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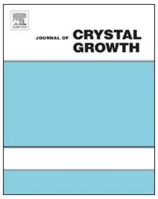

Large single crystal growth of $MnWO_4$-type materials from high-temperature solutions

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ABSTRACT

A simple high-temperature growth apparatus was constructed to obtain large crystals of chemically gradient (In, Na)-doped $MnWO_4$solid-solutions. This paper presents the crystal growth and characterisation of both $MnWO_4$and epitaxially grown (In, Na): $MnWO_4$crystals on $MnWO_4$. These large monolithic crystals were made in two steps: A $MnWO_4$ crystal was grown in the crystallographic main direction [001] applying the Czochralski method, followed by the top seeded growth of (In, Na): $MnWO_4$ solid-solutions with an oriented seed crystal of $MnWO_4$. Such a monolithic crystal will serve to fundamental investigation of coupling properties at boundaries between various multiferroic $MnWO_4$-type-solid-solutions.

1. Introduction

Manganese tungstate ($MnWO_4$, mineral name: huebnerite [1]) is paramagnetic at room temperature (RT) and features several antiferromagnetic phases below its Neel temperature (TN) ~13.5 K [2]. Among them, the so-called '*antiferromagnetic phase 2*' (AF*2*)exhibits a helical spin order between 7.6 K and 12.7 K, inducing a weak electric polarisation of 50–60 $\mu C/cm^2$ [3,32]. For this magnetoelectric (**ME**) coupling various $MnWO_4$-typesolid-solutions have been intensively studied [4–13] for potential application as data storage systems and high-sensitive magnetic sensors. In spite of a simple topology of $MnWO_4$ subtle changes of atomistic and magnetic properties in variously doped $MnWO_4$-family members are of interest. Recently, for instance, the nuclear structure of $MnWO_4$ has been re-considered in the polar space group symmetry P2 [14], instead of P2/cwhich has been widely accepted in literature [1–4,6–13,32]. On the other hand, the mechanism of multiferroicity in $MnWO_4$-type materials is still debated [15–18]. It is an important issue to determine crystallographic behaviour of magnetic Mn^{2+} and doping magnetic cations or non-magnetic replacements at the polar atomic site C_2. This is essential to the electric polarisation induced by the helical magnetic spin order at Mn^{2+} sites in AF*2*. Therefore it is necessary to elucidate spin-lattice coupling by analysing their nuclear and magnetic structures using both high-resolution X-ray and polarised neutron diffraction techniques. For the latter the availability of large high-quality single crystals is inevitable. To enhance the *ME* coupling in *AF2* additionally by magnetostriction it is desired to create chemical gradients in a zoned $MnWO_4$–type crystal called as *chemically gradient monolithic crystals*. It is highly interesting to characterize the change of its *ME* property by magnetostriction over several mm in thickness across chemical boundaries in such a solid-solution crystal.

For this purpose the top seeded solution growth (*TSSG*) [19] and the Czochralski (*CZ*) method [20] were applied in the current study. *TSSG* works well for compounds with high vapour pressure, as well as for those that cannot be grown from a congruent melt. In *TSSG* a seed crystal is dipped into an oversaturated solution while steadily cooling or evaporating the system. It is critical to provide a suitable solvent with a sufficient solubility. Using a high-temperature (*HT*) solution (flux) it is possible to remedy defects in the crystal [19]. However, substitutional or interstitial defects can be formed in crystals *TSSG*-grown when using chemically different solvents [21]. To prevent incorporation of solvent into the crystal a low growth rate is desired in *TSSG*. Accordingly this method requires a long synthesis time extended from several days up to a few months.

In the *CZ* growth the melt is pulled vertically against

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gravitational force towards a cooler region where the solid phase is stable. Therefore an appropriate pulling rate is applied, which determines the crystallisation velocity and the crystal diameter. This procedure can be performed using a *HT* solution as long as the temperature programme can be set to follow the liquidus curve. Rotation of the crystal and/or the crucible helps to transport the surplus of solvent away from the growth front. Optical observation is readily possible for controlling the crystal morphology during the growth process. In practice, however, a successful *CZ* growth is often retarded with much time-consuming trial-error in adjusting pulling rate, rotation speed and a suitable temperature programme [20,22–24].

Knowing advantages and disadvantages in these two different crystal growth methods, a low-cost, easy-performing *HT* crystal growth apparatus was constructed to produce large single crystals of $MnWO_4$ and (In, Na): $MnWO_4$ compounds. The crystal quality and refined structure models are described here based on results from electron microprobe analysis and X-ray diffraction studies.

2. Construction of a *HT* crystal growth apparatus

As shown in Fig. 1, the core of the new apparatus is a tubular heating element (*RAC 40/200 Kanthal, Sandvik*) for a maximal working temperature of 1300 °C. Two 50 mm thick insulating plates (*Fibrothal*) were attached to close the heating tube with a 40 mm hole bored through the upper plate. The heating core was wrapped with a thick layer of mineral wool and put into an aluminium case. At the upper part of the heating tube an additional alumina tube was mounted to steadily maintain high temperatures for preventing corrosion of the heating element from condensation of evaporated chemicals. The hole at the top plate was covered by a detachable steel lid. One central 8 mm and two further conical 3–5 mm holes were present on the lid for the pulling alumina rod and for optical observation, respectively. The illumination was realized with a focused 220 lm LED. A mirror was placed 15 mm above the observation hole diverting the picture of crucible and crystal over a glass lens to a magnification glass. The lens could be translated maximal ±5 mm along the optical path to focus different positions within the furnace. A sintered alumina pulling rod was connected to a motor for rotation movement. This motor was installed on the stage connected with a vertically aligned translation unit driven by a stepper motor. This setup allowed average pulling rates of 0–11 mm/h and a rotation of 0–150 rpm. A 25 ml Pt-crucible is put onto an alumina tube slightly above the maximum of the vertical temperature profile. A Pt-Pt/Rh thermocouple was positioned at a distance of 10 mm near the Pt-crucible. The whole construction was placed on a rugged basement where the power supply was installed with the control units for temperature (*Eurotherm* 3504) and translation (*LOGO! 24C, Siemens*).

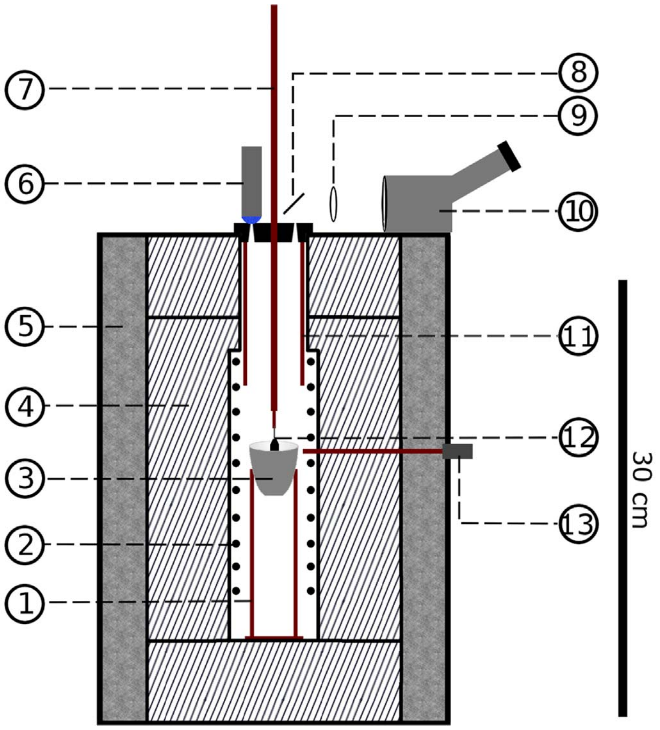

Fig. 1. Technical drawing of the constructed growth apparatus: (1) Alumina crucible holder (2) Heating wire (3) Pt-crucible (4) *Fibrothal* insolation (5) Mineral wool (6) LED light source (7) Alumina pulling rod (8) Mirror (9) Lens (10) Magnification glass (11) Alumina protection tube (12) Crystal (13) Pt-Pt/Rh thermocouple.

3. Crystal growth

3.1. *HT* solution

Melting points of $MnWO_4$-type compounds are relatively high about ~1300 °C. *HT* solutions were prepared according to previous works [3,25–32] using the educts MnO (99%, *Alfa Aesar*), In_2O_3 (99.9%, *Alfa Aesar*), WO_3 (99.8%, *Alfa Aesar*) and $Na_2WO_4 \cdot 2H_2O$ (98%, *Merck*). A solvent mixture of Na_2WO_4 and $Na_2W_2O_7$ was chosen for several important requirements to grow large crystals of $MnWO_4$, i.e. (1) a low eutectic melting point between 653 °C and 719 °C [33–36]; (2) a high solubility of $MnWO_4$; (3) formation of manganese oxides is retarded in the presence of $Na_2W_2O_7$; (4) chemically similar to the end crystal product $MnWO_4$; (5) non-toxicity of the resulting solution for working in ambient open air conditions; (6) low evaporation at working temperatures; (7) remaining solvent is easily removable from the crystal product, e.g. by washing with hot NaOH solution [25–32].

3.2. Seed preparation

Initial seed crystals were obtained via spontaneous nucleation of a supersaturated solution, where the used educts, as given in details in Table 1, were homogeneously ground up and filled into a Pt-crucible and allowed to react at 1050 °C for 12 h in a chamber furnace. Subsequently the reactants were cooled with a rate of 1 K/h to 860 °C and quenched to *RT* within the furnace. In this way, elongated rods of $MnWO_4$ crystals could be grown up to a maximal size of $15 \times 3 \times 3$ mm^3. Using these seed crystals an aggregate of larger massive $MnWO_4$ crystals were obtained from *TSSG*, denoted by a lab-code, TSX0 (Table 2). Thereof homogeneous parts were cut for seeding in the subsequent *CZ* experiments. By variation of growth conditions in a series of *CZ* growths (lab-coded by CZX#) a well-oriented single crystal of $MnWO_4$ could be grown finally, as summarised in Table 2.

3.3. *CZ* crystal growth of $MnWO_4$

The seed crystal was drilled on (010) for the perfect cleavage to make a small hole at the top affixed to a Pt-wire (Fig. 2a). The crystal was seeding and pulling in the preferred growth direction [001] to allow effective crystal growth. The Pt-crucible charged with the weighed starting reactants (Table 1) was positioned in the reaction chamber of the growth apparatus. The seed was hung about 2 cm above the crucible while homogenising the *HT* solution at 1100 °C for 14 h. Subsequently the working temperature was slowly lowered to 1080 °C until first small crystallites were observed on the surface of the solution. At this point the temperature