

Solvents for growing $\text{Al}_2(\text{WO}_4)_3$ single crystals from high-temperature solutions

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Abstract

The crystallization conditions of $\text{Al}_2(\text{WO}_4)_3$ from $\text{Li}_2\text{O}-\text{WO}_3$ solvents (molar ratio 30.0:70.0, 32.5:67.5, 35.0:65.0, 45.0:55.0 and 55.0:45.0) as well as from $\text{Na}_2\text{O}-\text{WO}_3$ solvents (molar ratio 25.0:75.0, 27.5:72.5, 30.0:70.0 and 32.5:67.5) have been investigated. The concentration and temperature regions of crystallization of $\text{Al}_2(\text{WO}_4)_3$ and the density, viscosity as well as the solution losses due to evaporation have been established. On the basis of the data obtained it has been concluded that the most suitable solvent for growing $\text{Al}_2(\text{WO}_4)_3$ single crystals is $\text{Na}_2\text{O}-\text{WO}_3$ with a molar ratio of 27.5:72.5.

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1. Introduction

The compound $\text{Al}_2(\text{WO}_4)_3$ is a material with various potential applications. The crystal structure of $\text{Al}_2(\text{WO}_4)_3$ is a $\text{Sc}_2(\text{WO}_4)_3$ -type with orthorhombic symmetry [1]. In this quasi-layered structure Al^{3+} is situated between the layers and could migrate relatively easily due to which $\text{Al}_2(\text{WO}_4)_3$ is a potential material for chemical sensors [2] and electrochemical energy cells [3,4].

It has been found that $\text{Al}_2(\text{WO}_4)_3$ has a volumetric coefficient of thermal expansion close to zero, which is based on a compensation for the expansion along one of the crystallographic directions accompanied by reduction along the other two directions [5].

In addition, Al^{3+} in $\text{Al}_2(\text{WO}_4)_3$ has octahedral surroundings and can easily be replaced by Me^{3+} ions of 3d-elements or by rare earth ions with a relatively small ionic radius: Er, Tm, Yb, Lu [6]. On this basis $\text{Al}_2(\text{WO}_4)_3$ is a potential laser matrix for solid state lasers with different applications [6,7].

An important peculiarity of $\text{Al}_2(\text{WO}_4)_3$ is that it may be the basis of solid solutions with $\text{Sc}_2(\text{WO}_4)_3$, $\text{In}_2(\text{WO}_4)_3$ and other

compounds having the same structure [8]. On the basis of such solutions one could find optimum chemical compositions with most pronounced desirable properties.

The successful application of $\text{Al}_2(\text{WO}_4)_3$ in the above fields needs detailed investigation of its properties mainly on single crystal samples with appropriate sizes and quality. Only the investigation of $\text{Al}_2(\text{WO}_4)_3$ single crystals could help elucidating the real ion conductivity or expansion in different directions, the results being not affected by the grain boundaries and the loss of orientation in the polycrystalline substance. Studies of optical and laser properties is possible on single crystal samples alone.

The growth of single crystals is directly associated with the way of melting of the compound. According to Waring [9], $\text{Al}_2(\text{WO}_4)_3$ melts congruently at 1254 °C. Nassau et al. [10] have found this temperature to be 1220 °C. Kislyakov and Lopatin [11] has established peritectic melting of $\text{Al}_2(\text{WO}_4)_3$ at 1320 °C.

Even when assuming congruent melting of $\text{Al}_2(\text{WO}_4)_3$, the attempts to grow single crystals from their own melt, failed in general. The main problem is the strong evaporation of WO_3 which essentially changes the melt composition and, besides, erodes the crystal formed and the seed [7,12]. Relatively better results have been obtained by a modified Czochralski method in the presence of excess WO_3 [8,12,13]. However, in this case again the authors have noticed problems associated with the evaporation of WO_3 .

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Growth of $\text{Al}_2(\text{WO}_4)_3$ by the flux method has been performed up to now with sodium polytungstate as solvent [6]. The crystals obtained ($3 \text{ mm} \times 3 \text{ mm} \times 1 \text{ mm}$) do not suffice for reliable studies.

Evidently, more detailed investigation on the properties of $\text{Al}_2(\text{WO}_4)_3$ and the solid solutions on its basis, determining its possible applications, are needed. These studies should be based on a reliable growth method of the single crystals. The present work reports the first attempts to find the most appropriate solvent for the growth of $\text{Al}_2(\text{WO}_4)_3$ single crystals by the flux method.

2. Experimental

Previous studies of part of the authors have established wide concentration regions of $\text{Al}_2(\text{WO}_4)_3$ crystallization in the systems $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{WO}_3$ [14] and $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{WO}_3$ [15]. The successful use of these systems for the growth of $\text{Al}_2(\text{WO}_4)_3$ single crystals requires the choice of the most suitable initial solution. For that purpose, a series of solutions have been investigated with respect to some of their characteristics such as: concentration and temperature region of crystallization of $\text{Al}_2(\text{WO}_4)_3$, neighbouring phases and conditions of homogenization, as well as density, viscosity and volatility of the solutions.

On the basis of these previous studies, five solvents containing Li_2O and WO_3 in a $\text{Li}_2\text{O}:\text{WO}_3$ molar ratio of 30.0:50.0, 32.5:67.5, 35.0:65.0 and 55.0:45.0 as well as four Na_2O and WO_3 containing solvents with a $\text{Na}_2\text{O}:\text{WO}_3$ ratio of 25.0:75.0, 27.5:72.5, 30.0:70.0 and 32.5:67.5 were chosen. Each of the solvents was used for preparing a series of solutions (about 10) differing in the concentration of $\text{Al}_2(\text{WO}_4)_3$. The homogenization conditions, type of crystallizing phase, crystallization temperature, solution density at the crystallization temperature and weight losses during the investigation (3–4 h) were determined for each solution. The viscosity of some of the solutions was also investigated.

The investigations proceeded in a resistance furnace with Kanthal heating elements whose temperature was controlled with an accuracy of $\pm 0.1^\circ\text{C}$ using an Eurotherm controller. The initial reagents for the solutions were Li_2CO_3 (Na_2CO_3), $\text{Al}(\text{OH})_3$ and WO_3 with a purity superior than 99%. Cylindrical platinum crucibles, 30 mm high, 20 mm in diameter, were used. The amount of the solutions for the separate experiments varied between 10 and 20 g, while the solution layer thickness was within 1–1.5 cm. Each series began with a solution with maximum concentration of $\text{Al}_2(\text{WO}_4)_3$. After homogenization and determination of the above mentioned properties, the solution was diluted by addition of the corresponding solvent. Subsequently the properties of the new composition were determined. The series continued with a step of 1–2 mol% till the appearance of a phase differing from $\text{Al}_2(\text{WO}_4)_3$.

The homogenization of the solution was achieved at a temperature exceeding the expected crystallization temperature (T_{cr}) by about 50°C .

The crystallization temperature was determined as the temperature of a phase appearance on the solution surface upon a Pt probe immersed in the solution. The accuracy of determination was $\pm 2^\circ\text{C}$. When necessary, the kind of the phase was determined by X-ray phase analysis.

The density of the solution was established by measuring the level of the given solution amount (determination of the solution volume). With a determination error of $\pm 20 \mu\text{m}$, the calculation error of the solution density was about 3%.

The viscosity of some solutions was determined with a viscometer whose working principle and calibration are described in another communication [16].

The weight losses by evaporation were determined for each solution by comparing the weight of the solution containing crucible before and after the solution treatment.

3. Results and discussion

3.1. The system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{WO}_3$

The crystallization temperatures (T_{cr}) depending on the concentration of $\text{Al}_2(\text{WO}_4)_3$ in the five solvents from the system

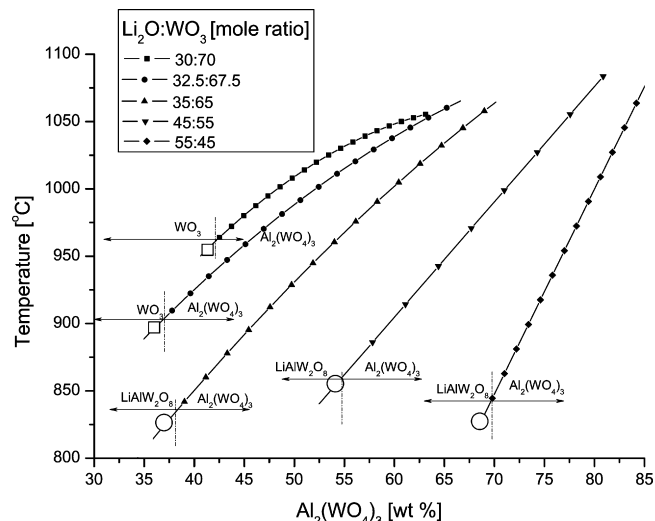


Fig. 1. Temperature dependence of the solubility of $\text{Al}_2(\text{WO}_4)_3$ in solvents of the system $\text{Li}_2\text{O}-\text{WO}_3$.

$\text{Li}_2\text{O}-\text{WO}_3$ are shown in Fig. 1. There is an almost linear dependence of T_{cr} on the concentration, the linearity being more pronounced with the solvent having a higher Li_2O concentration. With rising Li_2O content the solubility strongly increases. Thus, with solvent 30.0:70.0 the concentration of $\text{Al}_2(\text{WO}_4)_3$ is 62.5 wt.% while with solvent 55.0:45.0 this concentration is 84 wt.% at the same T_{cr} (1060°C). All solvents have sufficiently large concentration and temperature regions within which $\text{Al}_2(\text{WO}_4)_3$ alone crystallizes. For the solvent with $\text{Li}_2\text{O}:\text{WO}_3 = 30.0:70.0$ and 32.5:67.5 the phase next to $\text{Al}_2(\text{WO}_4)_3$ is WO_3 while for the remaining three solvents this phase is LiAlW_2O_8 .

On the basis of these data, the crystallization isotherms and the concentration limit of crystallization have been found (Fig. 2). To the right of the dotted line, L_1 denotes solutions whose homogenization up to 1150°C (the temperature of noticeable WO_3 evaporation) proves impossible. To the left of the solid line L_2 stands for solutions from which phases neighbouring to $\text{Al}_2(\text{WO}_4)_3$ crystallize. It is evident that the crystallization isotherms are almost parallel to the lines with the same Li_2O concentration, i.e. the Li_2O content is determining for the dissolution of $\text{Al}_2(\text{WO}_4)_3$.

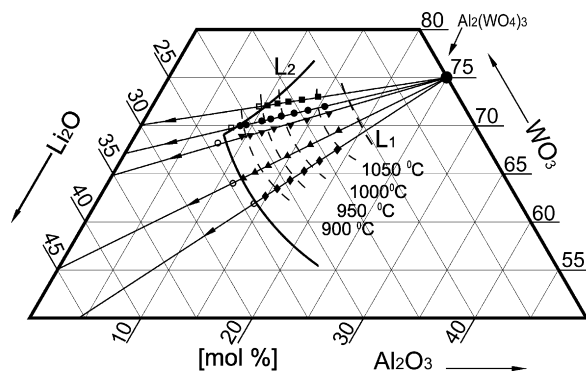


Fig. 2. Concentration and temperature regions of crystallization of $\text{Al}_2(\text{WO}_4)_3$ in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{WO}_3$.

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