Canadian Mineralogist
Vol. 28, pp. 87-91 (1990)

XRD AND XPS ANALYSES OF THE GROSSULAR–HYDROGROSSULAR SERIES

WEIJI CHENG

Department of Earth and Space Sciences, University of Science and Technology, Hefei, Anhui, Peoples' Republic of China

HUGH J. GREENWOOD

Department of Geological Sciences, University of British Columbia, Vancouver, British Columbia V6T 2B4

HONGLIANG HU AND DAVID C. FROST

Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Y6

ABSTRACT

Members of the grossular–hydrogrossular series $^{\mathrm{VIII}}\mathrm{Ca}_3{}^{\mathrm{VI}}\mathrm{Al}_2({}^{\mathrm{IV}}\mathrm{SiO}_4)_{3-x}(\mathrm{O}_4\mathrm{H}_4)_x$ ($x = 0, 0.2, 0.375, 0.4, 0.6, 0.75, 0.8, 1.0$) have been synthesized from oxide mixtures at temperatures between 270 and 745°C and pressures between 1 and 4 kbars. Products consist of a single phase over a narrow range of temperature and over a wide range of pressure. The unit-cell dimension increases with increasing (O_4H_4) content. The *d*-value of the (420) plane (d_{420}) is related to mole fraction of hydrogrossular (x_{HGr}) by the regression equation $d_{420} = 2.651 + 0.0289x_{\mathrm{HGr}} - 0.0180x^2_{\mathrm{HGr}} + 0.0411x^3_{\mathrm{HGr}}$. The excess volume of mixing can be described approximately as a symmetric solution using $V_{\mathrm{xs}} = -6.718x_{\mathrm{Hgr}}x_{\mathrm{Gr}}$ cm^{3}mol^{-1}, or more completely using an asymmetric model where $V_{\mathrm{xs}} = -9.700x_{\mathrm{Gr}}x_{\mathrm{HGr}}{}^2 + -3.507x_{\mathrm{Gr}}{}^2x_{\mathrm{HGr}}$ (cm^{3}mol^{-1}). Analyses by X-ray photoelectron spectroscopy (XPS) show that the binding energies of the Si and O core electrons are reduced with increasing (O_4H_4) content. Correlations between average chemical shift and the composition of hydrogrossular (x_{HGr}) are, for $\mathrm{O}^1\mathrm{S}_{1/2}$ and $\mathrm{Si}^2\mathrm{P}_{3/2}$: $S_{(\mathrm{O})} = 0.98 - 1.28x_{\mathrm{HGr}} + 0.36x^2_{\mathrm{HGr}}$, and $S_{(\mathrm{si})} = 4.77 - 1.13x_{\mathrm{HGr}} + 0.07x^2_{\mathrm{HGr}}$. There is no measurable difference in the XPS binding energies of Al core electrons for the solid solutions studied.

Keywords: grossular, hydrogrossular, XPS, XRD, nonideal solution, molar volume.

SOMMAIRE

Nous avons synthétisé des membres de la série grossulaire-hydrogrossulaire $^{\mathrm{VIII}}\mathrm{Ca}_3{}^{\mathrm{VI}}\mathrm{Al}_2({}^{\mathrm{IV}}\mathrm{SiO}_4)_{3-x}(\mathrm{O}_4\mathrm{H}_4)_x$ ($x = 0, 0.2, 0.375, 0.4, 0.6, 0.75, 0.8, 1.0$) à partir de mélanges d'oxydes entre 270 et 745°C et entre 1 et 4 kbars. Le produit est monophasé quelle que soit la pression, mais sur un intervalle restreint de température. Le paramètre réticulaire augmente avec une augmentation en proportion de (O_4H_4). La valeur de d_{420} dépend de la fraction molaire d'hydrogrossulaire selon la relation $d_{420} = 2.651 + 0.0289x_{\mathrm{HGr}} - 0.0180x^2_{\mathrm{HGr}} + 0.0411x^3_{\mathrm{HGr}}$. L'excès en volume de mélange correspond approximativement à un modèle de solution symétrique dans lequel $V_{\mathrm{xs}} = -6.718x_{\mathrm{HGr}}x_{\mathrm{Gr}}$ cm^{3}mol^{-1}, ou plus précisément à un modèle assymétrique dans lequel $V_{\mathrm{xs}} = -9.700x_{\mathrm{Gr}}x_{\mathrm{HGr}}{}^2 + -3.507x_{\mathrm{Gr}}{}^2x_{\mathrm{HGr}}$ cm^{3}mol^{-1}. Les analyses par spectroscopie des photoélectrons X montrent que l'énergie des liaisons des électrons du noyau des atomes de Si et de O diminue avec une augmentation en proportion de (O_4H_4). Les corrélations entre déplacement chimique moyen S et la teneur en hydrogrossulaire (x_{HGr}), pour $\mathrm{O}^1\mathrm{S}_{1/2}$ et $\mathrm{Si}^2\mathrm{P}_{3/2}$, sont: $S_{(\mathrm{O})} = 0.98 - 1.28x_{\mathrm{HGr}} + 0.36x^2_{\mathrm{HGr}}$, et $S_{(\mathrm{Si})} = 4.77 - 1.13x_{\mathrm{HGr}} + 0.07x^2_{\mathrm{HGr}}$. Il n'y a pas de différence importante entre les énergies de liaison des électrons du noyau des atomes d'aluminium dans cette solution solide.

(Traduit par la Rédaction)

Mots-clés: grossulaire, hydrogrossulaire, spectroscopie des photoélectrons X, diffraction X, solution non idéale, volume molaire.

INTRODUCTION

Hydrogrossular, which conforms to the formula $\mathrm{Ca}_3\mathrm{Al}_2(\mathrm{SiO}_4)_{3-x}(\mathrm{H}_4\mathrm{O}_4)_x$, exists as a continuous solid-solution between $\mathrm{Ca}_3\mathrm{Al}_2\mathrm{Si}_3\mathrm{O}_{12}$ (grossular) and $\mathrm{Ca}_3\mathrm{Al}_2(\mathrm{H}_4\mathrm{O}_4)_3$. In rodingites, hydrogrossular with $x = 1$ is commonly the most abundant mineral present (Coleman 1966), in association with fine-grained mixtures of other hydrous silicates, such as prehnite, vesuvianite and clinozoisite.

Numerous structural studies of the hydrogrossular series have been published (Weiss *et al.* 1964, Cohen-Addad *et al.* 1967, Foreman 1968, Novak & Gibbs 1971, Basso *et al.* 1983, Sacerdoti & Passaglia 1985, and Lager *et al.* 1987). Sacerdoti & Passaglia (1985) demonstrated a correlation between the degree of hydration in garnet and the relative lengths of the shared and unshared edges of octahedra. Shoji (1974) and Kobayashi & Shoji (1983) found that the *d*-value of the (420) plane may be used to determine the (H_4O_4) content in the hydrogrossular series. Infrared (IR) studies of the series (Zabinski 1966, Cohen-Addad *et al.* 1967, Moore *et al.* 1971, Harmon *et al.* 1982, Kobayashi & Shoji 1983) addressed the correlation between the position of the H-absorption band and the (O_4H_4) content of the hydrous garnet.

The work reported here provides a quantitative relation between the unit-cell dimension and com-

TABLE 1. CONDITIONS AND RESULTS OF SYNTHESES

Run	X_{HGr}	T°C	P Kbars	Days	$2\theta_{420}$ CuK⁻	d_{420} Å	Vol. cm^3/mol
HA-1	1.0	270	1	27	33.10	2.7064	
HA-2	1.0	300	2	25	33.16	2.7017	
HA-3	1.0	301	4	21	33.15	2.7024	
HA-4	1.0	330	4	21	33.16	2.7017	
HA-5	1.0	300	2	24	33.12	2.7048	
HA-6	1.0	298	1	24	33.14	2.7032	
HA-8	1.0	332	1	45	33.16	2.7017	
HA-9	1.0	302	1	61	33.14	2.7032	
					MEAN	**2.703**	**133.18** Vxs(0.00)
HB-1	0.8	370	1	41	33.39	2.6836	
HB-2	0.8	364	1	26	33.43	2.6805	
HB-4	0.8	330	4	21	33.41	2.6820	
HB-5	0.8	409	1	31	33.38	2.6844	
HB-7	0.8	372	2	63	33.41	2.6820	
					MEAN	**2.683**	**130.25** Vxs(-1.43)
HC-1	0.75	371	1	26	33.46	2.6781	
HC-3	0.75	372	1	42	33.44	2.6797	
HC-4	0.75	400	1	28	33.46	2.6781	
					MEAN	**2.679**	**129.67** Vxs(-1.63)
HD-2	0.6	420	4	20	33.54	2.6719	
HD-3	0.6	450	1	16	33.56	2.6704	
HD-4	0.6	409	1	31	33.55	2.6711	
HD-6	0.6	440	1	61	33.56	2.6704	
					MEAN	**2.671**	**128.51** Vxs(-1.65)
HE-1	0.4	450	1	35	33.64	2.6642	
HE-3	0.4	458	1	20	33.65	2.6634	
HE-4	0.4	482	2	18	33.68	2.6611	
HE-6	0.4	508	4	13	33.65	2.6634	
					MEAN	**2.663**	**127.36** Vxs(-1.30)
HF-1	.375	460	1	26	33.67	2.6619	
HF-2	.375	511	1	24	33.70	2.6596	
HF-3	.375	500	1	31	33.69	2.6604	
					MEAN	**2.661**	**127.07** Vxs(-1.40)
HG-1	0.2	562	1	31	33.76	2.6550	
HG-2	0.2	558	1	14	33.76	2.6550	
HG-3	0.2	508	4	13	33.76	2.6550	
HG-5	0.2	599	2	14	33.77	2.6542	
HG-7	0.2	566	1	47	33.74	2.6565	
					MEAN	**2.655**	**126.21** Vxs(-0.94)
HH-8	0.0	745	1	16	33.79	2.6527	
HH-9	0.0	748	1	12	33.81	2.6512	
HH-12	0.0	599	2	14	33.84	2.6489	
HH-13	0.0	745	4	11	33.84	2.6489	
HH-14	0.0	651	1	25	33.80	2.6520	
HH-16	0.0	602	1	25	33.82	2.6504	
					MEAN	**2.651**	**125.64** Vxs(0.0)

Note: HGr represents $Ca_3Al_2(SiO_4)_2O_4H_4$; Gr = $Ca_3Al_2(SiO_4)_3$, x_{HGr} = mole fraction HGr in solid solution, Molar volume in cm3/mole, Vxs = excess molar volume of mixing in cm3/mol.

position, and uses X-ray photoelectron spectroscopy analysis to examine the correlation between composition and binding energy of the core electrons of Si, O, and Al.

EXPERIMENTS

Members of the solid-solution series of $Ca_3Al_2(SiO_4)_{3-x}(H_4O_4)_x$ (x = 0, 0.2, 0.375, 0.4, 0.6, 0.75, 0.8, 1.0) were synthesized from oxide mixtures of CaO, Al_2O_3, SiO_2 and H_2O. Five-gram batches of an oxide mixture were prepared for each solid solution, then ground by hand under alcohol for at least 2 hours. For each synthesis, a sealed gold capsule containing between 10 and 30 mg of oxide mixture and excess distilled water (30 to 50 wt.%) was held at a temperature between 270 and 745°C and a pressure between 1 and 4 kbars for 14 to 40 days (Table 1).

The product of each synthesis experiment was examined with the optical microscope and X-ray powder diffraction (XRD). Some products were examined with a scanning electron microscope and electron microprobe. Only products consisting of a single homogeneous phase were used for further analysis by XRD and XPS (X-ray photoelectron spectroscopy).

The d-value of the (420) plane was measured by XRD using Cu$K\alpha$ radiation. The silicon peak at 28.47 2θ° was used as an internal standard. With a scanning rate of ½ degree 2θ per minute, the mean of three scans with increasing 2θ and three with decreasing 2θ was taken to yield the recorded measurement for each product.

For XPS analysis, the photoelectron spectra of $O^1S_{1/2}$, $Si^2P_{3/2}$ and $Al^2P_{3/2}$ were measured with a Varian IEE-15 spectrometer using Mg$K\alpha$ X rays as the exciting radiation. Fine powders of the samples were thinly dusted onto 3M tape (see Jorgensen 1971, for techniques). The carbon ^1S line at 284.0 eV (Jorgensen 1971) was used as the reference for the scale of binding energies, which are reproducible to within ±0.1 eV. Sample scans were averaged over 7 scans for $O^1S_{1/2}$, 100 scans for $Al^2P_{3/2}$ and 50 scans for $Si^2P_{3/2}$.

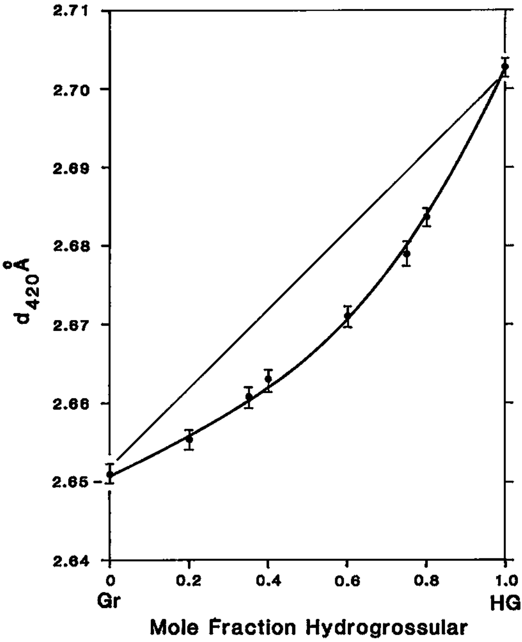

FIG. 1. Relation between d_{420} and composition of the grossular - hydrogrossular solid solution. Vertical line segments show the range of measured values. The curve represents a least-squares fit to the weighted means of the measurements with $d_{420} = 2.651 + 0.0289x_{HGr} - 0.0180x^2_{HGr} + 0.0411x^3_{HGr}$.

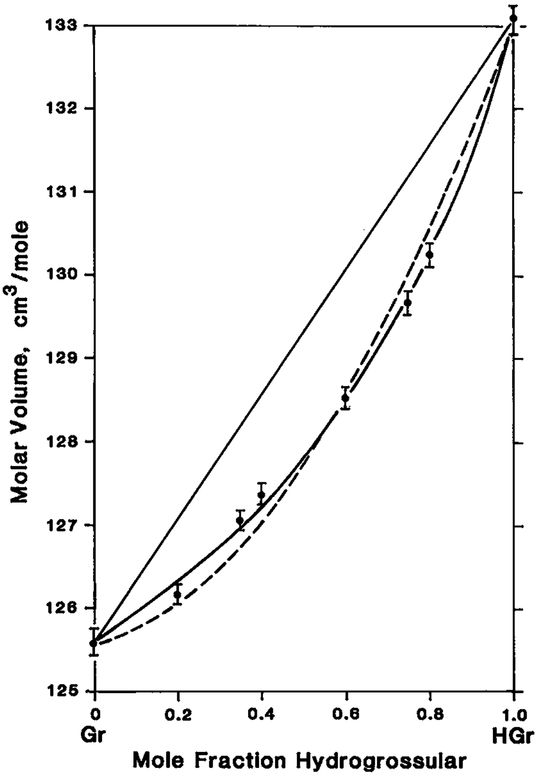

FIG. 2. Relation between molar volume and composition of the grossular - hydrogrossular solid solution. Two fits to the data are presented. The symmetric solution model with $Wv = -6.718$ cm^{3}mol^{-1} is shown dashed, and the asymmetric fit with $Wv_{12} = -3.507$ and $Wv_{21} = -9.700$ cm^{3}mol^{-1} is shown as a solid curve. See text for equations and discussion.

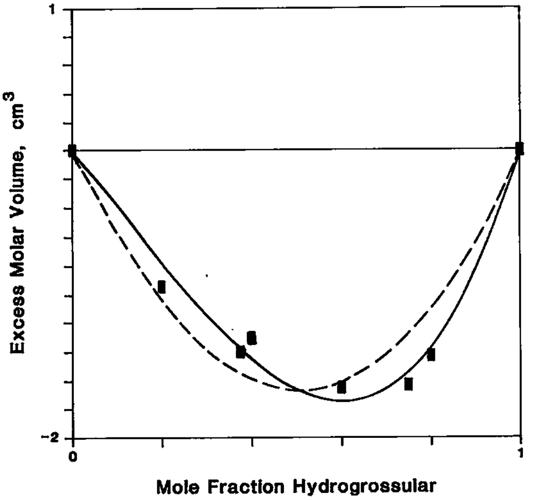

FIG. 3. The excess volume of mixing of the grossular - hydrogrossular series. Two regression fits have been made to the data. The dashed represents the symmetric model, and the solid curve, the asymmetric model. See caption for Fig. 2 and text for details.

TABLE 2. CHEMICAL SHIFTS IN BINDING ENERGIES OF O, Al, AND Si

	Oxygen			Aluminum			Silicon		
X_{HGr}	#1	#2	Avg	#1	#2	Avg	#1	#2	Avg
0.0	1.3	0.6	0.95	2.1	2.7	2.4	5.0	4.6	4.8
0.2	0.7	0.9	0.80	2.2	2.2	2.2	4.5	4.6	4.55
0.4	0.4	0.6	0.50	1.8	2.4	2.1	4.3	4.2	4.25
0.6	0.4	0.2	0.30	2.4	2.2	2.30	4.2	4.0	4.1
0.8	0.2	0.2	0.20	2.2	2.6	2.4	4.1	4.1	4.1
1.0	-0.3	0.4	0.05	1.5	2.0	1.75	3.2	4.0	3.6

Note: X_{HGr} = mole fraction hydrogrossular, XPS Data, electron volts, #1 and #2 are separate measurements on the same sample.

RESULTS AND DISCUSSION

The conditions of synthesis and physical properties of the synthesized hydrogrossular series are listed in Table 1. There is an approximate upper-temperature limit to the production of single-phase hydrogrossular solid-solution at each composition. For a given starting composition, additional phases formed with the hydrogrossular at the higher temperatures. There appears to be no effect due to pressure of synthesis. Single-phase hydrogrossular solid-solutions were obtained at temperatures below 300°C for $x_{HGr} = 1$, below 370°C for $x_{HGr} = 0.8$, below 430°C for $x_{HGr} = 0.6$, below 470°C for $x_{HGr} = 0.4$, and below 520°C for $x_{HGr} = 0.2$. End-member grossular can be synthesized over a temperature range from 600 to 795°C.

The value of d_{420} (Table 1) increases with increasing (O_4H_4) content, expressed by a least-squares fit:

$$d_{420} = 2.651 + 0.0289x_{HGr} - 0.0180x^2_{HGr} + 0.0411x^3_{HGr}$$

(Fig. 1). In this expression, x_{HGr} is the mole fraction of the hydrogrossular end-member [$Ca_3Al_2(SiO_4)_2(O_4H_4)$] defined by the structural formula $^{VIII}Ca_3{}^{VI}Al_2(^{IV}SiO_4)_{3-x}(O_4H_4)_x$. This expression may be used to derive the volume of the unit cell in Å^3 and the molar volume in cm^3 per mole (Fig. 2).

The relationship between molar volume and composition (Table 1, Figs. 2, 3) is nonlinear, indicating that the hydrogrossular series is a nonideal solid-solution. The excess volume (V_{XS}) may be

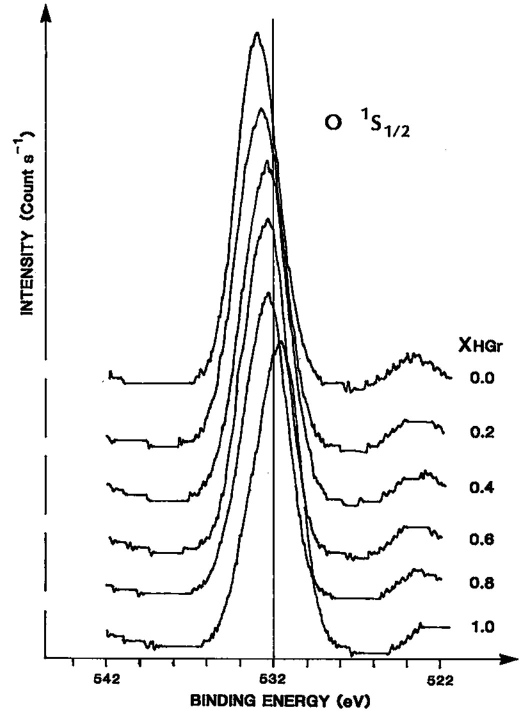

FIG. 4. Chemical shift of the $O^1S_{½}$ with (O_4H_4) content.

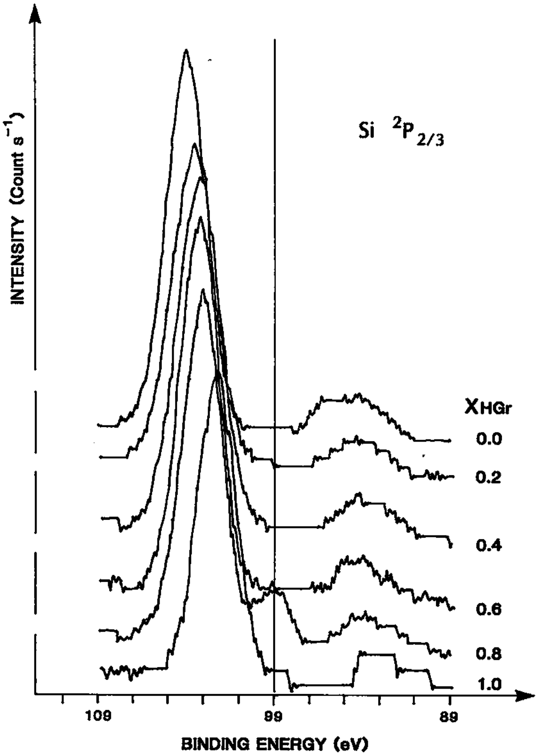

FIG. 5. Chemical shift of $Si^2P_{3/2}$ with (O_4H_4) content.

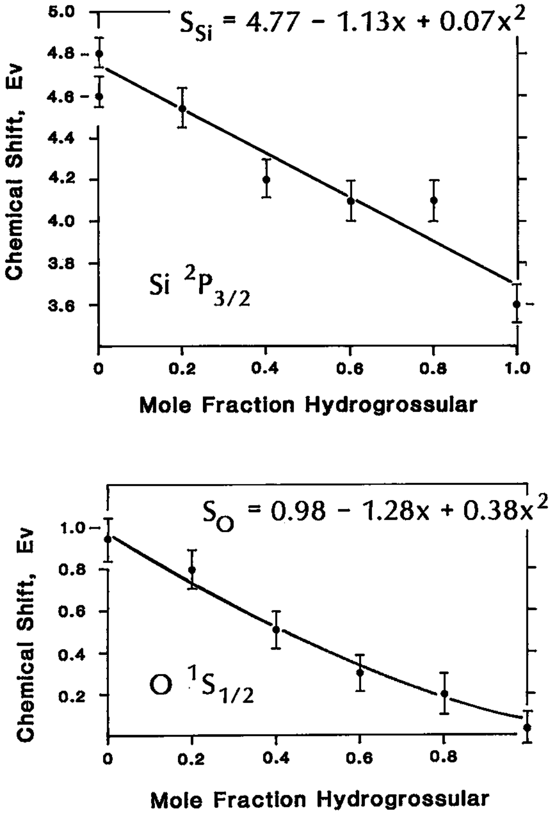

FIG. 6. Relation between chemical shifts and mole fraction hydrogrossular $[Ca_3Al_2(SiO_4)_2(O_4H_4)]$. (a) $Si^2P_{3/2}$; (b) $O^1S_{½}$.

defined by $V_{XS} = V_{SS} - V_{Gr} + x_{HGr}(V_{Gr} - V_{HGr})$, where x_{HGr} is the mole fraction of the $Ca_3Al_2(SiO_4)_2(O_4H_4)$ component, and V_{Gr} and V_{HGr} are the molar volumes of the end members of the series. The values of V_{SS} and V_{XS} calculated from experimental measurements are shown in Table 1. For the regular-solution model, $V_{XS} = x_{Gr}x_{HGr}Wv$. The volume term in the symmetric excess function, Wv, is -6.718 cm³ per mole on the basis of a least-squares fit to the excess-volume data of Table 1. Figure 3 illustrates the symmetric model (dashed curve). Alternatively, the volume data may be fitted more closely with an asymmetric model, where $V_{XS} = x_{Gr}x_{HGr}^2Wv_{21} + x_{Gr}^2x_{HGr}Wv_{12}$, with Wv_{21} = -9.700 and Wv_{12} = -3.507 cm³mol⁻¹. This model is illustrated in Figure 3 (solid curve). Because the symmetric (regular) solution model produces residuals that are well outside the precision of measurement, we favor the asymmetric model, which gives residuals approximately equal to the experimental precision of measurement.

XPS measurements show that the binding energies of the core electrons of Si and O decrease with increasing hydroxyl content (Table 2, Figs. 4, 5). Regression equations describing the chemical shifts are plotted in Figure 6. Quadratic expressions have been fitted because of the quadratic behavior of the volumetric properties, although the XPS data do not warrant more than a linear fit. There is no measurable shift of binding energies of the Al core electrons in the solid solutions studied.

In interpreting the XPS results it is important to note that both the XRD and the XPS peak shifts are averages over a very large number of unit cells. The enlargement of the unit cell due to hydroxyl substitution (Fig. 2) can be correlated mainly with the larger size of the OH-bearing "tetrahedral" groups (Lager *et al.* 1987). Similarly, the shifts in XPS peaks reflect a change in the proportions of SiO_4 and O_4H_4 groups.

Because the shift of the XPS $O^1S_{½}$ photoelectron peak is an average over all the oxygen atoms in the structure, the decrease in the binding energy of $O^1S_{½}$ with increase in (O_4H_4) content may be correlated with the increasing average distance between oxygen and other atoms as reflected by the measured expansion of the unit cell. The minimal change in the Al–O distance in the octahedra with the change in composition (1.924 Å *versus* 1.916 Å, Lager *et al.* 1987) corresponds with the small change in the binding energies of the core electrons of the Al atoms.

CONCLUSIONS

The results of XRD and XPS analyses show parallel monotonic changes in the *d*-value of the (420) plane, the molar volume and the binding energies of Si and O core electrons with (O_4H_4) content in the hydrogrossular series. These effects are what might be expected with the progressive loss of average bonding energy as fewer tetrahedral sites are occupied by Si^{4+}. The compositions and molar volumes of members of the hydrogrossular series may be calculated from XRD measurements using regression equations given in the text, with a precision of approximately 3 mole % HGr when *d*(420) is measured with a precision of 0.001 Å.

ACKNOWLEDGEMENTS

This study has been aided by funding from the Natural Sciences and Engineering Research Council of Canada to H.J. Greenwood (grant A–4222) and D.C. Frost (grant A–0954).

REFERENCES

BASSO, R., DELLA GIUSTA, A. & ZEFIRO, L. (1983): Crystal structure refinement of plazolite, a highly hydrated natural hydrogrossular. *Neues Jahrb. Mineral., Monatsh.*, 251-258.

COHEN-ADDAD, C., DUCROS, P. & BERTAUT, E.F. (1967): Étude de la substitution du groupement SiO_4 par $(OH)_4$ dans les composés $Al_2Ca_3(OH)_{12}$ et $Al_2Ca_3(SiO_4)_{2,16}(OH)_{3,36}$ de type grenat. *Acta Crystallogr.* **23**, 220-230.

COLEMAN, R.G. (1966): New Zealand serpentinites and associated metasomatic rocks. *N.Z. Geol. Surv. Bull.* **76**, 1-102.

FOREMAN, D.W. (1968): Neutron and X-ray diffraction study of $Ca_3Al_2(O_4D_4)_3$, a garnetoid. *J. Chem. Phys.* **48**, 3037-3041.

HARMON, K.M., GABRIELE, J.M. & NUTTALL, A.S. (1982): Hydrogen bonding. 14. Hydrogen bonding in the tetrahedral $O_4H_4^-$ cluster in hydrogrossular. *J. Molec. Struct.* **82**, 213-219.

LAGER, G.A., ARMBRUSTER, T. & FABER, J. (1987): Neutron and X-ray diffraction study of hydrogarnet $Ca_3Al_2(O_4H_4)_3$. *Am. Mineral.* **72**, 756- 765.

JORGENSEN, C.K. (1971): Photo-electron spectrometry of inorganic solids. *Chimia* **25**, 213-260.

KOBAYASHI, S. & SHOJI, T. (1983): Infrared analysis of the grossular–hydrogrossular series. *Mineral. J.* **11**, 331-343.

MOORE, R.K., WHITE, W.B. & LONG, T.V. (1971): Vibrational spectra of the common silicates. I. The garnets. *Am. Mineral.* **56**, 54-71.

NOVAK, G.A. & GIBBS, G.V. (1971): The crystal chemistry of the silicate garnets. *Am. Mineral.* **56**, 791-825.

SACERDOTI, M. & PASSAGLIA, E. (1985): The crystal structure of katoite and implications within the hydrogrossular group of minerals. *Bull. Minéral.* **108**, 1-8.

SHOJI, T. (1974): $Ca_3Al_2(SiO_4)_3$–$Ca_3Al_2(O_4H_4)_3$ series garnet: composition and stability. *J. Mineral. Soc. Japan* **11**, 359-372 (in Japanese).

WEISS, R., GRANDJEAN, D. & PALVIN, J.L. (1964): Structure de l'aluminate tricalcique hydraté, $3CaO\cdot Al_2O_3\cdot 6H_2O$. *Acta Crystallogr.* **17**, 1329-1330.

ZABINSKI, W. (1966): Hydrogarnets. *Pol. Akad. Nauk Oddzial Krakowie kom. Nauk Mineral.* **3**, 1-6.

Received May 11, 1989, revised manuscript accepted August 24, 1989.