed melts had not been proposed and the suggestion then made was that nucleation sites at the crucible surface were being removed. However, the induction behavior of $Pb_2V_2O_7$–V_2O_5 can be accounted for in terms of clusters which become smaller and fewer at soak temperatures both above and below the liquidus"; iii) the effect of successively using the same platinum crucible on nucleation and growth. It was concluded for the system $Pb_2V_2O_7/V_2O_5$ that nucleation sites are gradually removed from the crucible surface by dissolution of platinum into the flux [6]. It has been reported for $DyFeO_3$ crystals grown from flux [7], that this Pt precipitated as Pt grains on the crystal surface when the batches were cooled below the eutectic, in contact with the flux. But, when the batches were "hot-poured" (i.e. the flux was separated by inverting the crucibles at temperatures higher than the eutectic) there was no Pt deposit on the crystal surface. TG experiments [6] (for $TmVO_4$, $DyPO_4$ and Fe_2O_3, where crystallization took place on a Pt wire attached to an electrobalance arm and its tip immersed in the flux) confirmed that the condition of the platinum wire surface affects the crystallization temperature during programmed slow cooling. On a new wire, crystallization took place at lower temperatures (implying fewer nucleation sites) but for work-hardened wire (hardened and then used in the flux) crystallization temperature was higher than for a new wire i.e. more nucleation sites. The authors conclude that in order to obtain a small number of crystals either new crucibles or a long soak at high temperature is needed.

In this article we report the results of DTA experiments of WO_3 crystal growth (from flux) in the temperature range of 930–1170°C in order to try to clarify the effects of the addition of Pb^{2+} and of successively used crucibles.

Experimental

In order to attribute a specific event or a reaction to each of the DTA peaks temperatures, flux growth experiments were carried out. Interrupted flux growth experiments were carried out to observe whether or not WO_3 had crystallized above the interruption temperature. In uninterrupted experiments, the compositions were cooled from soak temperature to room temperature at $10°C\ h^{-1}$. Several flux growth experiments were carried out with thermal cycling (see later).

In DTA runs and flux growth experiments WO_3 (BDH Lab. Reagent) and NaF (BDH Analar) were used (as in [1]) with increasing amounts of Pb^{2+} added as PbF_2 (BDH Extra Pure). The molar ratios of the compositions used were:

100 WO_3:44 NaF:0 PbF_2; 100 WO_3:44 NaF:0.001 PbF_2;
100 WO_3:44 NaF:0.25 PbF_2 and 100 WO_3:44 NaF:5 PbF_2.

DTA data was obtained with a Stanton-Redcroft Pt–Rh wound furnace and a sample block assembly, a "home made" multi-step temperature programmer and controller and an amplifier for the DTA signal. A new Pt crucible was used for each composition. The crucibles had an upper lid welded under vacuum by electron beam, in order to facilitate many experiments with the same crucible without evaporation losses. The sample was heated to soak temperature (1170°C), left for 1 h soak time for each of the consecutive runs and cooled down sometimes below 600°C (past a second crystallization), sometimes below 300°C and sometimes to room temperature i.e. below the eutectic temperature. The cooling/heating rate was 25°C min^{-1}, because with smaller cooling/heating rates (i.e. 5 or 10°C) DTA peaks were hardly visible in the 1170–800°C temperature range. The crucibles were weighed before runs, after a few runs and after the last run. The change in mass was less than 1 mg for 200–400 mg samples.

The furnace used for flux growth was heated by Crusilite elements which provided a vertical temperature gradient so that the crucible base was several degrees cooler than the top. The stability was within 0.3°C.

Two new 20 ml platinum crucibles, free from lead contamination, were used starting with the first experiment (Table 1). Each crucible was covered with a tightly fitted lid (sometimes with and sometimes without an inner lid [8], as indicated in Table 1) to reduce evaporation and all this was covered by an inverted 50 ml platinum crucible to reduce temperature oscillations. A thermocouple was placed with its tip adjacent to the crucible base.

The platinum crucibles were held in a nearly closed brick boat located in the rear part of an sintered Al_2O_3 tube. This enabled: 1) a very fast hot-pouring process which interrupted a flux growth experiment, by making a 180° rotation at the hot-pouring temperature, withdrawing the whole set and letting it cool to room temperatures in several seconds; 2) Flux growth experiments with a cooling rate of 10°C h^{-1} down to room temperature.

In order to compare flux growth results with those of DTA, in a few experiments an initial thermal-cycling process was added, i.e. the liquid was cooled (after 1 h soak) at the rate of 20°C min^{-1} from 1170 to 930°C, then heated at the same rate to 1170°C, with 1 h soak time. This cycle was repeated 10 times and only then was the liquid slowly cooled from 1170°C to room temperature, at 10°C h^{-1}. This cycling simulates the effect of many consecutive DTA experiments with the same flux mixture.

X-ray powder diffraction was used to identify the crystals.

Table 1 Flux growth experiments

Batch number	Pb^{2+}amount mol[#]	Total mass/g	Mass loss/%	Soak temp./°C	Soak time/h	Hot pour/°C	Comments
a1	0	25	8.8	1170	1	1012	≈40WO_3 crystals. Largest 2×2 mm
a2	0.003	37	8.6	1160	1	1020	≈100WO_3 crystals
a3	0.25	37	6	1100	1.5	980	many small crystals
b1	0	25	6.0	1170	1	1070	no crystals on bottom and walls
b2	0.002	37	9	1170	1	1110	small thin WO_3 platelets
b3	0.01	35	5 *	1110	1.5	1110	no crystals on bottom and walls
b4	0.25	37	6 *	1100	1.5	1100	no crystals on bottom and walls
b5	0.25	37	5 *	1100	4	1100	material at bottom undissolved
b6	0.25	37	5 *	1110	4	1110	no crystals on bottom and walls
b7	0.25	22	6 *	1110	3	1110	no crystals on bottom and walls
b8	5	22	9 *	1110	3	1110	no crystals on bottom and walls
c1	5	1.6	6	1110	5	1110	no crystals on bottom and walls
d4	0	25	14*	1170	**	***	10 large crystals
d5	5	25	17*	1170	**	***	10 large crystals

[#] $XPbF_2$:100WO_3:44NaF;

* Crucibles with an inner lid.

** Ten soak cycles. See experimental part.

*** Cooling at 10°C h^{-1} to room temperature.

Results

DTA peaks are seen in two temperature ranges: 1000–1200°C and 600–700°C. This study deals with the peaks in the higher range (unlike [5] which only studied the lower range). As the temperatures of the peaks, the hights and the relative areas are different in different runs, a schematic DTA graph only is given in Fig. 1.

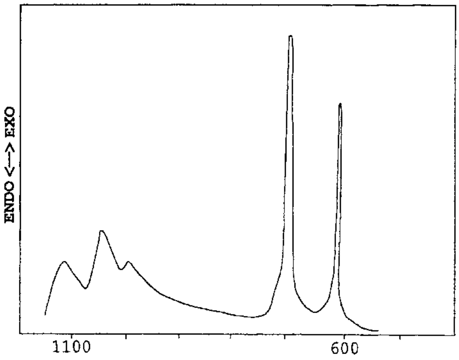

Fig. 1 DTA runs of WO_3–NaF (with or without lead) mixtures. A schematic graph

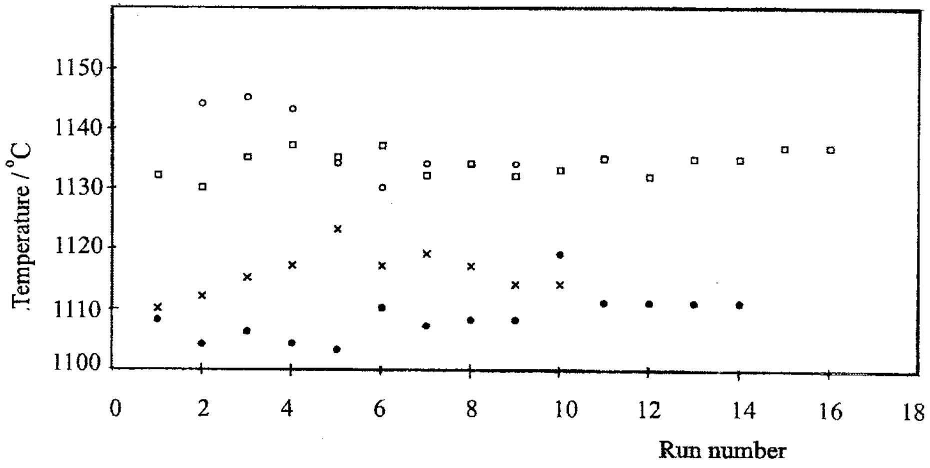

Fig. 2 Temperatures of the first DTA exotherms. Molar ratios of sample compositions:
• – $0PbF_2:100WO_3:44NaF$; × – $0.001PbF_2:100WO_3:44NaF$;
□ – $0.25PbF_2:100WO_3:44NaF$; ○ – $5PbF_2:100WO_3:44NaF$

During DTA runs two exothermic peaks clearly appear, on cooling, at high temperatures, above 1000°C. For samples without Pb^{2+}, usually only one sharp peak (the first) with a broad tail was observed and only rarely two peaks. The

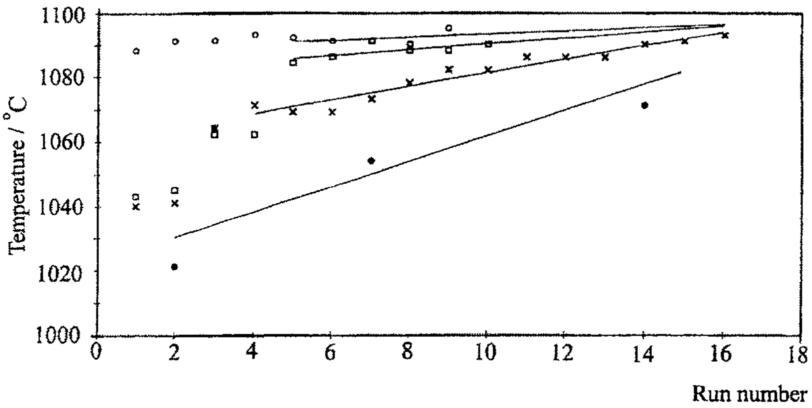

Fig. 3 Temperatures of the second DTA exotherms. Molar ratios of sample compositions:
• – $0PbF_2$:$100WO_3$:44NaF; × – $0.001PbF_2$:$100WO_3$:44NaF;
¤ – $0.25PbF_2$:$100WO_3$:44NaF; o – $5PbF_2$:$100WO_3$:44NaF

data relating to the first and second DTA peaks are summarized in Figs 2 and 3. A third exotherm, smaller and broader is sometimes observed (several times as a tail of the former peaks).

The first DTA exothermic peak appears between 1100 and 1150°C and its position remains fairly constant even after several runs. The temperature of this peak increases when Pb^{2+} is added.

The second exothermic DTA peak appears between 1020 and 1090°C. In the first run the temperature of the second peak depends on the Pb^{2+}concentration, but it rises with the number of runs and after several consecutive runs the position of this DTA peak is about the same for all dopant concentrations, about 1090°C, i.e. the same as that of the second peak for the sample with the highest PbF_2 concentration (5 PbF_2:100 WO_3:44 NaF).

The results of all types of flux growth experiments are summarized in Table 1.

Discussion

Experiments a1, a2 and a3 (Table 1) show that WO_3 certainly crystallizes above 980°C in each case.

The DTA curves showed (on cooling) a first high temperature peak between 1100 and 1150°C. From the hot-pouring experiments, it is clear that this is not a crystallization peak as no crystals were found on the walls and bottom of the crucibles on inverting the crucibles at 1100°C (experiments b1–b8). The original WO_3 was completely dissolved after soaking at 1100°C (experiments b1, b3–b8). The temperature at which the first DTA peak appeared varied with lead concentration and remained about the same in consecutive runs.

We suggest that this first exothermic peak may be attributed to heat released by some kind of organization reaction in the melt. Two models may be considered and based upon this study one cannot decide which is correct for the reorganization in the WO_3 system: i) the added Pb^{2+} ions serve as nucleation centers around which clusters of the solute are formed. That small amounts of lead ions can create clustering with heat evolution has been proved by Glasner *at al.* (as an example [2–4]) for Pb^{2+} added to aqueous alkali halides solutions. One should consider the possibility that this can also occur in melts. Some organization in the melt (even of pure WO_3) may occur, resulting in small clusters, the agglomeration of which later forms WO_3 crystals; ii) the added Pb^{2+} ions are located on the surface of the clusters and stabilize them. A work studying the crystalloluminescence of alkali halides in aqueous solutions with added Pb^{2+} [9] claims that the nucleus consists of an aggregation of ions in which the activating heavy metal impurity is located on the surface. This surface layer exerts a stabilizing action on the cluster and as a consequence metastable clusters, far bigger than the critical one, can temporarily exist. In this model, increasing the amount of lead would increase the size of the clusters and stabilize their formation at higher temperatures. One should consider the possibility that this can also occur in melts.

It was found in this study that the temperatures of crystallization of WO_3 from the WO_3-NaF compositions were 1020–1090°C (the second peaks). The second exothermic DTA peak is evidently due to heat of crystallization of WO_3, because only WO_3 crystals were obtained from all flux growth experiments in this high temperature range. This result is contrary to the conclusion of Wanklyn *et al.* [5]. It is now clear that the crystallization temperature of 698°C for WO_3 from WO_3-NaF compositions reported by them [5] is erroneous. The DTA peaks attributed by them to the crystallization of WO_3 are evidently due to the crystallization of a sodium wolframate compound (from the phase diagram, it is probably $Na_3W_4O_{13}$). The reason for this error seems to be the slow heating rates of their DTA runs. At these rates the peaks at the 1000–1200°C temperature range are hardly seen (in our study a rate of 25°C min^{-1} was used) while those at the 600–700°C range are large.

It was suggested [1] that obtaining a few large crystals of WO_3 by increasing the amount of Pb^{2+} was due to cluster formation and subsequent crystallization, according to Glasner's model for aqueous solutions. According to this model [2–4] in a solution of pure solute (i.e. no additive) there are many clusters of subcritical size, and if the temperature is lowered many clusters grow to a critical size, resulting in many small crystals. Increasing the number of nucleating impurity ions causes the formation of a higher number of subnuclei clusters of a smaller size (in fact aqueus alkali halide solutions with Pb^{2+} were kept for several days without crystallization taking place, as the building blocks were too small, below the critical size). The model predicts that only a few of the clusters will grow to a critical size (by combining with other small subnuclei clusters) resulting in a few, big crystals. Accordingly, crystallization temperatures will fall with the increase of Pb^{2+} concentration as smaller nuclei are formed. This seems to be in contrast with results obtained in our study from DTA runs. Generally speaking, the higher the Pb^{2+} concentration the higher was the crystallization temperature. After a few consecutive runs they all crystallized at the high temperature of crystallization of the composition with the highest lead concentration (5 PbF_2:100 WO_3:44 NaF), near 1090°C. Obviously, contrary to what was climed previously [1], Glasner's model cannot explain WO_3 growth as observed in our DTA runs. On the other hand, the results found in our study for DTA runs generally fit the model describing cluster formation with Pb^{2+} on the surface [9], predicting that the higher the Pb^{2+} concentration the bigger and fewer will the clusters be, enabling crystallization to occur at higher temperatures.

We propose that two factors acting simultaneously affect the nucleation and crystal growth of WO_3:1) Pb^{2+} concentration and 2) the number of nucleation sites on the Pt surface.

There was no difference in the thermal histories of the crucibles. Each sample was introduced into a new crucible which was sealed under vacuum and used for all runs. So, differences of thermal histories cannot explain the different results. The fact that the lines in Fig. 3 have different slopes shows that the amount of lead has an influence and the number of nucleation sites cannot solely explain the results otherwise all slopes should have been about equal.

The results of DTA runs can be explained in the following way: The nuclei- and the clusters-start forming at nucleation sites on the Pt surface and grow with the help of lead ions adsorbed on the nuclei surface. Pb^{2+} ions are spread (in the first runs) on a large number of nuclei, because the Pt surface provides many nucleation sites and so clusters will be relatively small resulting in a low crystallization temperature (Fig. 3). After consecutive runs some dissolution of the Pt surface occurs and so there are fewer nucleation sites, fewer nuclei form and so Pb^{2+} is concentrated on fewer clusters creating the effect of larger concentrations i.e. clusters grow bigger and crystallization temperatures become higher (Fig. 3). We suggest that this is the reason that in all batches (no matter what the lead concentration is) the crystallization temperatures become higher, reaching the temperature of the composition with the highest lead concentration (100 WO_3:44 NaF:5 PbF_2).

In a pure WO_3-flux mixture, the clusters, in the first runs, are small (because there is no Pb^{2+} to make them grow bigger) and so the crystallization temperatures are relatively low. With consecutive runs, where nucleation sites become scarce, fewer, larger, clusters are formed and so crystallization temperatures become higher (Fig. 3).

In flux growth experiments, experiments a1–a3 are a case of a short soak time and many nucleation sites. The lead is spread on a large number of sites, so the clusters will be small and hence many small crystals are formed. Experiments d4–d5 are cases of thermal cycling, i.e. a very long soak time. Most of the nucleation sites are destroyed. No matter what the Pb^{2+} concentration is (0 or 5) there are a very few nucleation sites and hence a small number of large crystals (in Fig. 3, after many soaks-runs- for both 0 and 5 lead concentrations the same crystallization temperature is obtained).

The influence of the number of nucleation sites (on the Pt crucible wall) on the nucleation (of $Pb_2V_2O_7$) in flux systems was studied (6). In consecutive DTA runs (at constant temperatures) there was an increase in induction times. The authors concluded that there are preferred nucleation sites on the surface of the platinum crucible, these being progressively removed at temperatures above the eutectic (by dissolution of platinum by the flux and recrystallization of the surface) and redeposited on cooling below the eutectic. This redeposition of Pt on the crystal surface was observed for $DyFeO_3$ [7]. Longer soak times lower the number of nucleation sites and so cause longer induction times which mean that (under constant cooling) crystallization has to occur at lower temperatures. This is opposed to the results of our study where, for the same Pb^{2+} concentration, successive runs caused higher crystallization temperatures (Fig. 1). Perhaps the reason is that the highest soak temperature for $Pb_2V_2O_7$ was only 853°C while in our study it was 1170°C i.e. nucleation sites could be removed more effectively. Perhaps the reason is the difference between crystal growth in the furnace, carried out under conditions of very slow cooling (10°C h^{-1}, i.e. close to equilibrium) and DTA runs with very fast cooling (25°C min^{-1}), under non-equilibrium conditions.

Conclusions

We believe this is the first study of flux growth experiments where exothermal effects are observed above the temperature of crystallization. Two factors simultaneously affect WO_3 growth from NaF flux doped with Pb^{2+}:1) Pb^{2+} concentration; 2) the number of nucleation sites on the Pt surface. In the presence of Pb^{2+}, the formation of clusters takes place at higher temperatures (bigger clusters being stabilized by adsorbed Pb ions). This in combination with the availability of nucleation sites on the platinum surface (the higher the soak temperature and the longer the soak time, the lower is their number) affect the temperature of crystallization and the size of the crystals. Thus higher Pb^{2+} concentrations and fewer nucleation sites result in fewer, larger WO_3 crystals.

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