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Cation Distribution by Powder X-Ray Diffraction in Uvarovite–Grossularite Garnets Solid Solutions Synthesized by the Sol–Gel Method

J. Carda[1] and G. Monros

Departamento de Ciencias Experimentales, Area Química Inorgánica, Universitat Jaume I, Apdo. 224, 12080 Castellon, Spain

V. Esteve

Departamento de Ciencias Experimentales, Area de Cristalografía y Mineralogía, Universitat Jaume I, Apdo. 224, 12080 Castellon, Spain

and J. M. Amigo

Departamento de Geología, Area de Cristalografía y Mineralogía, Universitat de València, C/. Dr. Moliner, 45 Burjassot, Valencia, Spain

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Nominal compositions of uvarovite–grossularite solid–solutions $Ca_3(Cr_{1-x}Al_x)_2Si_3O_{12}$, series $x = 0$ to $x = 1$, have been prepared by sol–gel method and fired up to 1000°C. Five of these structures ($x = 0$ to 0.5) have been refined using the Rietveld method from X-ray powder diffraction data taken with a Siemens D-500 diffractometer. The limit of solid solutions of these structures has been stabilized in 20% mole grossularite. The unit cell is cubic, *Ia3d* (230), $Z = 8$, $a = 12.0205(5)$ to 11.9903(18) for the five structures presented.

INTRODUCTION

Garnet structures have been widely studied the last thirty years (1, 2). The unit cell of $A_3B_2C_3O_{12}$ garnets contains 160 atoms: large cations (Ca^{2+}, Y^{3+}, Nd^{3+}, etc.) fill dodecahedral *A*-sites, intermediate-sized cations (Cr^{3+}, Al^{3+}, Gd^{3+}, etc.) octahedral *B*-sites, and smaller cations (Si^{4+}, Ga^{3+}, etc.) tetrahedral *C*-sites (3). The important physical properties of these components are a good reason for trying to design new solid solutions with interesting optical, magnetic, or electrical properties (4–7).

In this sense, recently, Carda *et al.* (8) have investigated methods for obtaining different garnet structures with applications to the ceramic pigments industry.

The systematic determination of crystallographic properties with this class of materials is extremely important and generally very useful in order to assign the cation site-occupancies, and consequently to develop new properties. Thus, several authors have focused their attention on determining garnet structures by multiple regression analysis. They have used the fitting of crystallographic data to identify errors in assigned cation site occupancies, valence, and spin states, to calculate the ionic radii, and to show the possible existence of new components (9, 10).

These multicomponent systems, generally react slowly (11). Therefore, it is very difficult to reach thermodynamic equilibrium, giving rise to the presence of heterogeneities either as residual starting materials or local variations of particle composition (12). In this sense, the first aim of this work is the preparation of this crystalline phase by sol–gel methods. This one is very interesting and it permits the obtainment of higher homogeneities in the starting mixtures and low processing temperatures (13).

The second aim of this work is to determine, by powder X-ray diffraction data, using the Rietveld method, the cation distribution in a solid–solution series of uvarovite and grossularite garnets ($Ca_3\,(Cr_{1-x}\,Al_x)_2\,Si_3\,O_{12}$, $x = 0$ to 1) synthesized at atmospheric pressure by the sol–gel process.

2. EXPERIMENTAL

2.1. Preparation and Characterization of Samples

A total of nine compositions were prepared along join uvarovite ($Ca_3Cr_2Si_3O_{12}$)–grossularite ($Ca_3Al_2Si_3O_{12}$) garnets (UVA–GROS), as is shown in Table 1.

All samples were synthesized by the sol–gel method, from silicium alkoxide (TEOS, Aldrich 99%) and calcium chlorides, chromium and aluminum chlorides salts (($CaCl_2 \cdot 2H_2O$), Merck 99.5%; $CrCl_3 \cdot 6H_2O$, Baker 100% and $AlCl_3 \cdot 6H_2O$, Merck 99%).

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[1] To whom correspondence should be addressed.

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TABLE 1
Nominal Compositions Prepared from the $Ca_3(Cr_{1-x}Al_x)_2\ Si_3O_{12}$ System

Sample	x	mole% UVA	Nominal composition
1	0.00	100	$Ca_3Cr_2Si_3O_{12}$
2	0.15	85	$Ca_3Cr_{1.7}Al_{0.3}Si_3O_{12}$
3	0.25	75	$Ca_3Cr_{1.5}Al_{0.5}Si_3O_{12}$
4	0.35	65	$Ca_3Cr_{1.3}Al_{0.7}Si_3O_{12}$
5	0.50	50	$Ca_3CrAlSi_3O_{12}$
6	0.65	35	$Ca_3Cr_{0.7}Al_{1.3}Si_3O_{12}$
7	0.75	25	$Ca_3Cr_{0.5}Al_{1.5}Si_3O_{12}$
8	0.85	15	$Ca_3Cr_{0.3}Al_{1.7}Si_3O_{12}$
9	1.00	0	$Ca_3Al_2Si_3O_{12}$

TABLE 2
Observed Phases after Thermal Treated Samples at 1000°C/for 30 Days

Sample	Observed phases
1	UVA (s)
2	UVA–$GROS_{ss}$(s) + $\alpha CaSiO_3$(vw)
3	UVA–$GROS_{ss}$(s) + $\alpha CaSiO_3$(vw)
4	UVA–$GROS_{ss}$(s) + $\alpha CaSiO_3$(vw)
5	UVA–$GROS_{ss}$(s) + $\alpha CaSiO_3$(vw) + Gh(vw)
6	UVA–$GROS_{ss}$(m) + $\alpha CaSiO_3$(vw) + Gh(m)
7	UVA–$GROS_{ss}$(m) + $\alpha CaSiO_3$(vw) + Gh(m)
8	UVA–$GROS_{ss}$(w) + $\alpha CaSiO_3$(vw) + Gh(s)
9	$\alpha CaSiO_3$(s) + Gh(s)

Note. Peaks intensity: (s), strong; (m), medium; (w), weak; (vw), very weak Gh, $Ca_2Al_2SiO_7$.

Figure 1 shows the experimental process to prepare the gels.

Stoichiometric amounts of TEOS and salts were prepared. TEOS was mixed with ethanol (TEOS/Ethanol = 4 : 8 V/V) in a glass vessel and refluxing for 24 hr. The chloride salts, previously dissolved in ethanol, were added to the solution of TEOS. The resulting solution was heated at 70°C and stirred for 24 hr; then the acid catalyst in HCl 3 *M* form (alkoxide/catalyst molar ratios here used were 1 : 0.099) was added, while keeping the same conditions until gelling occurred. All gels were dried afterwards at room temperature.

The dried gels were calcinated in an electric muffle furnace at 500°C/2 days, 800°C/7 days, 1000°C/14 days, and 1000°C/30 days. After each stage the samples were ground. This procedure was sufficient to reach equilibrium in every case (8).

The microstructure and microanalysis of gels (dry and fired) were studied by SEM/EDX (Hitachi, H-2500 model; Kevex Quantum 2000) and TEM/STEM/EDX configuration (Hitachi H-5000 model, Kevex Quantum 2000) as reported in previous publications (12, 14).

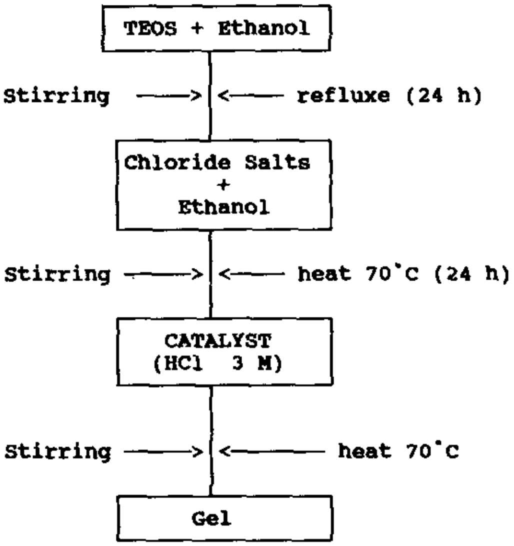

FIG. 1. Processing carried out for the preparation of gels.

2.2. X-Ray Powder Analysis

X-ray diffraction data (XRD) were obtained on dried material that was ground to 80 μm. Samples were manually pressed into standard Siemens D500 sample holders. The powder XRD patterns were taken at room temperature with a Siemens D500 X-ray powder diffractometer with a Bragg–Brentano geometry using Cu$K\alpha$ radiation (40 kV, 20 mA, divergence slit, 1°; detector slit, 0.05°), scintillation detector, and a secondary crystal graphite monochromator, using corundum as internal standard.

Intensities were collected by step-scanning from 20° to 80° (2θ) with a step size of 0.08° (2θ) and a counting time of 3 sec for each step for angular position determination and 0.05° (2θ) and 10 sec counting time for determination of intensities. The goniometer was controlled by the Siemens DIFFRAC AT software, which makes the integration of the diffraction peaks and the background correction.

The unambiguously indexed reflexions were used in several cycles of unit cell parameter refinement by using the Burnham least squares refinement program LCLSQ 30 (version 8.4) (15) running on a compatible PC.

The solid solution ratio has been determined by the Rietveld method (16), by using the WYRIET version for PC-AT computers (17) of the DBW3.2S-8804 program from Wiles *et al.* (18).

The structural model and initial structural parameters were taken from Hawthorne (9) as follows: space group $Ia3d$ (230); Z = 8 unit formula $Ca_3(Cr_{1-x}Al_x)_2Si_3O_{12}$; cell parameter a = 12 Å; Ca atom is in the Wyckoff 24c special position. Cr and Al atoms are in the 16a special positions,

TABLE 3

Refined Structure Parameters, R-values, and Bond Distances (Å) for $Ca_3(Cr_{1-x}Al_x)_2Si_3O_{12}$ Solid Solution

Sample	1	2	3	4	5
Nominal composition[a]	1.00	0.85	0.75	0.65	0.50
a, Å	12.0205(5)	11.9947(10)	11.9939(9)	11.9910(16)	11.9903(18)
B overall	0.27(10)	0.49(13)	0.71(12)	0.71(14)	0.57(16)
O: x	0.0396(5)	0.0390(7)	0.0396(6)	0.0401(8)	0.0423(8)
y	0.0472(5)	0.0483(6)	0.0477(5)	0.0487(7)	0.0474(7)
z	0.6559(4)	0.6549(6)	0.6553(5)	0.6553(7)	0.6603(13)
Ca–O 4×	2.349(6)	2.542(9)	2.544(7)	2.552(10)	2.542(12)
4×	2.511(6)	2.700(8)	2.707(7)	2.695(9)	2.727(10)
R^{3+}–O 6×	2.015(5)	2.168(8)	2.173(7)	2.178(9)	2.240(16)
Si–O 4×	1.630(6)	1.780(8)	1.769(7)	1.769(10)	1.700(14)
Calculated composition[a,b]	1.00	0.83	0.82	0.81	0.77
R_{B}[c]	6.61	6.47	7.68	8.25	15.83
R_{P}[d]	12.65	13.44	13.16	16.32	13.35
R_{wp}[e]	18.86	22.06	18.34	22.46	18.61
R_{wp} (expected)	10.13	9.61	9.43	9.22	8.78
S[f]	1.86	2.30	1.94	2.44	2.12

[a] Molar fraction of Cr located at the octahedrally coordinated position 16*a*.

[b] Calculated Cr^{3+} occupancy at the octahedral position by Rietveld refinement.

[c] Rietveld Bragg agreement index.

[d] Rietveld profile agreement index.

[e] Weighted Rietveld profile agreement index.

[f] Goodness of fit.

Si atom is in the 24*d* special position and O atom is in general position 96*h*. The scattering factor for Al^{3+} was taken from the International Tables for X-Ray Crystallography (19). In the last Rietveld refinement, a scale factor, two theta zero, three background parameters, three unit cell parameters, the form profile and an asymmetry parameter were varied. Diffraction profiles were modelled by using a pseudo-Voigt function that was corrected for peak asymmetry for angles less than 80° (2θ); U, V, W, and K parameters were varied. In addition to these nonstructural parameters, the x, y, and z positional parameters of oxygen and the overall thermal parameter were varied.

3. RESULTS AND DISCUSSION

Table 2 shows the evolution of phases after heating at 1000°C during 30 days.

Major evolution in the synthesis of these phases have not been observed with longer time of thermal treatment or high temperature (up to 1300°C), as was reported in previous papers (12, 14).

These results agree well with those obtained by Huckenholz and Knittel (11) heating at 1200°C for 120 days. These authors obtain the solid solution at 700°C and 1 kBar pressure for grossularite enriched compositions, in the present work we synthesized garnets solid solutions at lower temperatures and at atmospheric pressure. In the case of nominal grossularite composition it has not been possible to obtain this phase under the present experimental conditions.

This fact could be due to strong Si–O covalent bonding which does not allow deformation of the (SiO_4) polyhedra deformation and therefore prevents the introduction of Al into such a structure (1).

In general, the formation of a small residual phase of α-$CaSiO_3$ is due to the slow reaction rates of these multicomponent systems, even when using the sol–gel methods. The large reaction times required can lead to a loss of volatile components and, consequently, produce changes from the starting stoichiometry. From sample 5 there can be seen small peaks corresponding to residual phases $Ca_2Al_2SiO_7$ (gehlenite) together with α-$CaSiO_3$. This fact indicates only a small amount of aluminum goes into the solid solutions.

Table 3 displays the unit cell parameters derived from the refinement using all the observed reflections and the structure refined parameters, bonding distances, final atomic positions of O, overall thermal parameters, and R_p, R_{wp}, and R_{Bragg} factors. Plots of raw, calculated, and difference data for sample 3 are given in Fig. 2.

Ratios between R_B, R_{wp} (expected), and R_{wp} indicate that the structural parameters obtained are correct. Due

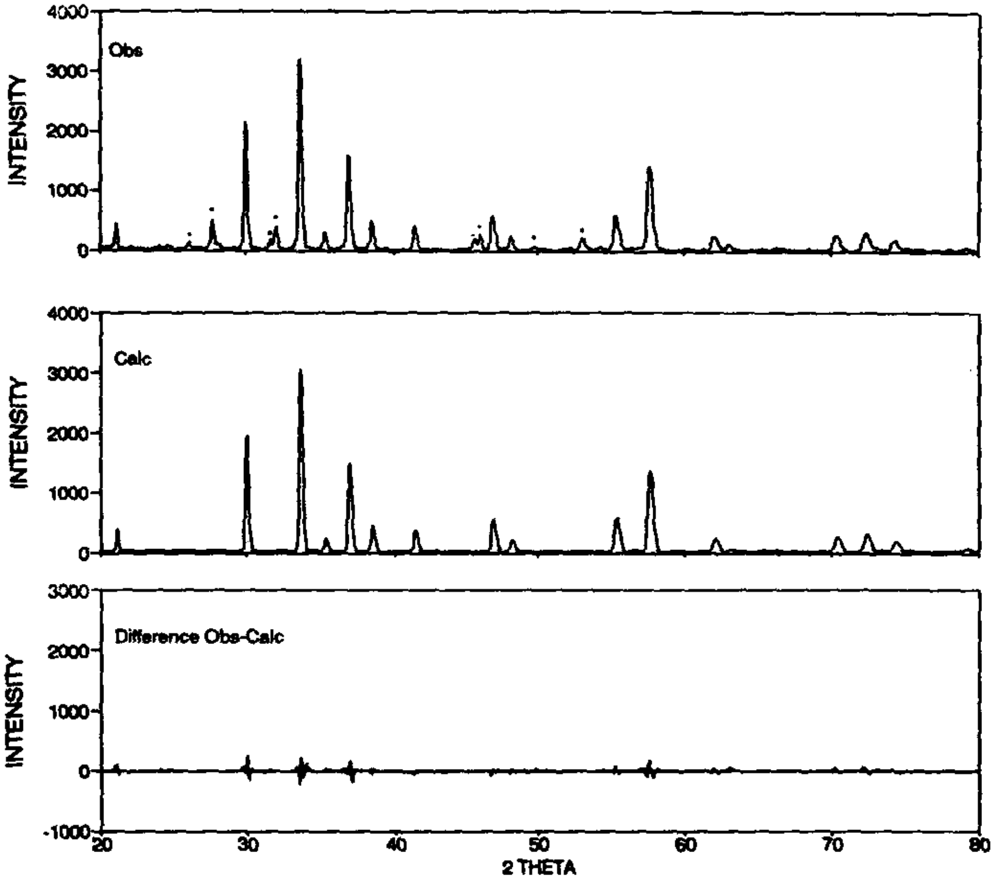

FIG. 2. Powder diffraction data for sample 3. Presented are raw data (Obs), calculated data (Calc) and a difference plot (Difference Obs-Calc). Peaks marked with · correspond to α-$CaSiO_3$.

to quality of the experimental data, only overall thermal factors are calculated.

From the lattice parameters data and occupation factors, the solid solution limit has been defined by the Rietveld method in 20% mole grossularite in our experimental conditions.

The decrease of a-values is in accordance with substitution of chromium for aluminum in octahedral site due to smaller size of Al^{3+} (0.67 Å) than Cr^{3+} (0.755 Å), in sixfold coordination (20).

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