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Czochralski growth of pure and doped lead tungstate single crystals

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In this paper we report the growth of pure and doped lead tungstate ($PbWO_4$) single crystals by the Czochralski method, using a resistive heating system. Variations in the nature of crystal cracking were observed. These structural defects are related to the seed rotation, crystal pulling rate and the axial temperature gradient. A gradual decrease in the optical quality (from top to bottom) of the growing crystal was observed. Repeated growth processes and the high purity of the starting materials ($Pb(NO_3)_2$ and Na_2WO_4) yielded transparent crystals. Doped lead tungstate crystals were grown for luminescence studies.

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1. Introduction

The lead tungstate single crystals (pure and doped) have very useful applications as scintillation detectors [1,2], medical imaging sensors [3] and laser active media [4]. Due to the fact that the physical properties of $PbWO_4$ crystals are so delicate that even small changes of the crystal growth conditions can lead to great variations in its scintillating properties, much attention has been paid to the crystal growth process for obtaining high quality crystals for high energy physics [5,6]. The doping of the $PbWO_4$ single crystals with different ions is a procedure which may compensate defects in structure to eliminate unwanted impurities or to change scintillation properties [7,8].

2. Experimental procedure

For the growing of pure and doped $PbWO_4$ single crystals we have applied the Czochralski technique, using a home-made experimental device. This device allows the variation of the pulling rate between 4 - 10 mm/h and of the rotation rate between 4 - 12 rpm. The starting material was melted in a platinum crucible with a volume of 40 ml (cm^3), using an electric furnace with kanthal A wire as heating element generating 1200 W of electric power.

For the initial crystal growth experiments, the $PbWO_4$ starting material was synthesized by us from $Pb(NO_3)_2$ (chem. pure, “Reactivul” Bucuresti) and Na_2WO_4, according to the reaction:

$$Pb(NO_3)_2 + Na_2WO_4 = PbWO_{4\ (precipitate)} + 2\ NaNO_3$$

Sodium tungstate was synthesized from Na_2CO_3 (pro analysis, “Reactivul” Bucuresti) and WO_3 (puriss 99.9%, Fluka) according to:

$$Na_2CO_3 + WO_3 = Na_2WO_4 + CO_2$$

The obtained Na_2WO_4 and $Pb(NO_3)_2$ were purified by repeated recrystallization from bidistilled water.

In addition to the source material synthesized by us, we also used lead tungstate 99.9% from Aldrich.

The presence of paramagentic impurities was evidenced by ESR measurements.

The experimental setup allows for the growth process to take place in inert atmosphere (argon or nitrogen gas). The doped $PbWO_4$ single crystals were obtained by introducing the dopants into the melt in the corresponding oxide form. Thus the Mn^{2+} and Gd^{3+} doped $PbWO_4$ single crystals were grown by mixing MnO and Gd_2O_3 with the starting material.

3. Results and discussion

In nature, the lead tungstate crystals can be found in two crystalline forms, either tetragonal stolzite, crystallized in a scheelite-type structure (space group $I4_1/a$) [9], or monoclinic raspite (space group $P2_1/a$) [10]. The synthetic $PbWO_4$ crystals which can be grown by deposition from solution or by pulling from melt have scheelite-type structure. The raspite phase changes irreversibly into stolzite phase at about 400°C. There are four molecules in the unit cell with the cell parameters $a = b = 0.54619$ nm, $c = 1.2049$ nm. The $PbWO_4$ single crystals grown by Czochralski technique crack more easily along the *c*-axis (due to a higher thermal expansion coefficient) as compared to the *a*-axis.

For the initial growth experiment we used a piece of kanthal wire instead of a seed crystal. The polycrystalline sample formed at the wire’s end was reduced in diameter several times in order to reduce the number of crystals in the sample. The remaining crystals were grown further on.

From the resulting polycrystalline sample, small single crystalline pieces were cleaved, in order to be used as the first seed crystals. Unfortunately, the use of kanthal wire instead of seed crystal has as a detrimental effect the impurification of the melt. The use of a platinum wire instead eliminates this disadvantage.

Fig. 1 shows the picture of the first $PbWO_4$ single crystal obtained by us with kanthal wire instead of seed crystal. This crystal has a dark reddish-brown color, its intensity increasing from top (where the crystallization process was initiated) to bottom (the lower part of the crystal). Very likely this coloration can be attributed to the presence of Fe^{3+} and Gd^{3+} ions as impurities in the crystal.

Fig. 1. Lead tungstate crystal obtained by pulling from melt, using kanthal wire instead of a seed crystal (as a consequence, the intense coloration due to impurification).

Two main lines of work were investigated in order to obtain colorless lead tungstate single crystals, as follows.

One was to carry out repeated pullings using only the upper part of the previously grown crystals. After 6 - 8 consecutive grown processes, the paramagnetic impurities were eliminated, at least from the upper part of the obtained single crystals. This was proved by ESR measurements. Nevertheless, the purified crystals were still colored, having a light yellow shade, which persists even after thermal treatments of 3 - 4 hours in argon or oxygen at 900 ^{o}C.

Photographs of some $PbWO_4$ crystals of this type can be seen in Fig. 2.

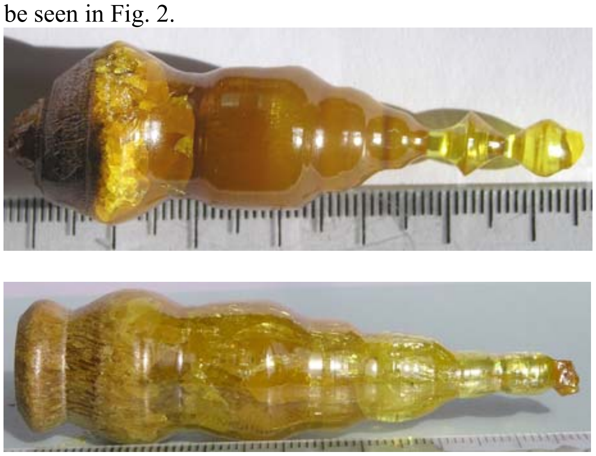

Fig. 2. $PbWO_4$ crystals obtained after repeated pullings from selected crystalline material (the clearer upper part, free of paramagnetic impurities, is evidenced).

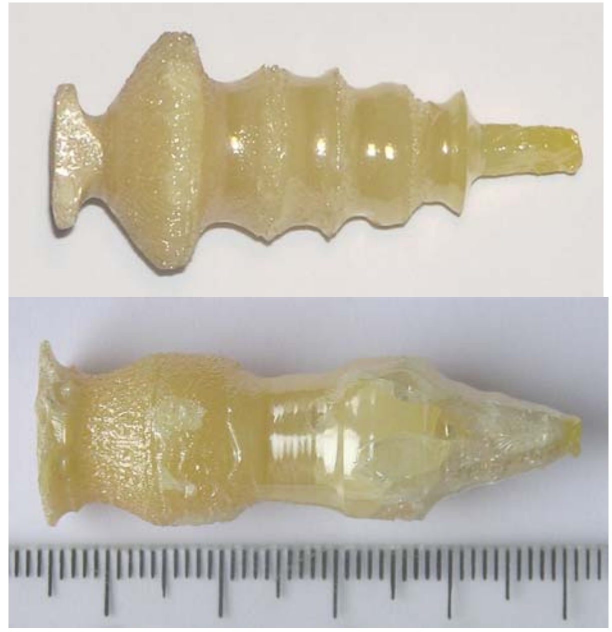

Fig. 3. $PbWO_4$ crystals obtained from ultrapurified starting materials (single crystals of Na_2WO_4 and $Pb(NO_3)_2$, grown from aqueous solutions).

The second line of work consisted in very carefull purification of the starting materials, Na_2WO_4 and $Pb(NO_3)_2$ respectively, by repeated recrystallization from water solutions. In the case of $Pb(NO_3)_2$, single crystals of $5\times10\times10$ mm^3 were grown. The $PbWO_4$ crystals obtained in this case were almost colorless (Fig. 3).

The growth processes were performed at various pulling rates and vertical temperature gradients. The different vertical temperature gradient distributions were obtained by using a good heat conducting rod between the seed crystal and the its metallic support and by adjusting the flow rate of the cooling water. We have found that higher values of pulling rate and vertical temperature gradient are causing more cracks in the crystal.

4. Conclusions

We have successfully grown good quality single crystals of lead tungstate, having 6 - 15 mm in diameter and 30 – 70 mm long, by pulling from melt using the Czochralski technique.

The good quality of these crystals can be obtained either by: *(i)* successive pullings, in combination with the selection of the pure upper part after each step, or by *(ii)* using ultrapure single crystalline starting materials (Na_2WO_4 and $Pb(NO_3)_2$), grown from aqueous solutions. This second solution is better than the first one.

The doped crystals were obtained by introducing the corresponding oxide in the melt. Therefore the Mn^{2+} and Gd^{3+} doped single crystals were obtained by adding MnO and Gd_2O_3 into the melt.

After a thermal treatment of 3 – 4 hours at 900 °C, in argon and oxygen atmosphere, the light yellow colour of the obtained single crystals remained unchanged.

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