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Novel solvents for the single crystal growth of germanate phases by the flux method

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ABSTRACT

A series of alkali-borate ($Na_2O \cdot B_2O_3$, $Na_2O \cdot 1.5B_2O_3$, $Na_2O \cdot 2B_2O_3$ and $Li_2O \cdot B_2O_3$), and a series of alkali-molybdate ($Na_2O \cdot 1.5MoO_3$, $Na_2O \cdot 2MoO_3$ and $Li_2O \cdot MoO_3$) solvents were studied with a view to find out the suitable conditions for growing single crystals from germanate phases by the flux method. The ternary systems solvent-CaO–GeO_2 were investigated and crystallization temperature and crystalized phase were determined. As a main result the concentration and temperature regions of crystallization of calcium germanates ($Ca_5Ge_3O_{11}$, $CaGeO_3$) and of some alkali germanates (Li_2GeO_3, Li_2CaGeO_4, $Na_2CaGe_6O_{14}$) were experimentally determined for a first time. The conditions found for Ca_2GeO_4 growth are significantly more favorable than those known so far. Additionally during this study, two novel unknown phases were obtained. X-ray diffractograms of the novel phases are presented. The obtained conditions are a basis for successful single crystal growth by the flux method for all mentioned germanate compounds.

1. Introduction

Solid-state lasers emitting in the spectral region of 1.1–1.6 µm find increasing applications in medicine, ecology, telecommunications, instrument-building, etc. [1–3]. Several single crystals doped with ions of the transition elements emit in this region. Of major importance among them are single crystals doped with Cr^{4+}. The laser media most often used so far are Cr^{4+} doped Mg_2SiO_4 (forsterite) and $Y_3Al_5O_{12}$ (YAG) [4,5]. These media have, however, several drawbacks, e.g., low quantum yield due to non-emitting transitions; presence of Cr^{3+} in the matrix and limited doping capacity with Cr^{4+}. Last but not least are the problems of crystal growth related to the high melting temperatures of these two compounds [6,7]. Recently, a number of compounds have been studied as potential substitutes for Mg_2SiO_4 and $Y_3Al_5O_{12}$. Very few of these studies have, however, yielded positive results. A major group of compounds with potential application are the Cr^{4+} doped compounds with olivine structure. Unfortunately, most of these compounds display drawbacks such as incongruent melting, phase transitions, and non-radiative emission. For example, single crystal growth of Mg_2GeO_4 is accompanied by significant evaporation of GeO_2 [8]; $CaMgSiO_4$ melts incongruently [9]; Ca_2SiO_4 undergoes several polymorphous transitions [10].

The only material with olivine structure (besides forsterite) that has provided single crystals of satisfactory size and quality and has demonstrated laser emission of high efficiency is Cr^{4+}:Ca_2GeO_4 [11,12]. As a representative of the olivines, this compound also undergoes a phase transition, but at a higher temperature (1450 °C). The low-temperature modification with olivine structure is very suitable to be doped with Cr^{4+}; germanium is situated in the required tetrahedral environment and Cr^{4+} and Ge^{4+} are of the same valence state and have close ionic radii (0.041 и 0.039 nm, respectively). Moreover, the large ionic radius of Ca^{2+} does not allow its substitution by Cr^{3+} and Cr^{2+}, which are undesirable for this application [13].

Attempts have been made to grow single crystals of Cr^{4+}:Ca_2GeO_4 by the flux method at temperatures lower than 1450 °C (the phase transition temperature). The reported studies show that the use of $CaCl_2$ as a solvent is not appropriate due to the intense evaporation of $CaCl_2$ and the formation of hygroscopic phases that enter in the crystal and destroying it [14,15]. When CaF_2 is used as a solvent, crystal growth should be carried out at a temperature above 1350 °C, where solvent evaporation takes place; moreover, the process should take place in an iridium crucible in a nitrogen atmosphere [16]. The use of a lithium-molybdate solvent is also reported, but no details on solution chemical composition are given [17].

The main aim of the present work was to find out a novel, more appropriate solvent for the growth of single crystals of Ca_2GeO_4 by studying a series of alkali-borate and alkali-molybdate solvents. During the studies, appropriate conditions for the growth of other germanates with potential applications, such as $Ca_5Ge_3O_{11}$, $CaGeO_3$,

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Li_2GeO_3, Li_2CaGeO_4, and $Na_2CaGe_6O_{14}$, were also found. Additionally, as a result of the studies, two novel phases, unknown so far, were discovered.

2. Experimental

First a group of alkali-borate compounds ($Na_2O \cdot B_2O_3$, $Na_2O \cdot 1.5B_2O_3$, $Na_2O \cdot 2B_2O_3$ and $Li_2O \cdot B_2O_3$) were examined as solvents. It is known that these solvents are characterized by relatively low melting temperatures and high dissolving capacity of a number of compounds of different compositions. The number of solvents was limited to the compositions shown above, because both the viscosity of solvents with a higher B_2O_3 content and the volatility of solvents with a higher alkali oxide content increased.

The second group of solvents included alkali-molybdate compounds ($Na_2O \cdot 1.5MoO_3$, $Na_2O \cdot 2MoO_3$ and $Li_2O \cdot MoO_3$). These solvents are also characterized by low melting temperatures, but their dissolving capacity is lower than that of the alkali-borate solvents. On the other hand, the viscosity of the solutions based on the molybdate solvents is significantly lower, which considerably facilitates the mass transfer during crystal growth. As a result, irrespective of the lower concentrations of dissolved solids in this case, the crystals grow with a considerably higher rate and display a better quality. The compositions of the alkali-molybdate solvents were also limited, as shown above, because of the sharp decrease in solubility at higher MoO_3 contents and the increased evaporation at higher alkali oxide contents (established in the preliminary experiments).

The crystallization temperature was limited to 1150 °C, i.e. a temperature of solution homogenization was about 1200 °C. The evaporation of the solutions at a crystallization temperature above 1150 °C during the prolonged flux process would lead to poorly controlled growth conditions and low reproducibility of the results. The concentration borders are shown on the figures.

The main purpose of the study was to find out the temperature and concentration regions of crystallization of lithium-, sodium- and calcium-germanate phases with potential application as solid-state laser media (matrices). Germanates containing Mg and Zn, as well as Al, Ga, Sc and In will be the subject of future studies.

The ternary systems solvent-CaO–GeO_2 were subjected to spontaneous crystallization as homogeneous solutions upon lowering their temperature down to the crystallization temperature (saturation temperature). The following starting reagents were used: Li_2CO_3 (99.99%), Na_2CO_3 (99.6%), H_3BO_3 (99.9%), MoO_3 (99.9%), $CaCO_3$ (99.5%) and GeO_2 (99.999%).

The reagents in a total amount of 20–25 g were weighed with a precision of ± 0.01 g. They were mechanically mixed and were transferred to a platinum crucible of 3 cm diameter and 3 cm height. Depending on the composition and the temperature of the final solution, the depth of the solution was about 1 cm. A vertical Kanthal resistance furnace capable of temperatures up to 1250 °C with programmable temperature control and precision of 0.1 °C (controller-programmer type EUROTHERM 2704) was used. After decomposition of the carbonates and the boric acid, the solution was homogenized for 1–3 h at a temperature exceeding the assumed crystallization temperature by about 50 °C. An indication that a homogeneous solution was obtained was the solidification of the solution as a transparent glassy mass without any non-dissolved particles to be seen when the platinum probe was removed and observed under microscope (× 100). The “sticking” of the platinum probe to the bottom of the crucible was an additional evidence for the lack of particles on the bottom. A reliable proof of homogeneity was the transparency of the obtained solution which allowed seeing the bottom through the solution under special irradiation. By step-wise lowering of the temperature (in most cases by 10 °C every 30 min), the temperature of primary crystallization was determined by the appearance of nuclei on the immersed platinum probe. The appearance of the first crystals on the platinum probe immersed in the solution was assured by the temperature difference between the solution layer at the hot bottom and walls of the crucible and the colder center on the solution surface. The temperature of the solution with the immersed platinum probe and the first nuclei was raised by a step of 5 °C every 30 min up to the temperature when the nuclei started to dissolve. Then the temperature was reduced back using the same step until a growth of the nuclei was observed again. In this way the temperature of saturation (liquidus temperature) was determined with an accuracy of ± 5 °C. It was established that the metastable zone in this system comprises about 10–15 °C, i.e. the real temperature of the first crystallization is 10–15 °C above that when the first appearance of nuclei on the pure platinum probe was observed. The latter were separated mechanically, cleaned in hot water, dried and submitted for X-ray phase analysis. Powder XRD data were recorded in the range from 10 to 80° (2θ) with a constant step of 0.02° and 1 s/step counting time at room temperature on a Shimadzu XRD-7000 powder diffractometer using filtered Cu Kα radiation.

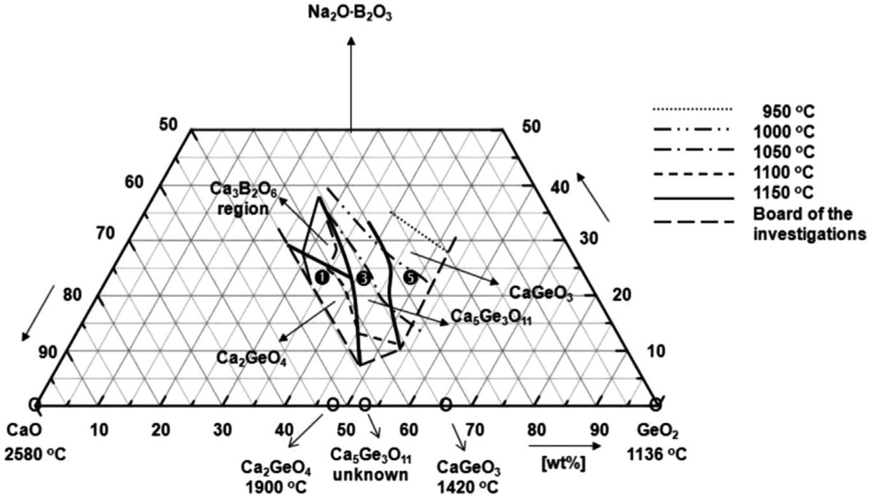

Fig. 1. Temperature and concentration regions of crystallization in the system $Na_2O \cdot B_2O_3$–CaO–GeO_2. Some calcium germinate compounds and its melting temperatures are shown on the bottom axes.