Crystal Chemistry of Birefringent Uvarovite Solid Solutions

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Abstract: The crystal chemistry of five optically anisotropic uvarovite samples from different localities (California, Finland, Russia, and Switzerland) were studied with electron-probe microanalysis (EPMA) and the Rietveld method. Monochromatic synchrotron high-resolution powder X-ray diffraction (HRPXRD) data were used, and Rietveld refinement was carried out with the cubic space group, Ia̅3d. The general formula for garnet is \([\text{X}^3\text{Y}^2\text{Z}^3\text{O}_{12}]\). Uvarovite has the ideal formula, \(\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}\), which may be written as \(\text{Ca}_3(\text{Cr,Al,Fe})_2(\text{Si}_3\text{O}_{12})\) because of solid solutions. HRPXRD traces show multiple cubic garnet phases in each sample that has a heterogeneous chemical composition. The optical and back-scattered electron (BSE) images and elemental maps contain lamellar and concentric zoning as well as patchy intergrowths. With increasing \(a\) unit-cell parameter for uvarovite solid solutions, the Z–O distance remains constant, and the average \(<\text{X–O}>\) distance increases slightly in response to the \(\text{Cr}^{3+} \leftrightarrow \text{Al}^{3+}\) cation substitution in the Y site. The Y–O distance increases most because \(\text{Cr}^{3+}\) (radius = 0.615 Å) is larger than \(\text{Al}^{3+}\) (radius = 0.545 Å) cations. The \(\text{Fe}^{3+}\) (radius = 0.645 Å) cation is also involved in this substitution. Structural mismatch between the cubic garnet phases in the samples gives rise to strain-induced optical anisotropy.

Keywords: uvarovite; grossular; andradite; garnet; optical anisotropy; intergrowths of multiple cubic phases; Rietveld refinements; Synchrotron high-resolution powder X-ray diffraction (HRPXRD); structure; chemistry

1. Introduction

Several studies have documented birefringent garnets with lamellar or oscillatory features, which were referred to as “chemical zoning” instead of separate phases, e.g., [1–4]. Such birefringent garnets appear to contain a few cubic garnet phases that grow as oscillatory zoning or by re-sorption and re-precipitation that gives rise to patchy features, e.g., [5–7].

Birefringence in garnet was reported over a century ago, e.g., [8,9], but the origin remains questionable. Some almandine, grossular, spessartine, andradite, uvarovite, and hydrogarnet samples are anisotropic under cross-polarized light, which may indicate that they are not optically cubic, e.g., [10–13]. Several reasons were given for the birefringence, but the main one appears to be cation orders in the X and Y sites that cause a symmetry reduction, e.g., [1,10,14,15]. Other suggested reasons for the birefringence in garnet were discussed and are not repeated here [16].

Six birefringent uvarovite samples were investigated with various experimental techniques, and the results were presented [17–19]. The water content in these samples ranges from 0.07 to 0.34 wt. %, and they exhibit no compositional zoning. Their selected-area electron diffraction (SAED) patterns are consistent with cubic symmetry. Microwinning was not observed in their high-resolution transmission electron microscopy (HRTEM) images. Hydroxyl groups are not the primary cause for the anisotropic behavior in uvarovite, but cation ordering on the Y octahedral positions causes birefringence, as indicated by single-crystal X-ray diffraction studies [19]. The structure of their uvarovite samples was
refined in various noncubic space groups, including triclinic, monoclinic, and orthorhombic, and it was concluded that partial long-range Cr$^{3+}$/Al ordering on the Y site was the most prominent noncubic feature. The structure of a synthetic uvarovite was refined in the cubic space group [18]. Crystal structures that were refined in unnecessarily low symmetry space groups were heavily criticized [20,21].

Diffraction peaks from garnets showing split reflections were observed, e.g., [11,22–27]. Recently, multi-phase intergrowths of two or three cubic garnet phases were observed with HRPXRD; all birefringent garnets showed split reflections [5,7,16,28,29].

The structure consists of alternating ZO$_4$ tetrahedra and YO$_6$ octahedra with X atoms forming XO$_8$ dodecahedra (Figure 1). The eight O atoms in the XO$_8$ dodecahedron occur at the corners of a distorted cube. Each O atom is four-coordinated tetrahedrally by two X, one Y, and one Z cation. The O atom occupies a general position, whereas the cations are located at special positions with fixed atom coordinates. If substitution with a different size cation occurs on the Y site in uvarovite solid solutions, for example, then the Y–O distance changes significantly, whereas the Z–O and average <X–O> distances change by minor amounts [7]. Nomenclature of the garnet supergroup was recently given [34].

![Figure 1](image-url). Part of the garnet structure viewed down the c axis, showing the linkages of the various polyhedra (X = yellow dodecahedra, Y = pink octahedra, Z = green tetrahedra, and grey spheres = O atoms).

This study examines the crystal chemistry of five optically anisotropic uvarovite samples from different localities. Each sample contains multiple cubic garnet phases, but one crystal fragment is an isotropic cubic phase. This work is part of a large study on garnet-group minerals [35–39]. Briefly, this study indicates that intergrowth of multiple cubic phases in a crystal of uvarovite causes strain-induced optical anisotropy.
2. Experimental Methods

2.1. Sample Description

The localities and some characteristics of the five uvarovite samples used in this study are given (Table 1). The crystals were a few millimeters in size and varied in color from light to dark green. The specimen of sample 5 contained crystals that were either dark (5a and 5b were intergrowths of two cubic phases) or light green (5c was a cubic, isotropic phase). All the other samples were birefringent, so they were not optically cubic (Figure 2).

| Sample # | Locality |
|----------|----------|
| 1. Russia-A | Sarany, near Perm, Russia; Royal Ontario Museum (ROM #M51847) sample. |
| 2. Switzerland | Zermatt area, Switzerland (ROM #M33537). |
| 3. Russia-B | Sarany, Urals, Russia. |
| 4. Finland | Outokumpo, Finland. |
| 5a, 5b. California | Jacksonville, Toulumne Co., California, USA. These crystals are dark green. |
| 5c. California | Jacksonville, Toulumne Co., California, USA. The crystals are light green, isotropic, and chemically homogeneous. All crystals from sample 5 are from the same hand specimen. |

All the samples (a few millimeters in size) are light to dark green in color. They are birefringent and chemically heterogeneous, except for sample 5c.

![Figure 2](image_url) (a) PPL (b) XPL 100 µm

**Figure 2.** (a) Plane-polarized (PPL) and (b) cross-polarized (XPL) light images for uvarovite (Uv) sample 1 from Russia. The images are from a double-sided polished thin section of 50 µm thickness. Except for sample 5c, all the other Uv samples are birefringent in XPL.
2.2. Electron-Probe Microanalysis (EPMA)

Quantitative chemical compositions, backscattered electron (BSE) images, and X-ray elemental maps were collected with a JEOL JXA-8200 WD-ED electron-probe microanalyzer (EPMA) (JEOL, Tokyo, Japan). Point analyses were obtained with the wavelength-dispersive (WD) method. The JEOL operating program on a Solaris platform was used for ZAF correction and data reduction. The operating conditions were 15 kV accelerating voltage, 20 nA beam current, and 5 μm beam diameter. The counting time was 20 s on peak and 10 s on background. Relative analytical errors were 1% for major elements and 5% for minor elements. The following standards were used: almandine-pyrope (MgKα), grossular (CaKα), almandine (FeKα, AlKα, and SiKα), rutile (TiKα), spessartine (MnKα), chromite (CrKα), and zircon (ZrLα). EPMA data were analyzed with the spreadsheet of Locock [40], and some data points are given in Table 2. The variations of the cations in the Y site are shown graphically together with an indication of the number of data points measured.

2.3. Synchrotron High-Resolution Powder X-Ray Diffraction (HRPXRD)

The samples were studied with HRPXRD that was performed at beamline 11-BM, Advanced Photon Source (APS), Argonne National Laboratory (ANL). A small fragment (about 2 mm in diameter) of the sample was crushed to a fine powder using a corundum mortar and pestle. The crushed sample was loaded into a Kapton capillary (0.8 mm internal diameter) and rotated during the experiment at a rate of 90 rotations per second. Data were collected at 22 °C to a maximum 2θ of about 50° with a step size of 0.001° and a step time of 0.1 s per step. HRPXRD traces were collected with a unique multianalyzer detection assembly consisting of twelve independent silicon (111) crystal analyzers and LaCl₃ scintillation detectors that reduced the angular range to be scanned and allowed for rapid acquisition of data. A silicon (NIST 640c) and alumina (NIST 676a) standard (ratio of 1/3Si:2/3Al₂O₃ by weight) was used to calibrate the instrument and refine the monochromatic wavelength (λ = 0.41390(2) or 0.41424(2) Å) used in the experiment (see Table 3). Additional details of the experimental setup are given elsewhere [41–43]. The above experimental techniques were used to characterize many minerals [44–56].

2.4. Rietveld Structure Refinement

HRPXRD data were analyzed with the Rietveld method [57], as implemented in the GSAS program [58], and using the EXPGUI interface [59]. Scattering curves for neutral atoms were used. The starting atom coordinates, cell parameter, and space group, Ia₃d, were taken from [31]. The background was modeled using a shifted Chebyshev polynomial (eight terms). In the GSAS program, the reflection-peak profiles were fitted using a pseudo-Voigt (type-3) profile-shape function [60,61]. A full-matrix, least-squares refinement was carried out by varying the parameters in the following sequence: a scale factor, unit cell parameter, atom coordinates, and isotropic displacement parameters. No impurities or unindexed peaks were observed in the samples. When more than one phase was detected in the traces, the separate phases were refined together with the site occupancy factors (sofs) in terms of the dominant atoms in the X, Y, and Z sites. In the multiphase samples, the isotropic displacement parameter, U, for similar sites were constrained to be equal. Toward the end of the refinement, all parameters were allowed to vary simultaneously, and the refinement converged.
Table 2. Electron-probe microanalysis (EPMA) results for the five uvarovite samples † (including grossular (Grs) and andradite (Adr)) used in this study. Some samples contain more than one garnet phase (φ).

| Oxide (wt. %) | φ1a | φ1b | φ2a | φ2b | φ3a | φ3b | φ3c | φ4a | φ4b | φ4c | φ4d | φ5a | φ5b, c |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| CaO          | 33.54 | 33.66 | 34.89 | 33.78 | 35.71 | 35.23 | 34.75 | 33.55 | 33.42 | 32.94 | 33.94 | 33.52 | 32.60 |
| MnO          | 0.07 | 0.05 | 0.51 | 0.31 | 0.05 | 0.08 | 0.06 | 0.69 | 0.55 | 0.47 | 0.52 | 0.03 | 0.10 |
| MgO          | 0.06 | 0.03 | 0.20 | 0.11 | 0.00 | 0.00 | 0.00 | 0.10 | 0.10 | 0.08 | 0.08 | 0.10 | 0.02 |
| Cr₂O₃        | 17.95 | 21.85 | 3.82 | 15.73 | 12.58 | 14.41 | 17.45 | 20.30 | 22.73 | 0.28 | 10.46 |
| Al₂O₃        | 6.59 | 4.79 | 12.79 | 6.59 | 12.48 | 10.83 | 8.47 | 10.33 | 8.26 | 6.03 | 5.31 | 0.89 | 0.79 |
| Fe₂O₃        | 0.83 | 0.63 | 9.46 | 5.47 | 0.97 | 0.94 | 0.66 | 0.52 | 0.51 | 0.47 | 0.44 | 30.06 | 18.38 |
| TiO₂         | 1.92 | 0.93 | 0.27 | 0.13 | 0.20 | 0.20 | 0.18 | 0.50 | 0.33 | 0.14 | 0.12 | 0.11 | 0.21 |
| ZrO₂         | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| SiO₂         | 36.07 | 36.15 | 38.12 | 36.62 | 38.30 | 37.81 | 37.28 | 36.65 | 36.43 | 35.77 | 36.95 | 35.97 | 35.02 |
| ∑            | 97.06 | 98.09 | 100.07 | 98.75 | 100.28 | 99.74 | 99.40 | 96.81 | 97.20 | 96.44 | 100.11 | 100.88 | 97.70 |

| Cations for 12 O atoms (apfu) | Ca²⁺ | Mn²⁺ | Mg²⁺ | ΣX | Cr³⁺ | Al³⁺ | Fe³⁺ | Ti⁴⁺ | Zr⁴⁺ | V³⁺ | ΣY | Si⁴⁺ = Z |
|-------------------------------|------|------|------|-----|------|------|------|------|------|------|-----|----------|
| Ca²⁺                          | 2.989 | 0.005 | 0.007 | 3.000 | 1.180 | 0.052 | 0.120 | 0.001 | 0.000 | 0.000 | 2.000 | 3.000 |
| Mn²⁺                          | 2.993 | 0.034 | 0.024 | 3.000 | 1.434 | 0.468 | 0.058 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| Mg²⁺                          | 2.942 | 0.022 | 0.013 | 3.000 | 0.238 | 0.560 | 0.016 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| ΣX                            | 2.965 | 0.003 | 0.000 | 3.000 | 1.019 | 0.337 | 0.008 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| Cr³⁺                          | 2.997 | 0.005 | 0.000 | 3.000 | 0.779 | 0.057 | 0.012 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| Al³⁺                          | 2.995 | 0.004 | 0.000 | 3.000 | 0.919 | 0.056 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| Fe³⁺                          | 2.943 | 0.000 | 0.000 | 3.000 | 1.146 | 0.040 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| Ti⁴⁺                          | 2.944 | 0.000 | 0.000 | 3.000 | 0.933 | 0.032 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| Zr⁴⁺                          | 2.960 | 0.000 | 0.000 | 3.000 | 1.346 | 0.030 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| V³⁺                           | 2.952 | 0.000 | 0.000 | 3.000 | 1.459 | 0.027 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| ΣY                            | 2.996 | 0.000 | 0.000 | 3.000 | 0.507 | 0.007 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |
| Si⁴⁺ = Z                      | 2.933 | 0.000 | 0.000 | 3.000 | 0.709 | 0.014 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 3.000 |

End-member mole %

|                  | Uvarovite (Uv) | Grossular (Grs) | Andradite (Adr) | F(000) |
|------------------|----------------|-----------------|-----------------|--------|
|                  | 59 72 12 51    | 32 23 57 31    | 3 2 28 17      | 143 145 |
|                  | 46 57 47 57    | 50 40 48 38    | 3 3 2 2        | 137 144 |
|                  | 67 73 1 35     | 28 24 4 4      | 1 1 4 1      | 139 141 |
|                  | 73 1 35        | 28 24 4 4      | 1 1 4 1      | 141 144 |
|                  | 1 35           | 28 24 4 4      | 1 1 4 1      | 145 153 |
|                  | 35 1        | 28 24 4 4      | 1 1 4 1      | 151 151 |

† Samples 1, 2, and 5 contain two phases; sample 3 contains three phases; and sample 4 contains four phases. F(000) is the total number of electrons.
### Table 3. High-resolution powder X-ray diffraction (HRPXRD) data and Rietveld refinement statistical indicators for five uvarovite samples.

| Sample Location | 1. Russia-A (ROM #M51847) | 2. Switzerland (ROM #M33537) | 3. Russia-B | 4. Finland | 5a, b. California | 5c. California |
|-----------------|-----------------------------|---------------------------------|-------------|-----------|----------------|--------------|
|                 | \( \phi \ 1a \) | \( \phi \ 1b \) | \( \phi \ 2a \) | \( \phi \ 2b \) | \( \phi \ 3a \) | \( \phi \ 3b \) | \( \phi \ 3c \) |
| wt. %           | 41.6(5) | 58.4(3) | 85.2(1) | 14.8(2) | 29.2(5) | 34.8(9) | 36.0(4) |
| \( a \) (Å)     | 11.9617(1) | 11.97226(8) | 11.94509(2) | 11.96731(9) | 11.91603(9) | 11.92890(6) | 11.9405(1) |
| \( \Delta a \) (Å) | — | 0.0106\(^{b-a}\) | — | 0.0222\(^{b-a}\) | — | 0.0129\(^{b-a}\) | 0.0116\(^{b}\) |
| \( b \) LY      | 4.85 | 6.88 | 11.50 | 17.31 | 16.30 | 13.53 | 16.27 |
| Reduced \( \chi^2 \) | 2.310 | 1.163 | 1.437 |
| \( cR \) (\( F^2 \)) | 0.0497 | 0.0601 | 0.0868 |
| \( N_{\text{obs}} \) | 1361 | 1390 | 2017 |
| \( \lambda \) (Å) | 0.41390(2) | 0.41390(2) | 0.41424(2) |
| Data points | 47992 | 47992 | 47996 |
| \( \phi \) \(4a\) | 1.2(6) | 13.0(3) | 61.7(3) | 24.0(4) | 25.1(2) | 74.9(1) | 100.0 |
| \( a \) (Å)     | 11.9200(1) | 11.9400(1) | 11.95213(3) | 11.95942(5) | 12.03656(3) | 12.05168(2) | 12.05247(1) |
| \( \Delta a \) (Å) | — | 0.0200\(^{b}\) | 0.0121\(^{b}\) | 0.0073\(^{d-c}\) | — | 0.0151\(^{b-a}\) | 0.0008\(^{b}\) |
| \( b \) LY      | 7.27 | 12.04 | 8.53 | 6.95 | 10.65 | 10.91 | 8.82 |
| Reduced \( \chi^2 \) | 1.558 | 1.180 | 3.098 |
| \( cR \) (\( F^2 \)) | 0.0425 | 0.0385 | 686 |
| \( N_{\text{obs}} \) | 2656 | 1366 | 686 |
| \( \lambda \) (Å) | 0.41424(2) | 0.41424(2) | 0.41424(2) |
| Data points | 47996 | 47996 | 686 |

Sample 5 from California contains dark (5a, b) and light (5c) green crystals. Phase 5c has structural parameters that are the same as phase 5b. \(^a\) The strain and birefringence are proportional to \( \Delta a = (\bar{a}_{\text{substrate}} - \bar{a}_{\text{film}}) [62]. \(^b\) The profile term LY is a measure of strain. The minor phase is under more strain than the dominant phase. \(^c\) \( R \) (\( F^2 \)) = Overall R-structure factor based on observed and calculated structure amplitudes \( = \left( \sum(F_o^2 - F_c^2)/\sum(F_o^2) \right)^{1/2} \). \(^d\) \( \theta \) range = 2–50°.
3. Results

The samples appeared homogeneous in plane-polarized light (PPL), but they were birefringent under cross-polarized light (XPL) with lamellae (Figure 2). Sample 5c was isotropic and was a single cubic phase. The back-scattered electron (BSE) images contained light and dark areas that indicated different compositions (Figure 3). These BSE images showed patchy features (e.g., Figure 3a) or lamellar features that represented different compositions (Figure 3b,c). The brighter areas (higher mean atomic number) corresponded to Cr/Fe-rich uvarovite, whereas the darker areas (lower mean atomic number) corresponded to Al-rich uvarovite, \( \text{Ca}_3\{\text{Al}, \text{Cr}, \text{Fe}\}_2\text{Si}_3\text{O}_{12} \).

![Figure 3](image)

**Figure 3.** Back-scattered electron (BSE) images showing well-defined lamellar features in all the images. (a) Uv sample 1 from Russia-A, (b) Uv sample 3 from Russia-B, and (c) Uv sample 5 from California. The crystals in (a) also contain patchy features that arise from dissolution and re-precipitation. The scale bars are shown.

The BSE image and X-ray elemental maps showed the distribution of Al, Cr, and Ti atoms for sample 1 (Figure 4) and sample 5 (Figure 5). Concentric and lamellar features clearly showed a heterogeneous distribution of the Al atoms (Figure 4b). The lamellar features indicated epitaxial growth and represented two different compositions that were visible in the images. Two separate compositions can be deduced from the elemental maps and quantitative spot analyses (Table 2; Figure 6). The EPMA compositions from the various points were not averaged because of their heterogeneous distribution in each sample. Instead, a composition for each phase in a sample was given (Table 2), and the distribution of the cations in the Y site was shown (Figure 6). After examining EPMA and HRPXRD results, probable compositions were given for each phase in Table 2.
Figure 4. Uv sample 1 from Russia: (a) BSE image contains light and dark concentric features that indicate different compositions. The X-ray elemental maps show the distribution of (b) Al, (c) Cr\(^{3+}\), and (d) Ti\(^{4+}\) atoms that occur in the Y site. The Fe\(^{3+}\) map is homogeneous and is not shown. The concentric features indicate epitaxial growth and two different compositions are observed (Table 2). The scale bar in (a) is 100 μm.
Instead of lamellar or epitaxial features, sample 5 displayed patchy features with heterogeneous distribution of Al atoms (Figure 5). This sample contained two cubic phases. It was possible to find a light green crystal fragment that was a cubic isotropic phase (i.e., sample 5c).

The complete HRPXRD traces for the samples are given (Figure 7). The expanded traces showed that each reflection peak was split because each sample contained different cubic phases (Figure 8). Sample 5c represented a single cubic phase because the peaks were sharp, narrow, and symmetrical (Figures 7f and 8f).

The unit-cell parameters and the Rietveld refinement statistical indicators for the phases in the five samples are given (Table 3). Their atom coordinates, isotropic displacement parameters, and sefs are given (Table 4). Bond distances and angles for each phase are listed (Table 5). The unit cell parameters and bond distances are displayed (Figure 9).

Figure 5. Uv sample 2 from Switzerland: (a) BSE image contains light and dark patches that indicate different compositions. The X-ray elemental maps show the inverse distribution of (b) Al and (c) Cr atoms. The Fe and Mg maps are homogeneous and are not shown. The light and dark patches are formed by dissolution and re-precipitation of the Uv crystals. The scale bar in (a) is 50 μm.
Figure 6. Variations for the dominant Y-site cations for the five Uv samples: (a) 1. Russia-A, (b) 2. Switzerland, (c) 3. Russia-B, (d) 4. Finland, and (e) 5. California. For each EPMA data point, apfu were obtained from each sample (some are given in Table 2), and the cations on the Y site are shown graphically. The point analyses are ordered in terms of the dominant Y-site cation.
Figure 7. Complete HRPXRD traces for the five Uv samples: (a) 1. Russia-A, (b) 2. Switzerland, (c) 3. Russia-B, (d) 4. Finland, (e) 5a, b. California, and (f) 5c. California. The difference curve ($I_{\text{obs}} - I_{\text{calc}}$) is shown at the bottom of each trace. Short vertical lines indicate allowed reflection positions. The intensities and difference curves that are above 20° 2θ are multiplied by 5. The inserts contain the 400 reflection that occurs at a low 2θ angle, and the range is the same for each sample.
Figure 8. Expanded scale for the same set of reflections for five samples: (a) 1. Russia-A, (b) 2. Switzerland, (c) 3. Russia-B, (d) 4. Finland, (e) 5a, b. California, and (f) 5c. California. For the multiple-phase cubic samples, each reflection peak is split, asymmetrical, or broad (a, b, and e = two phases, c = three phases, d = four phases), whereas a cubic single-phase garnet has sharp, narrow, and symmetrical peaks (f).
Figure 9. Structural variations for five uvarovite samples that occur between grossular (Grs; \(a = 11.845(1) \text{ Å} \) [31]) and andradite (Adr; \(a = 12.06259(1) \text{ Å} \) [7]) (dashed vertical lines). A dashed vertical line for a synthetic uvarovite (Uv) is shown (\(a = 11.997 \text{ Å} \) [18]). The (a) average \(<X–O>\), (b) mean \(<D–O>\), (c) \(Y–O\), and (d) \(Z–O\) distances vary linearly with the \(a\) unit cell parameter. The intervals on the y-axis are the same in each plot (0.11 Å). The \(Z–O\) distances are nearly constant. The \(<X–O>\) and \(<D–O>\) distances change by small amounts, but the \(Y–O\) distances change the most and show the most scatter. Phase 1b and, in particular, phase 2b may contain minor amounts of \((O_4H_4)\) hydrogarnet substitution because their \(Z–O\) distance increases as their \(Y–O\) distance decreases. Error bars are smaller than the symbols.
| Table 4. Atom coordinates, isotropic displacement parameters, \( U \times 100 \) (Å²), and sofs for five uvarovite samples (including Grs and Adr). |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Russia-A | 2. Switzerland | 3. Russia-B | 4. Finland | 5a, b. California | 5c. California |
| \( \phi_1 \) a | \( \phi_1 \) b | \( \phi_2 \) a | \( \phi_2 \) b | \( \phi_3 \) c | \( \phi_4 \) a | \( \phi_4 \) b | \( \phi_4 \) c | \( \phi_4 \) d | \( \phi_5 \) a | \( \phi_5 \) b | \( \phi_5 \) c | \( \phi_5 \) d |
| Ca(X) | Y | U | Cr | 0.44(1) | 0.44(1) | 0.474(4) | 0.447(1) | 0.47(1) | 0.47(1) | 0.453(7) | 0.453(7) | 0.453(7) | 0.453(7) | 0.463(9) | 0.463(9) | 0.440(9) |
| Y | U | 0.206(6) | 0.206(6) | 0.331(6)Al | 0.331(6)Al | 0.183(8)Cr | 0.183(8)Cr | 0.184(4)Cr | 0.184(4)Cr | 0.184(4)Cr | 0.184(4)Cr | 0.274(4)Fe | 0.274(4)Fe | 0.275(5)Fe |
| Si(Z) | Si | U | Y | 0.27(1) | 0.27(1) | 0.29(1) | 0.29(1) | 0.23(2) | 0.23(2) | 0.30(1) | 0.40(1) | 0.30(1) | 0.30(1) | 0.30(1) | 0.30(1) | 0.32(1) | 0.32(1) | 0.36(1) |
| O | O | x | x | 0.0396(1) | 0.0398(1) | 0.0385(3) | 0.0384(2) | 0.0398(1) | 0.036(2) | 0.042(2) | 0.042(2) | 0.037(2) | 0.037(2) | 0.038(2) | 0.038(2) | 0.039(8) | 0.03937(6) | 0.03956(5) |
| y | y | 0.045(1) | 0.048(1) | 0.0465(2) | 0.0479(2) | 0.0479(1) | 0.042(2) | 0.050(2) | 0.046(2) | 0.0464(2) | 0.0464(2) | 0.0479(1) | 0.0483(1) | 0.0483(5) | 0.04838(4) |
| z | z | 0.654(1) | 0.652(1) | 0.6530(3) | 0.652(2) | 0.6532(2) | 0.6522(2) | 0.6532(2) | 0.654(2) | 0.6548(2) | 0.6548(2) | 0.6533(2) | 0.654(2) | 0.654(2) | 0.6550(2) | 0.6552(4) |
| Ca(X) | Ca | Y | Cr | U | 0.82(2) | 0.82(2) | 0.85(2) | 0.85(2) | 0.80(2) | 0.80(2) | 0.80(2) | 0.80(2) | 0.80(1) | 0.80(1) | 0.80(1) | 0.80(1) | 0.85(1) | 0.85(1) | 0.88(2) |
| Y | sof | 0.773(3) | 0.825(2) | Al | 1.397(2) | 1.595(8) | 0.661(3) | 0.722(4) | 0.708(3) | 0.632(2) | 0.731(4) | 0.810(5) | 0.818(3) | 0.881(3) | 0.909(1) | 0.905(1)Fe |
| Si(Z) | sof | 0.950(4) | 0.908(3) | 0.92(2) | 0.932(5) | 0.944(4) | 0.888(5) | 0.943(5) | 0.89(2) | 0.907(6) | 0.930(2) | 0.932(4) | 0.946(4) | 0.936(2) | 0.937(2) |
| Ca(X) | EPMA | 0.999 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Y | EPMA | 0.850Cr | 0.892Cr | 1.386Al | 1.603Al | 0.738Cr | 0.770Cr | 0.817Cr | 0.770Cr | 0.817Cr | 0.862Cr | 0.885Cr | 0.977Fe | 0.948Fe | 0.948Fe |
| Si(Z) | EPMA | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| X | \( \Delta \) (sof) | -0.073 | -0.038 | -0.347 | -0.046 | -0.939 | 0.010 | -0.103 | -0.203 | -0.083 | -0.037 | -0.101 | -0.056 | -0.059 | -0.059 |
| Y | \( \Delta \) (sof) | -0.077 | -0.067 | 0.011 | -0.08 | -0.077 | -0.048 | -0.19(4) | -0.086 | -0.057 | -0.067 | -0.096 | -0.039 | -0.039 |
| Z | \( \Delta \) (sof) | -0.070 | -0.092 | -0.076 | -0.068 | -0.056 | -0.112 | -0.110 | -0.093 | -0.070 | -0.068 | -0.054 | -0.064 | -0.064 |
| \( \Delta \) c | | -0.15 | -0.8 | -0.9 | -0.9 | -1.9 | 0.2 | -2.1 | -4.1 | -1.7 | -0.7 | -2.0 | -1.1 | -1.2 | -1.2 |
| Y | \( \Delta \) c | -1.8 | -1.6 | 0.1 | -0.1 | -1.8 | -1.1 | -2.6 | -3.4 | -2.1 | -1.4 | -1.6 | -2.5 | -1.0 | -1.0 |
| Z | \( \Delta \) c | -1.0 | -1.3 | -1.1 | -1.0 | -0.8 | -1.6 | -0.8 | -1.5 | -1.3 | -1.0 | -1.0 | -0.8 | -0.9 | -0.9 |

1a \( \pm 1b = \) difference between sofs obtained by refinements for the two phases. A significant difference occurs in the Y site. \( O(\text{sof}) = 1.0 \). 4 X at (0, 1/4, 5/6) with Ca dominant, Y at (0, 0, 1/2) with Cr or Al dominant, and Z at (1/6, 0, 3/4) with Si dominant. For each sample, the U for the same site in each phase was constrained to be equal. 5 \( \Delta (\text{sof}) = \text{sof} \) (HRPXRD refinement) \( \pm \) sofs (EPMA). 6 \( \Delta e = \) electrons (HRPXRD refinement) \( \pm \) electrons (EPMA). 7 Phase 4a was a small amount of 1.2(6) wt. %, so the atom coordinates were fixed to those of phase 4b.
Table 5. Selected bond distances (Å) and angles (°) for five uvarovite samples.

|       | 1. Russia-A | 2. Switzerland | 3. Russia-B |
|-------|-------------|----------------|-------------|
|       | φ1a | φ1b    | 1a – 1b | φ2a | φ2b    | 2a – 2b | φ3a | φ3b    | φ3c |
| Z–O   | ×4  | 1.627(2) | 1.659(1) | −0.032 | 1.6487(6) | 1.666(3) | −0.017 | 1.639(2) | 1.649(2) | 1.645(2) |
| Y–O   | ×6  | 1.980(2) | 1.974(1) | 0.006  | 1.9649(6) | 1.962(2) | 0.003  | 1.970(2) | 1.935(2) | 1.989(2) |
| X–O   | ×4  | 2.345(2) | 2.353(1) | −0.008 | 2.3382(5) | 2.351(2) | −0.013 | 2.349(2) | 2.312(2) | 2.375(2) |
| X'–O  | ×4  | 2.518(2) | 2.481(1) | 0.037  | 2.4963(5) | 2.483(2) | 0.013  | 2.477(2) | 2.538(2) | 2.451(2) |
| <X–O> | [8]  | 2.432   | 2.417    | 0.015  | 2.4173    | 2.417    | 0.000  | 2.413    | 2.425    | 2.413    |
| a<Y–O> | [4]  | 2.118   | 2.117    | 0.001  | 2.1120    | 2.116    | −0.004 | 2.109    | 2.109    | 2.115    |
| ∠Y–O–Z| ×1  | 135.7(1) | 133.96(7)| 1.74   | 134.84(3) | 134.2(1) | 0.64   | 134.5(1) | 136.8(1) | 133.1(1) |

4. Finland

|       | φ4a | φ4b    | φ4c    | φ4d    | φ5a    | 5a – 5b | φ5b    | 5a – 5b | 5b – 5c |
|-------|-----|--------|--------|--------|--------|---------|--------|---------|---------|
| Z–O   | ×4  | 1.644(2) | 1.639(3) | 1.646(1) | 1.644(2) | 1.652(2) | 1.6478(7) | 0.004  | 1.6445(6) | 0.003  |
| Y–O   | ×6  | 1.989(2) | 1.982(3) | 1.971(1) | 1.989(2) | 2.005(2) | 2.0138(7) | −0.009 | 2.0169(6) | −0.003 |
| X–O   | ×4  | 2.332(2) | 2.320(3) | 2.340(1) | 2.332(2) | 2.356(2) | 2.3610(7) | −0.005 | 2.3621(5) | −0.001 |
| X′–O  | ×4  | 2.487(2) | 2.496(3) | 2.497(1) | 2.487(2) | 2.498(2) | 2.5019(7) | −0.004 | 2.5031(5) | −0.001 |
| <X–O> | [8]  | 2.410   | 2.408    | 2.419    | 2.410    | 2.427    | 2.4315    | −0.005 | 2.4326    | −0.001 |
| a<D–O>| [4]  | 2.113   | 2.109    | 2.114    | 2.113    | 2.128    | 2.1311    | −0.003 | 2.1317    | −0.001 |
| ∠Y–O–Z| ×1  | 133.6(1) | 134.2(2) | 134.78(5) | 133.6(1) | 133.6(1) | 133.59(4) | 0.01   | 133.62(3) | −0.03  |

1a – 1b = difference between phases 1a and 1b, etc. Significant difference occurs for the Y–O distance (see Figure 9). * a<D–O> = [(Z–O) + (Y–O) + (X–O) + (X′–O)]/4, which is the average distance from the four-coordinated O atom.
4. Discussion

Both the EPMA results and the HRPXRD data indicated that all the uvarovite samples were chemically heterogeneous. EPMA point analyses were used to obtain an estimate of the individual phase composition (Table 2; Figure 6).

There are several assumptions made in calculating a chemical formula for garnet using EPMA data so that the formula is stoichiometric with no atom vacancies and results in a general formula, $X_3Y_2Z_3O_{12}$. Cation vacancies are possible in garnets and are well-known in hydrogarnets, e.g., [63–67]. Atom vacancies are common in minerals, and this is tested by refining the cation sof as the O-atom sof is set to 1 (Table 4). Using all the atoms obtained by EPMA, sof s are calculated in terms of the dominant atoms in the X(Ca), Y(Cr/Al/Fe), and Z(Si) sites and then converted to electrons (Table 4). The $\Delta$e values for these sites are reported in the last three lines in Table 4. The agreement between EPMA and refinements results are quite good, except for phases that occur in such small amounts that their structures cannot be refined with sufficient accuracy (e.g., phase 4a).

Complete HRPXRD traces are shown for the five samples (Figure 7). A single cubic isotropic phase is observed for sample 5c (Figures 7f and 8f). The expanded HRPXRD traces clearly show multiple cubic phases (Figure 8). Each peak in the birefringent uvarovite samples is split, but the isotropic sample 5c shows sharp, symmetric, and narrow peaks. The split reflections indicate multiple cubic phases: samples 1, 2, and 5 contain two phases; sample 3 contains three phases; and sample 4 contains four phases. Different compositions corresponding to the different cubic uvarovite phases were also observed in BSE images and point analyses (Table 1; Figure 6).

Vacancies in the Z site (<10%), if real, may indicate minor (O$_4$H$_4$) substituting for the SiO$_4$ group. If (O$_4$H$_4$) substitution occurs, then Z(sof) is <1, the unit cell edge increases, the Si–O bond distance increases, and, simultaneously, the Y–O distance decreases from their corresponding values in the hydrous phase [63]. Based on these criteria, (O$_4$H$_4$) substitutions appear to be insignificant in our samples except for phases 2b and 1b (Table 5, Figure 9).

Data from this study are shown in Figure 9, which was previously developed to show the structural variations across the entire cubic garnet-group minerals, including cubic hydrogarnets [7,63]. Figure 9 was constructed with data taken from the literature, e.g., [30,31,64–89]. All the single-crystal structure refinements of garnets were done in the cubic space group, $Ia3d$, and only single phases were observed with the single-crystal method, which is not appropriate for studying a multiple-phase assemblage because of the complications that arise from diffraction of the different phases. The bond distances obtained by single-crystal and HRPXRD methods are similar. Multiple phases in grossular could not be observed with TEM [10] but were easily observed with HRPXRD (this study; [28]). Multiphases also occur in other minerals such as apatite [90], genthelvite [91], and nepheline [92].

The O atom is at a general position in the garnet structure, and the coordinates for all the cation sites are fixed. Because each O atom is four-coordinated by one Z, one Y, and two X sites in a tetrahedral configuration, substitution on any one cation site has only minor effects on the other sites, as reflected in their bond distances [7]. The Z–O distances are nearly constant and are within the range 1.64 to 1.65 Å because the Z site is nearly filled with Si atoms (Figure 9). The X site is nearly filled with Ca atoms, so the <$X$--$O$> distance increases slightly in response to substitution in the Y site (Figure 9). Therefore, the Z and X sites have minor influence on the structural variations in uvarovite solid solutions, which is controlled mainly by Cr, Al, and Fe atoms in the Y site. Sample 5 from California plots close to end-member andradite, so it is inappropriate to call it uvarovite, especially for phase 5a, which is Adr$_{94}$Gr$_{4}$Uv$_{1}$ (Table 2).

Sample 5 contains two cubic phases. Phases 5b and 5c have unit cell parameters, and bond distances are identical to each other (5b and 5c in Table 5; Figure 9). Phase 5a contains less Fe$^{3+}$ cations than phases 5b or 5c (Table 4). This difference results in large differences in the sof s for the Y site (Table 4) and Y–O distances (Figure 9). The Z–O and average <$X$–$O$> distances are nearly the same for all phases in sample 5 because they contain similar numbers of Si and Ca atoms, respectively (Table 4;
The larger unit cell parameters of phases 5b and 5c over 5a results from a larger number of Fe atoms in phases 5b and 5c. This difference in unit cell parameters is 0.015 Å (Table 3).

The Y–O distance increases the most because of the substitutions of large Fe$^{3+}$ (radius = 0.645 Å) and Cr$^{3+}$ (radius = 0.615 Å) cations for smaller Al$^{3+}$ (radius = 0.535 Å) cations, as required for solid solutions between anhydrous grossular (Ca$_3$Al$_2$Si$_3$O$_{12}$), uvarovite (Ca$_3$Cr$_2$Si$_3$O$_{12}$), and andradite (Ca$_3$Fe$^{3+}_2$Si$_3$O$_{12}$). For some samples, there appears to be an increase in Z–O distance and a corresponding decrease in Y–O distance, which may indicate minor hydrogarnet substitution [28,64,65]. A good example is phase 2b (Figure 9).

The <D–O> distances (<D–O> = [(Z–O) + (Y–O) + (X–O) + (X’–O)]/4) vary linearly with the a unit cell parameter [16]. All data points shown in Figure 9 essentially fall on the linear line for <D–O>, but the other distances (Z–O, <X–O>, and Y–O) show varying degrees of scatter. Better coordination of the O atom over the cations appears to be important for the garnet structure.

Lamellar “zones” in grossular–andradite (Grs–Adr) solid solutions are Al$^{3+}$- or Fe$^{3+}$-rich, and they have an inverse relation with regard to these cations occupying the Y site, e.g., [1,3,4,24,93]. In order to simulate cation order in garnets, many single-crystal studies were done in space groups with symmetries that were lower than cubic (see Introduction). However, this study, as well as our other studies on garnets, show that such lamellar “zones” represent two or three different cubic phases [5,7,16,28]. The different cubic phases are evident from HRPXRD traces (Figures 7 and 8) and BSE images (Figures 3–5). Oscillatory zoning in garnet-group minerals may be primary growth features, as these are similar to those observed in erythrite [94]. The patchy features observed in BSE images may arise from secondary dissolution and re-precipitation.

Hirai and Nakazawa [24] observed stratified (110) layers in an iridescent grandite garnet, where the layers were composed of Fe-rich (Adr$_{87}$) and Al-rich (Adr$_{78}$) lamellae. Their selected-area electron diffraction (SAED) pattern showed two phases because spots were split normal to the lamellae. From the split reflections, the difference in unit cell size for the two phases was about 0.02 Å. They interpreted the lamellae as arising from exsolution [23,24] instead of oscillatory zoning, e.g., [1–4]. In our studies on andradites that contained lamellae, two or three different cubic phases were observed [5,16].

5. Conclusions

Uvarovite garnets have cubic symmetry and can exist as a single-phase or an intergrowth of a few cubic uvarovite phases, which occurs as epitaxial growth features (“chemical zoning”) instead of exsolution (e.g., Figure 3b,c). The different phases can also form by hydrothermal alteration where the original phase is dissolved, re-precipitated, and occurs as patchy features (e.g., Figures 3a, 4 and 5). Such patchy features were observed in other garnets [6,33]. Single-phase uvarovite is optically isotropic, whereas the multiphase uvarovite samples are anisotropic because of the strain arising from structural mismatch (differences in unit cell parameters and bond distances). The coexistence of multicubic phases is caused by compositional variations at the Y site (Al, Cr, and Fe substitutions) that also control the structural variations because the atoms occupying the Y site have different sizes.

Garnets exist in various geological environments and have extensive uses in society. The birefringence problem in garnet has perplexed researchers for over a century. This study on uvarovite garnet shows that structural mismatch between the cubic phases in the intergrowths gives rise to strain-induced birefringence. The presence of these different phases can easily be detected with high-resolution synchrotron X-rays. This study also clarifies that uvarovite garnet is cubic, which is in contrast to recent studies that claim the presence of low symmetry that arises from cation ordering.

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