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Morphology of flux-grown vanadate garnets

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Abstract

The morphologies of vanadate garnets ($NaCa_2M_2V_3O_{12}$, M = Ni, Mg or Co) were studied by growing well-formed crystals from sodium vanadate flux. The first rank F-faces were determined by growing crystals at low supersaturation levels and were found to be the {1 1 0} face at lower temperature and the {2 1 1} face at higher temperature. This change was ascribed to a change in the ratio of the bond lengths at the octahedral site to that of the dodecahedral site with increasing temperature. When crystals grew larger in the lower temperature region, predominantly {2 1 1} faces appeared in addition to {1 1 0} faces, whereas in the higher temperature region, {1 1 0} faces were predominant over {2 1 1} faces. The reason for these phenomena was ascribed to the surface kinetics caused by an increase in the rate of mineral nutrient transport to the surface of the crystal with increasing crystal size.

Keywords: A1. Crystal morphology; A2. Growth from high-temperature solutions; A2. Single crystal growth; B1. Inorganic compounds; B1. Minerals; B1. Vanadates

1. Introduction

The basic morphologies of various garnet crystal specimens are either {1 1 0} or {2 1 1}, or a combination of both. It is very important to determine the relative morphological importance of the {1 1 0} and {2 1 1} faces, because both are F-faces. A particular study of the relationship between morphology, composition and paragenesis in silicate garnets was made by Kostov [1]. Kostov showed that the morphologies of $Mg_3Al_2Si_3O_{12}$, $Fe_3^{2+}Al_2Si_3O_{12}$ and $Mn_3Al_2Si_3O_{12}$ are {2 1 1}, of $Ca_3Al_2Si_3O_{12}$ is {1 1 0} and of $Ca_3Fe_2^{3+}Si_3O_{12}$ is {1 1 0} ≈ {2 1 1}. According to Chase and Osmer [2], $Y_3Ga_5O_{12}$ and $Y_3Fe_5O_{12}$ have a {2 1 1} morphology and $Y_3Al_5O_{12}$ has a {1 1 0} ≈ {2 1 1} morphology. They found that small tetrahedral metal ions favor a crystalline {1 1 0} habit and large tetrahedral metal ions favor a {2 1 1} habit. The effective ionic radius of the tetrahedral V metal ion (0.355 Å) is between that of Si (0.26 Å) and those of Al (0.39 Å), Ga (0.47 Å) and Fe (0.49 Å). Therefore, considering these morphological tendencies, an investigation of the morphology of vanadate garnets presents an interesting study.

Regarding the rank order of faces {1 1 0} and {2 1 1}, Hergt and Görnert [3] found that the predominance of the {1 1 0} face significantly increased with increasing growth temperature for flux-grown $Y_3Ga_5O_{12}$ and $Y_3Fe_5O_{12}$ garnets. Based on experimental determination of growth rate anisotropy, they concluded that the {1 1 0} face roughens at an even higher temperature than the {2 1 1} face. However, based on the kinetic statistical mechanical sublattice model for $Y_3Fe_5O_{12}$ garnets, Cherepanova et al. [4] showed that at high temperatures, faces of the {2 1 1} form will be dominant if growth on {1 1 0} occurs in single layers. At lower temperatures, for example 1173 K, and perhaps below this temperature, interlacing occurs and consequently growth occurs in double steps. Therefore, it can be predicted that {2 1 1} and {1 1 0} faces will dominate the habit of garnet crystals at lower temperatures. In the light of these contradictory conclusions that have been described in the literature, we propose to experimentally determine the relative importance of the temperature dependence of {1 1 0} and {2 1 1} faces in vanadate garnets [3].

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By measuring 133 garnets from Fort Wrangell and Alaska, Pabst [5] concluded that there was excellent correlation between morphology and size. These garnets all showed both {1 1 0} and {2 1 1} faces, and it was found that the predominance of {1 1 0} increased with the size of the garnet. There was no compositional variation in the garnets to which differences in morphology might be attributed, and the morphological differences between large and small garnets were not associated with any environmental differences. Therefore, based on these findings, we have an interest to examine the correlation of morphology with size in flux-grown vanadate garnets.

In order to clarify and solve unclear points or contradictions for the morphology of the garnets, it is very important to determine the rank order of the {1 1 0} and {2 1 1} faces [3]. To determine the rank order, vanadate garnet single crystals $NaCa_2M_2V_3O_{12}$ (M = Ni, Mg or Co) grown at low supersaturation levels using a $NaVO_3$ flux were examined. The relationship between the rank order of the {1 1 0} and {2 1 1} faces and the crystal structure change with substitution of ions and increasing temperature was also clarified. Furthermore, the correlation between morphology and size was determined by consideration of the rank order of the F-face and the surface kinetics in the growth process.

2. Experimental procedure

2.1. Solubility

The solubility of vanadate garnet in $NaVO_3$ was determined by measuring the mass loss of vanadate garnet in $NaVO_3$ melts at temperatures between 630 and 800 °C, using the method reported by Oishi and Sugiura [6]. Mixtures of excess crystals (0.5–2 mm in size, 0.5–1 g) of vanadate garnet prepared by the flux method [7] and $NaVO_3$ powder (ca. 5 g) were placed in platinum crucibles. After dissolution had proceeded for 10 h at controlled temperature, undissolved crystals were present upon quenching. The undissolved crystals were separated from the solidified saturated solution in warm water and then reweighed. The loss in mass due to dissolution represents the solubility at that temperature.

2.2. Flux growth

Reagent-grade Na_2CO_3, $CaCO_3$, NiO, MgO, CoO and V_2O_5 were used for flux growth of vanadate garnet crystals. Firstly, vanadate garnets and $NaVO_3$ were synthesized by solid-state reaction [8]. Stoichiometric amounts for the desired composition of each vanadate garnet or $NaVO_3$ were placed together with acetone and nylon balls in a polyethylene bottle and mixed well using a ball mill. Solid-state reactions were performed for 50 h at 850 °C and for 20 h at 560 °C for vanadate garnet and $NaVO_3$, respectively.

Secondly, flux growth was conducted as follows. The vanadate garnet powder was used as a solute and $NaVO_3$ powder was used as a flux. Mixtures of solute and $NaVO_3$ were prepared in molar ratios ($R = 100 \times \text{solute}/(NaVO_3 + \text{solute})$) of 0.3–0.9 mol%. All mixtures had a mass of 20 g and were placed in 30 cm^3 platinum crucibles. The crucible was then positioned in a vertical electric furnace with silicon carbide heating elements. The temperature-control apparatus consisted of a thermocouple that was positioned halfway along the furnace tube, and a KP1000 Controller/Programmer (CHINO Co.) with precision of ±0.1 °C. An additional reference thermocouple, used to monitor the furnace temperature, was positioned under the platinum crucible. Temperature calibration was conducted by measuring the melting temperature of $NaVO_3$. The run-to-run temperature reproducibility was within ±1 °C.

Crystal growth was conducted as follows. The furnace was heated at a rate of approximately 100 °C/h to a temperature 50 °C higher than the saturation temperature. The furnace was held at this temperature for 20 h (soaking), then rapidly cooled (over ca. 0.5 h) to a maintained cut-off temperature and held for 50 h (crystal growth). Following this, the crucible was removed from the furnace and quenched using water.

The crystalline products were separated by dissolving the flux in warm water. The resulting crystals were examined using an optical microscope, and the crystal phases were identified using X-ray diffraction (XRD).

In the present study, a solubility curve was used to obtain the objective yields. To determine the rank order of the F-face, experiments were conducted at the lowest level of supersaturation that was possible. That is, on a molar ratio R that was expected to result in yields as small as ca. 0.002 g at the cut-off temperature. However, in order to obtain relatively large crystals, experiments were also conducted on a molar ratio R that was expected to result in yields of ca. 0.02–0.03 g at the cut-off temperature.

3. Results and discussion

3.1. Solubility of vanadate garnets in $NaVO_3$

Mixtures of excess crystals of vanadate garnet and $NaVO_3$ powder were maintained for 2, 5 and 10 h at 630 °C in order to determine the time for equilibration. The solubility for each garnet at 630 °C was the same for the mixtures maintained for 5 and 10 h, so that the solubility was determined at a temperature higher than 630 °C by maintaining mixtures for 10 h at each temperature. Evaporation of $NaVO_3$ did not occur.

The dependence of solubility on temperature is shown in Fig. 1. Solubility was measured between 630 and 800 °C. The solubility was found to gradually increase with increasing temperature. The objective yields were calculated by using the determined solubility curves. The use of $NaVO_3$ as a flux for crystallization of the corresponding vanadate garnets was suitable, because both components of