

Correlation between structural parameters of garnet and garnet-like structures

DOROTA A. PAWLAK,^{a,b} KRZYSZTOF WOŹNIAK^{a*} AND ZYGMUNT FRUKACZ^b

^aDepartment of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warszawa, Poland, and ^bInstitute of Electronic Materials Technology, ul. Wólczyńska 133, 01-919 Warszawa, Poland. E-mail: kwozniak@chem.uw.edu.pl

(Received 11 November 1998; accepted 8 April 1999)

Abstract

Statistical analysis of structural parameters of garnet and garnet-like structures retrieved from the Inorganic Crystal Structure Database has revealed strong correlations between them. The degree of correlation depends on doping site and garnet type. Structural parameters are not equally sensitive to changes imposed by doping. The strongest correlation exists between the unit-cell parameter and the doping-ion radius. In the case of doping at the dodecahedral sites, the most sensitive parameter is the shortest dodecahedral distance. Principal component analysis (PCA) clearly shows that the first component explains most of the variation of structural data. It has a geometric basis and correlates with the effective radii of the doping ion. Partial correlation helps to identify the strongest relations between pairs of variables when the influence of other structural variables on them is controlled. It appears that in some cases partial correlation has a different sign when compared with the results of the standard correlation technique.

1. Introduction

Natural garnets are beautiful precious stones. Artificial garnets doped with different rare-earth ions are used as lasing materials. Garnet structure has been investigated for many years. Apart from investigations under normal temperature and pressure conditions, other studies have been carried out. Studies of aluminium silicate garnets at various temperatures (Meagher, 1975; Armbruster & Geiger, 1993; Rodić *et al.*, 1991) were made in order to understand the relationship of the crystal structures of minerals to their thermal expansions. Investigations of variations in the garnet structure, and other physical properties of garnets, with pressure (Hazen & Finger, 1978) were also accomplished. There was a hypothesis that structural changes in aluminium silicate garnets as a function of heating are comparable to changes owing to chemical substitution at the dodecahedral site, *i.e.* that temperature, pressure and composition may be structurally analogous variables (Hazen, 1976). Latter studies of this subject (Meagher, 1975; Hazen & Finger, 1978) have shown that the $R_3Al_2Si_3O_{12}$ (where $R = Ca, Mg$)

garnet structure responds differently to changes in temperature, pressure and composition.

In this work we investigate the relationship between the composition of the garnet and its structure. We are mostly interested in artificial non-silicate garnets used for different purposes (laser materials). Some 250 garnet structures have already been solved and described. They can be retrieved from the Inorganic Crystal Structure Database (ICSD: Bergerhoff *et al.*, 1983; Bergerhoff & Sievers, 1989) and we believe that this is a sufficient sample for use in deducing structural generalizations.

It appears that the relative size of ions and their concentrations are of primary importance. The problem is that the X-ray and neutron diffraction methods routinely used for structure determinations are often unable to supply reliable information regarding small amounts of doping ions. However, in spite of this obvious disadvantage of low sensitivity to similar ions, there should be an indirect way of deducing this information from structural data obtained by diffraction methods.

The objectives of this work are:

- (a) to show how replacement of ions located at different sites affects the garnet structure,
- (b) to examine what types of correlation exist between the geometrical parameters of garnets and, in particular,
- (c) to understand the structural consequences of doping.

We would like to show which geometrical parameters of the garnet structure 'feel' most the change of an ion at one particular site. We also want to show, using principal component analysis, the total reaction of the garnet structure to doping. We hope to show a simple way of estimating dopant concentrations based on the analysis of structural data (even in cases when it is impossible to refine doping-ion occupation factors).

1.1. Details of the garnet structure

Garnets have a formula $\{A\}_3\{B\}_2\{C\}_3O_{12}$, where $\{A\}$ denotes an ion A located at dodecahedral sites [24(c) in Wyckoff notation], $\{B\}$ is an ion B at octahedral sites [16(a)] and $\{C\}$ is an ion C located at tetrahedral sites [24(d)]. O atoms occur in general positions [96(h)]. Garnets crystallize in space group $Ia\bar{3}d$, one of the most

Table 1. ICSD collection codes of garnet structures investigated in this work

Collection code										
2012	6110	6113	6150	9232	9233	9234	9235	9236	9237	9238
14342	14343	18111	20090	20214	20215	20216	22277	23845	23846	23847
23848	23849	23851	23853	23854	23856	23857	24940	24941	24942	24943
24944	24945	24946	27363	27364	27365	27366	27367	27368	27369	27370
27682	28017	28030	28089	28090	28091	28092	28176	29248	29249	29250
29251	30106	30107	30108	31238	31239	33550	33602	33603	34837	34838
34840	34841	34842	34843	34844	37145	39193	39336	39337	60302	61782
62615	62616	63037	63038	66253	66255	66647	66672	67045	67102	67103
67441	67653	71256	71257	71258	71887	71888	71889	71890	71891	71892
71893	71894	71895	71896	73240	73815	73816	73817	74603	74604	74605
74606	75640	75641	75642	75643	75644	75645	75646	78054	78055	100258
100614	100615	100616	100617	100618	100619	100620	100621	200341	200342	200343
200344	200345	200346	200347	202850	202959					

symmetric space groups of the cubic system. A , B and C cations occupy particular sites, depending on cation radii. In most natural garnets, and also in artificially obtained crystals with the garnet structure, the same sites can be occupied in a statistical manner by more than one type of ion.

Garnets form a very important structure and have been investigated for many years (Geller, 1967). However, even detailed studies of a single structure of one garnet cannot provide as much significant information as can be obtained from a large sample of structures analysed together. Thus, our work is based on data retrieved from the ICSD (version of April 1996), which contains 249 solved and refined garnet and garnet-like structures (Table 1), and two structures of yttrium aluminium garnets (YAGs) solved and refined in our laboratory (Pawlak *et al.*, 1998). We have, however, included only those structures which have a cited crystallographic R factor ≤ 0.07 , leaving 140 structures for further analysis. This total sample was divided into subsets according to different factors, such as type of structure, type of sites *etc.*, and these subsets were analysed separately. All crystals studied at different temperatures or with different pressure have been excluded in all subsamples. In the case of the total sample, the exclusion of data points obtained for temperatures and pressures different from normal does not significantly change the correlation coefficient and slopes obtained for all data points.

There is one independent dodecahedral site in the garnet structure (Fig. 1). It can be characterized by two different classes of the central ion (A)...oxygen atom (O) interatomic distance. There are four shorter $A-O$ distances and four longer ones (Fig. 1a). In the case of octahedral sites all six central ion (B)...oxygen atom (O) $B-O$ distances are equal (Fig. 1b). For a tetrahedral site all four central ion (C)...oxygen atom (O) $C-O$ distances are also equal (Fig. 1c). We denote these structural parameters using Wyckoff notation as $c-h_{sh}$, $c-h_l$, $a-h$, $d-h$ (where $A \rightarrow c$, $B \rightarrow a$, $C \rightarrow d$, $O \rightarrow h$) and reserve the u.c.p. abbreviation for the unit-cell parameter.

2. Results and discussion

2.1. Correlation analysis

2.1.1. *Total sample.* Table 2 contains the correlation coefficients (R) for pairwise linear regressions between all structural parameters. There is a strong positive correlation ($R = 0.87-0.96$) between each interatomic distance and the unit-cell parameter, *i.e.* an increase of the interatomic distance is always associated with an increase of the unit-cell parameter. The largest R values are associated with $c-h_{sh}$ and $a-h$ versus u.c.p. ($R = 0.96$ and 0.91 , respectively; see Fig. 2), but the correlation for the $d-h$ and $c-h_l$ distances, although slightly weaker, is still very significant ($R = 0.86$ and 0.82 , respectively). All R values quoted in this paper are significant from a statistical point of view.

The highest correlation between interatomic distances occurs for $c-h_{sh}$ and $c-h_l$ ($R = 0.93$; Fig. 3). However, the relationship between the $a-h$ and $c-h_{sh}$ distances is appreciable ($R = 0.89$), as is that between the $c-h_l$ and $a-h$ variables ($R = 0.77$). We also note that correlation involving the $d-h$ interatomic distance are weaker than the relations for the other parameters. In general, when one of the parameters changes, all the other parameters also change in the same direction with similar magnitude, as shown by the slopes of the linear relationships in Table 3.

The slopes of the linear relationships between structural parameters are almost equal to unity, with the

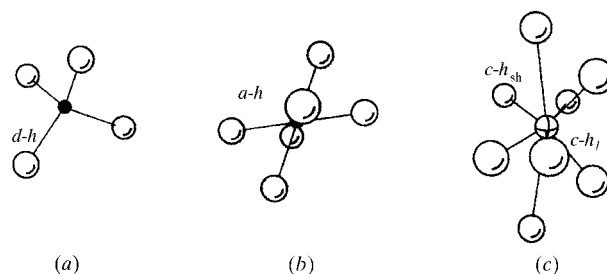


Fig. 1. Definition of structural parameters characteristic of particular sites: (a) dodecahedral, (b) octahedral and (c) tetrahedral.

Table 2. Correlation coefficients for four different samples of data: all data; $\{A\}_3Al_5O_{12}$; $\{A\}_3Fe_5O_{12}$, where $A = Y$ or lanthanide ions; $Y_3X_5O_{12}$, where $X = Al, Sc, Fe, Ga, In$

All values are significant at the confidence level $\alpha = 95\%$. $a-h$: interatomic distance between a cation occupying an octahedral site and the nearest O atom (in general position); $d-h$: interatomic distance between a cation in a tetrahedral site and the nearest O atom; $c-h_{sh}$: shorter interatomic distance between a cation in a dodecahedral site and the nearest O atom; $c-h_l$: longer interatomic distance between a cation in a dodecahedral site and the second nearest O atom; u.c.p. unit-cell parameter.

Column	All data I	$\{A\}_3Al_5O_{12}$ II	$\{A\}_3Al_5O_{12}$, where $A = 100\%$ of one element III	$\{A\}_3Fe_5O_{12}$ IV	$\{A\}_3Fe_5O_{12}$, where $A = 100\%$ of one element V	$Y_3(B)_5O_{12}$ VI
Number of data points	140	15	8	9	8	10
$a-h$ versus $d-h$	0.64 (6)	—	—	—	—	0.94 (2)
$a-h$ versus $c-h_{sh}$	0.89 (3)	—	—	—	—	0.87 (2)
$a-h$ versus $c-h_l$	0.77 (5)	—	—	—	—	—
$d-h$ versus $c-h_{sh}$	0.69 (7)	0.638 (5)	0.640 (7)	0.749 (6)	0.796 (6)	0.96 (1)
$d-h$ versus $c-h_l$	0.46 (9)	0.599 (5)	—	—	0.668 (7)	—
$c-h_{sh}$ versus $c-h_l$	0.93 (3)	0.924 (5)	0.947 (7)	0.974 (6)	0.975 (6)	—
$a-h$ versus u.c.p.	0.91 (3)	—	—	—	—	0.980 (9)
$d-h$ versus u.c.p.	0.86 (5)	0.722 (4)	0.720 (6)	0.702 (7)	0.740 (7)	0.988 (7)
$c-h_{sh}$ versus u.c.p.	0.96 (2)	0.941 (5)	0.943 (7)	0.988 (4)	0.988 (4)	0.931 (7)
$c-h_l$ versus u.c.p.	0.82 (4)	0.903 (8)	0.91 (1)	0.976 (7)	0.980 (7)	—

exception of the relations with u.c.p., which is, of course, ca 10 times larger than the interatomic distance parameters. The least sensitive parameter is the $d-h$ interatomic distance. Slopes of plots involving $d-h$ show the largest deviation from unity.

2.1.2. $\{A\}_3Al_5O_{12}$ subset. Here we consider the correlation for the subset containing 15 structures of garnets with the general formula $\{A\}_3Al_5O_{12}$, where $A =$

Y, Pr, Nd, Gd, Tb, Ho, Er, Yb, Lu. In some cases two ions occupy the $\{A\}$ position. Compounds in this subset are doped with different lanthanide ions in the range of doping from 0 to 100% (see column II of Table 2). As doping takes place in the dodecahedral sites (replacement of yttrium ions), one would expect the greatest changes to occur for the Y—O ($c-h$) interatomic distances, and this is the case. The best correlation for interatomic distances is for $c-h_{sh}$ and $c-h_l$ ($R = 0.924$), i.e. an increase in the shorter Y—O distance also brings about an increase of the longer one.

Column III of Table 2 shows the correlation coefficients for those structures having only one type of ion occupying the dodecahedral sites. In general, the correlation is quite similar to the previous case, although the correlations involving the $d-h$ parameter are not significant owing to the small number of data points. Two data points obscure the other relations for this subsample, which is why the relations look rather like tendencies. According to these tendencies an increase in $c-h_{sh}$ is associated with an increase in $d-h$. A similar relationship can also be observed for the $c-h_l$ and $d-h$ distances ($R = 0.638$ and 0.599 , respectively). There is no correlation for the octahedral $a-h$ distance. Thus, the change of cation at the dodecahedral sites enforces the changes of shorter and longer distances of the dodecahedral sites and weaker changes of the $d-h$ distance of the tetrahedral site. We have not found even a secondary sensitivity of the octahedral sites to doping at the dodecahedral sites. Similar conclusions can be drawn from the correlation between interatomic distances and the u.c.p. The strongest influence on the u.c.p. is exerted by $c-h_{sh}$ and $c-h_l$ ($R = 0.941$ and 0.903 , respectively; Fig. 4), the $d-h$ distance has a weaker effect ($R = 0.722$) and there is no correlation with the $a-h$ parameter.

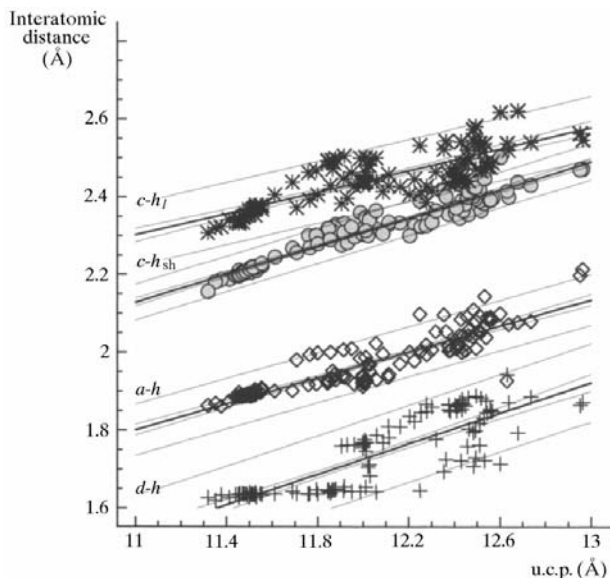


Fig. 2. Linear relations between interatomic distances and u.c.p. for the total sample. The number of data points is equal to 140. The correlation coefficients and slopes are given in Tables 2 and 3. All distances are given in Å. Confidence intervals for slopes and tolerance intervals are all at the significance level $\alpha = 0.05$.

Table 3. Slopes of linear relationships between structural parameters of garnets

Column	All data I	$\{A\}_3\text{Al}_5\text{O}_{12}$ II	$\{A\}_3\text{Al}_5\text{O}_{12}$, where $A = 100\%$ of one element III	$\{A\}_3\text{Fe}_5\text{O}_{12}$ IV	$\{A\}_3\text{Fe}_5\text{O}_{12}$, where $A = 100\%$ of one element V	$\text{Y}_3(\text{B})_5\text{O}_{12}$ VI
Number of data points	140	15	8	9	8	10
a - h versus d - h	0.52 (5)	–	–	–	–	1.0 (1)
a - h versus c - h_{sh}	0.87 (4)	–	–	–	–	2.1 (4)
a - h versus c - h_l	0.84 (6)	–	–	–	–	–
d - h versus c - h_{sh}	0.84 (7)	0.3 (1)	0.3 (1)	0.3 (1)	0.30 (9)	2.2 (2)
d - h versus c - h_l	0.6 (1)	0.20 (7)	–	–	0.19 (9)	–
c - h_{sh} versus c - h_l	1.05 (3)	0.68 (8)	0.7 (1)	0.75 (7)	0.76 (7)	–
a - h versus u.c.p.	0.168 (7)	–	–	–	–	0.27 (2)
d - h versus u.c.p.	0.20 (1)	0.10 (3)	0.10 (4)	0.07 (3)	0.08 (3)	0.25 (1)
c - h_{sh} versus u.c.p.	0.181 (5)	0.28 (3)	0.29 (4)	0.27 (2)	0.27 (2)	0.10 (1)
c - h_l versus u.c.p.	0.138 (8)	0.37 (5)	0.36 (7)	0.35 (3)	0.35 (3)	–

The slopes obtained for d - h , c - h_{sh} and c - h_l , versus u.c.p. relationships are equal to 0.10, 0.28 and 0.37, respectively. The relative magnitude of these slopes can be associated with the angles formed by particular structural parameters and the directions of crystallographic axes. In the case of the interatomic distances the greatest change is observed for the c - h_{sh} dependence on the c - h_l distance (slope = 0.68). The other slopes are smaller (ranging from 0.2 to 0.3), so these relations resemble the dependencies between geometrical parameters and the u.c.p.

2.1.3. $\{A\}_3\text{Fe}_5\text{O}_{12}$ subset. For this subset results similar to those for the yttrium aluminium garnets can be expected. Unfortunately, only 11 structures in the ICSD

fulfil our criteria. $\{A\}$ represents Y, Sm, Eu, Tb, Dy, Yb and Lu located at dodecahedral sites. Column IV of Table 2 contains the correlation coefficients for the $\{A\}_3\text{Fe}_5\text{O}_{12}$ subset with one or more type(s) of ion(s) at the dodecahedral positions, whereas column V of this table consists of the cases having $A = 100\%$ of ions of one element. It appears that the correlation between c - h_{sh} and c - h_l ($R = 0.974$; Fig. 5.), d - h and c - h_{sh} distances ($R = 0.749$), as well as between c - h_{sh} , c - h_l , d - h and the u.c.p. ($R = 0.988$, 0.976 and 0.702 , respectively), are qualitatively the same (quantitatively somewhat better than those for $\{A\}_3\text{Al}_5\text{O}_{12}$). Also, in this case the a - h distance appears to be independent of doping in dode-

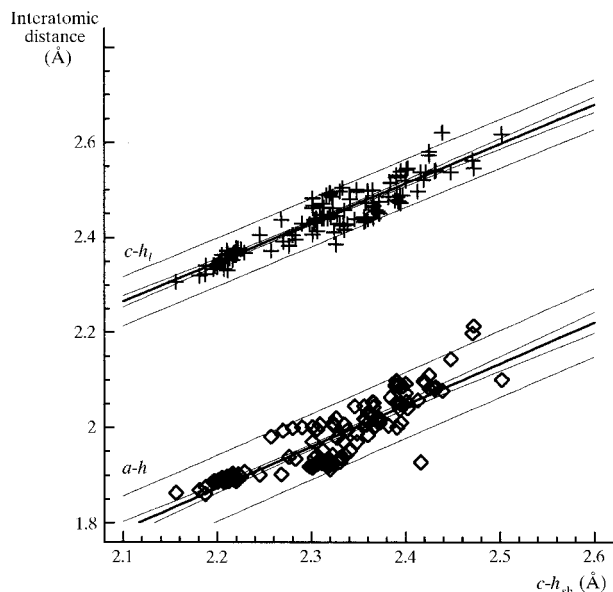


Fig. 3. Linear relations between interatomic distances for the total sample: c - h_l and a - h versus c - h_{sh} . The number of data points is equal to 140. The correlation coefficients and slopes are given in Tables 2 and 3. All distances are given in Å. Confidence intervals for slopes and tolerance intervals are all at the significance level $\alpha = 0.05$.

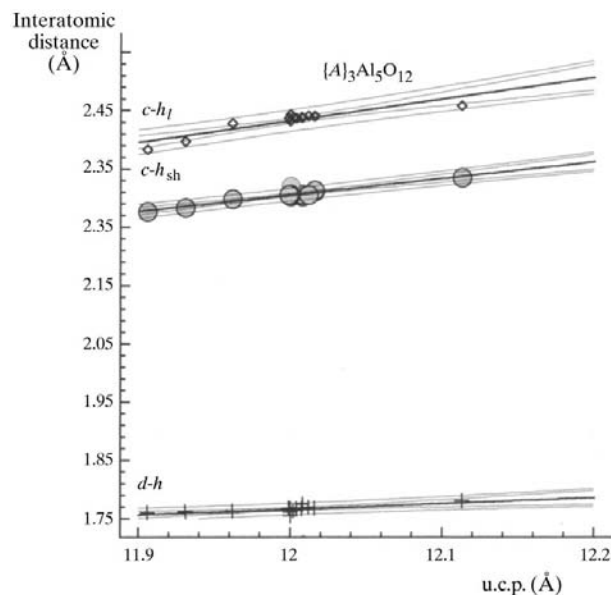


Fig. 4. Linear relations between interatomic distances, with the exception of a - h which do not correlate, and u.c.p for the $\{A\}_3\text{Al}_5\text{O}_{12}$ subsample. The correlation coefficients and slopes are given in Tables 2 and 3. All distances and the u.c.p. are given in Å. Confidence intervals for slopes and tolerance intervals are all at the significance level $\alpha = 0.05$.

cahedral sites. The slopes of the relations obtained for $d-h$, $c-h_{sh}$, $c-h_l$ versus u.c.p. are almost the same as in the case of $\{A\}_3Al_5O_{12}$ (0.07, 0.27 and 0.35, respectively). This reflects great structural similarity between these two subsamples.

2.1.4. $Y_3[(B)]_5O_{12}$ subset. For this subset $[(B)]$ denotes Al, Sc, Fe, Ga, In occupying either the octahedral and/or tetrahedral sites. There are only 10 structures in this subset. These crystals can have both of these sites doped with one or more type of ion. The strongest effects then can be expected for the parameters associated with these sites. In fact, the changes of both $a-h$ and $d-h$ distances mostly affect the u.c.p. ($R = 0.980$ and 0.88 , respectively; Fig. 6a). Also the $c-h_{sh}$ distance is correlated with the u.c.p. ($R = 0.931$). Surprisingly, the $c-h_l$ distance does not correlate with the u.c.p. The best correlation between the interatomic distances is for $d-h$ and $a-h$ ($R = 0.94$), which can be expected and both these distances correlate with the $c-h_{sh}$ distance ($R = 0.96$ and 0.87 , respectively; Fig. 6b). The $c-h_l$ interatomic distance does not correlate with any of the other distances or with the unit-cell parameter because doping for this subsample takes place either at octahedral or tetrahedral sites and the changes of the dodecahedral parameters have only secondary character.

From the slopes of simple regressions between the $a-h$, $d-h$, $c-h_{sh}$ distances and the unit-cell parameter (0.27, 0.25 and 0.10, respectively) one can see that small changes of the u.c.p. are associated with quite large changes of the $a-h$ and $d-h$ distances. Larger changes of

the $a-h$ and $d-h$ distances are required to give the same change of the u.c.p. The slopes of simple regressions between the interatomic distances suggest that marked changes of the $a-h$ distance are associated with similar changes of $d-h$ and small changes of the $c-h_{sh}$ distances (slopes = 1.0 and 2.1, respectively). Moreover, a

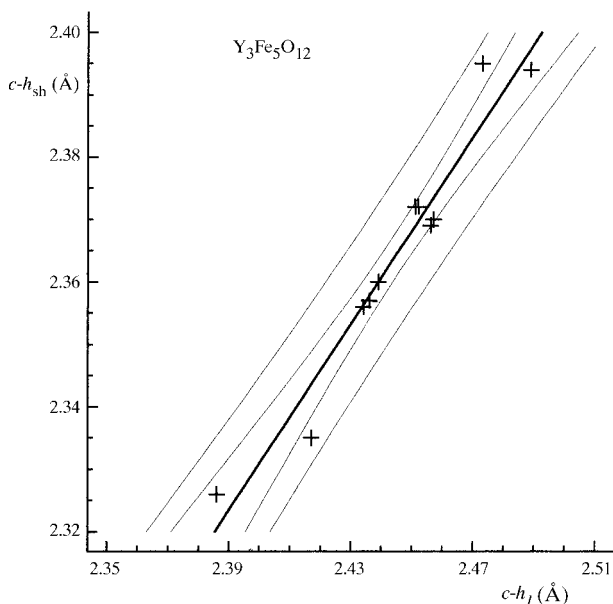
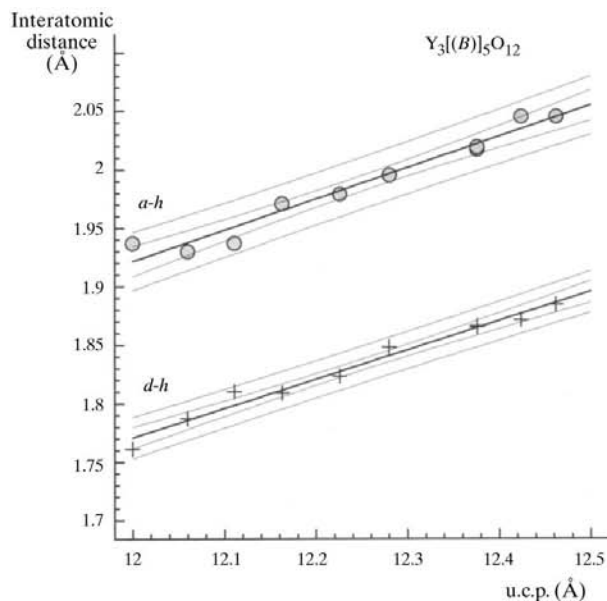
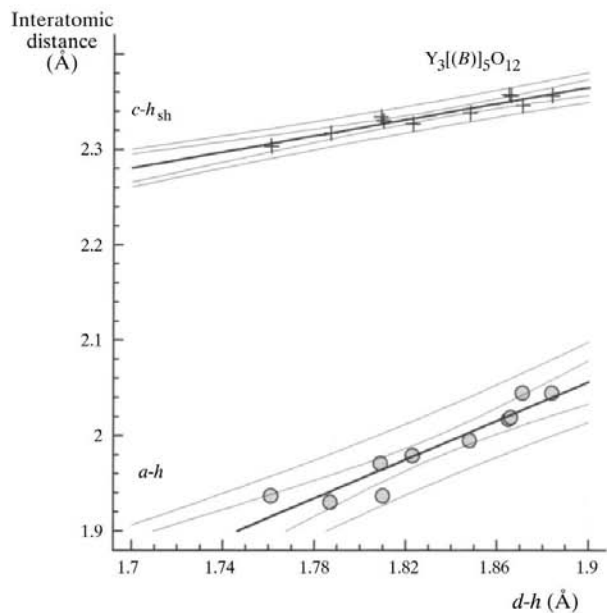


Fig. 5. Linear relations between $c-h_{sh}$ and $c-h_l$ interatomic distances for the $\{A\}_3Fe_5O_{12}$ subsample. The correlation coefficients and slopes are given in Tables 2 and 3. All distances are given in Å. Confidence intervals for slope and tolerance interval are both at the significance level $\alpha = 0.05$.



(a)



(b)

Fig. 6. Linear relations for the $Y_3[(B)]_5O_{12}$ subsample: (a) $a-h$ and $d-h$ versus u.c.p.; (b) $c-h_{sh}$ and $a-h$ versus $d-h$. The correlation coefficients and slopes are given in Tables 2 and 3. All distances and the u.c.p. are given in Å. Confidence intervals for slopes and tolerance intervals are all at the significance level $\alpha = 0.05$.

substantial change of d - h is needed to observe a change of the c - h_{sh} distance (slope = 2.2). The a - h and d - h distances are approximately twice as sensitive as c - h_{sh} .

The basic reason for all these changes in all the cases described above is the variation of doping/replacing ion radius. This issue will be dealt with in the next section.

2.2. Dependence on radius of the dopant ion

For those subsets which have only one void partially or fully occupied by a dopant/replacement ion, it is possible to correlate structural parameters with the radius of that ion. We have used the Shannon (1976) and Espinosa (1962) values of ionic radii. As the correlation between them is very high ($R = 0.999$) we present relations with the radii given by Shannon. The correlation is possible only for the $\{A\}_3\text{Al}_5\text{O}_{12}$ and $\{A\}_3\text{Fe}_5\text{O}_{12}$ subsets. We have divided both subsets into two groups: (a) those which contain crystal structures with the full replacement of ions in dodecahedral voids and (b) those in which the concentration of doping ions is small (very much less than 100%). We also analyse a group of gallium garnets $\{A\}_3\text{Ga}_5\text{O}_{12}$, consisting of six structures found in the ICSD.

In the case of the $\{A\}_3\text{Al}_5\text{O}_{12}$ and $\{A\}_3\text{Fe}_5\text{O}_{12}$ subsets with $A \neq 100\%$ of one element, all equivalent correlations are quite good and similar for both subsamples. Some data points, however, deviate significantly from the best lines, see Fig. 7(a). This results from partial doping. Thus, one has to take into account not only the dopant radius, but also the concentration of the dopant. To account for this we will apply, rather than a dopant radius, 'an effective radius' r_{Ef} defined in the following manner

$$r_{\text{Ef}} = R_H + (r - R_H)(d/100) \quad (\text{in general}) \quad (1a)$$

$$r_{\text{Ef}} = R_H + (r - R_H)(x/3) \quad (\text{for the dodecahedral sites only}), \quad (1b)$$

where r is a dopant ion radius, d the dopant concentration (in atomic %), R_H the host ion radius [when doping takes place at the yttrium sites, this is the Y^{3+} ionic radius, $R_{\text{Y}(\text{cr-crystal radius})} = 1.159 \text{ \AA}$] and x the number in the chemical formula of a garnet.

This simple approach works very well when applied to the data points deviating from the best line obtained for particular subsets. Some of the data points, those describing partial doping, deviate far less from the regression line (Fig. 7b).

In our opinion, this linear dependence can have a predictive power when it is verified with a series of doped YAGs with known concentrations. This is a very important point because quite often it is difficult to establish the concentration of doping ions with X-ray or neutron diffraction owing to a statistical distribution of dopants in the structure and small differences between

the electron densities of the doping and host ions. There seems to be an indirect way of obtaining structural information from the values of u.c.p. and c - h_{sh} or c - h_l parameters, which is illustrated in Fig. 7.

It can be seen in Fig. 7(b) that two data points remain off line. These points represent some YAGs doped with a specific amount of neodymium. However, with the help of the regression lines one can estimate this unknown quantity by: (a) projection of these points on the best line, which gives the values of effective radii for both points; (b) recalculation of the unknown concentration from the effective radii values using (1). This method is strongly dependent on the number of data points defining the regression line: the more data points there are, the more reliable the regression line. In order to obtain the most reliable slope and intercept we are going to investigate, with single crystal and powder X-ray diffraction methods, a whole series of garnets doped with different amounts of the rare earth elements.

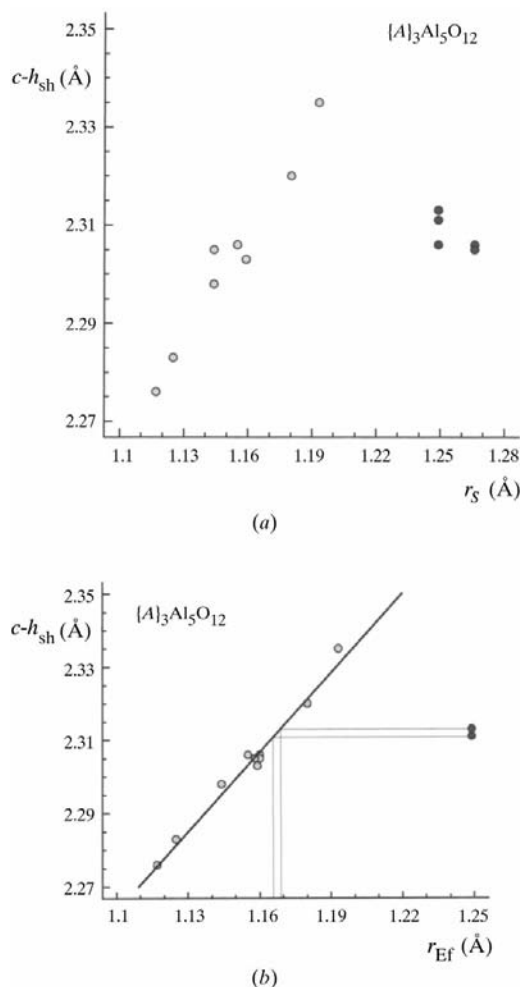


Fig. 7. Linear relations for the $\{A\}_3\text{Al}_5\text{O}_{12}$ subsample between (a) interatomic distance c - h_{sh} and r_S , and (b) c - h_{sh} and r_{Ef} . All values are given in Å.

Table 4. Correlation coefficients for relations between structural parameters of garnets and the effective doping-ion radii

	$\{A\}_3\text{Fe}_5\text{O}_{12}$, where $A = 100\%$ of one element	$\{A\}_3\text{Fe}_5\text{O}_{12}$	$\{A\}_3\text{Al}_5\text{O}_{12}$, where $A = 100\%$ of one element	$\{A\}_3\text{Al}_5\text{O}_{12}$	$\{A\}_3\text{Ga}_5\text{O}_{12}$, where $A = 100\%$ of one element
Number of data points	8	9	8	15	6
a - h versus r_{Ef}	–	–	–	–	–
d - h versus r_{Ef}	0.75 (7)	0.709 (7)	–	0.65 (5)	0.894 (3)
c - h_{sh} versus r_{Ef}	0.993 (3)	0.992 (3)	0.989 (3)	0.983 (3)	0.991 (5)
c - h_l versus r_{Ef}	0.978 (7)	0.975 (7)	0.957 (8)	0.941 (7)	0.981 (7)
u.c.p. versus r_{Ef}	0.998 (5)	0.998 (5)	0.93 (3)	0.93 (2)	0.997 (7)

Table 5. Slopes of linear relationships between structural parameters of garnets and the effective doping-ion radii

	$\{A\}_3\text{Fe}_5\text{O}_{12}$, where $A = 100\%$ of one element	$\{A\}_3\text{Fe}_5\text{O}_{12}$	$\{A\}_3\text{Al}_5\text{O}_{12}$, where $A = 100\%$ of one element	$\{A\}_3\text{Al}_5\text{O}_{12}$	$\{A\}_3\text{Ga}_5\text{O}_{12}$, where $A = 100\%$ of one element
Number of data points	8	9	8	15	6
a - h versus r_{Ef}	–	–	–	–	–
d - h versus r_{Ef}	0.20 (7)	0.19 (7)	–	0.22 (7)	0.17 (4)
c - h_{sh} versus r_{Ef}	0.69 (3)	0.70 (3)	0.73 (4)	0.73 (4)	0.91 (6)
c - h_l versus r_{Ef}	0.88 (8)	0.89 (8)	0.9 (1)	0.95 (9)	0.92 (9)
u.c.p. versus r_{Ef}	2.52 (6)	2.52 (5)	2.3 (4)	2.3 (3)	2.50 (9)

In Table 4 we present correlation coefficients (and the slopes in Table 5) for the relations between structural parameters of the garnets and the effective ion radii. For the $\{A\}_3\text{Fe}_5\text{O}_{12}$ subsample, the c - h_{sh} and c - h_l distances correlate very well with the effective dopant radius, r_{Ef} ($R = 0.991$ and 0.974 , respectively; Figs. 8a and 8b). However, the highest correlation coefficient with this parameter has the unit-cell parameter ($R = 0.996$, Fig. 8c). A small change in the doping-ion radius results in a large increase of the unit-cell parameter (slope = 2.50). Both the distances c - h_l and c - h_{sh} are also quite sensitive (slopes equal to 0.51 and 0.66, respectively). To a certain extent the c - h_{sh} is even superior to the u.c.p. because its dependencies on the effective radius have slopes characteristic of a particular class of garnet (Fig. 8a). The slopes for equivalent dependencies, obtained for u.c.p., are the same. Unexpectedly, in the case of the c - h_l distance not only the slopes, but also the full linear relationships do not differ for all types of garnets. Even the changes in size of the main cations (Ga, Fe, Al) in the crystal lattice do not affect these dependencies. There is, naturally, no correlation between the octahedral distances and the dopant radius.

2.3. Principal component analysis

As can be seen from Table 2, most of the structural parameters are interrelated. Most of them also correlate with the Shannon radius for the doping ion. In fact, when a given garnet site is doped all structural parameters defining the garnet structure are changed. This total effect of doping can be rationalized using principal

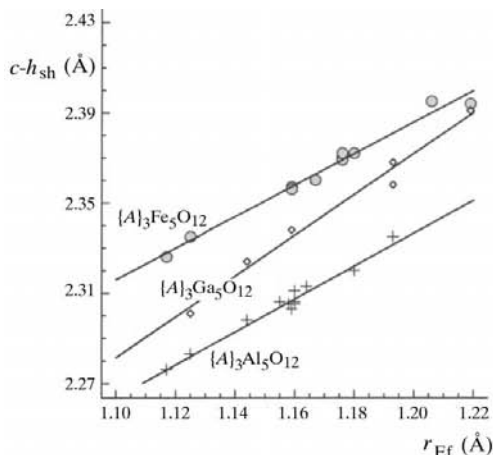
component analysis. PCA forms linear combinations of the parameters analysed so as to account for the overall variance in the sample using the minimum number of principal components (PCs). Such linear combinations of variables have coefficients defining the relative magnitude of the involvement of particular parameters in each PC. The first component describes the largest amount of variance, then the next component, orthogonal to the first, is calculated to account for variance left unexplained by the first, and so on.

The percentage of data variance rationalized by the first component for the total sample is 80% (Table 6). In the case of the subsets, var(PC1) varies from 63 to 74%. The second components explain only some 14–26% and will not be analysed in detail.

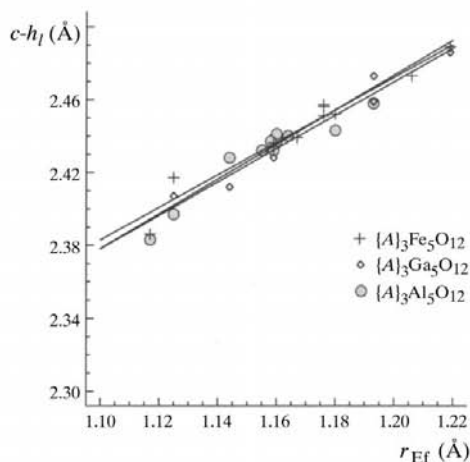
The PC scores of the first component correlate very well with the Shannon radii and even better with the ‘effective’ ion radii (Table 7). Both types of scores – those with and without rotation – have very similar values of correlation coefficients. All the correlation coefficients, except one, have their absolute values higher than 95%. These correlations clearly show that most of the changes in the structures of garnets are due to doping. This is illustrated in Fig. 9.

2.4. Partial correlation

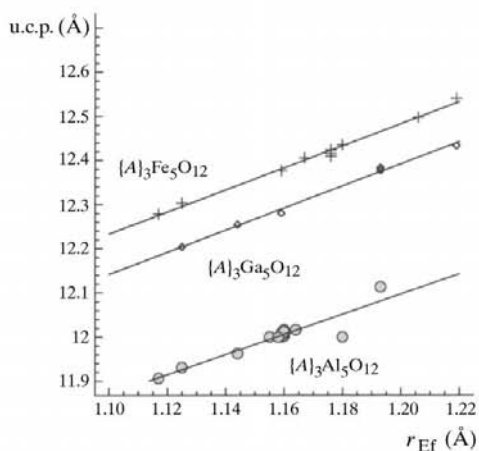
The results of partial correlation (Spiegel, 1961; Czermiński *et al.*, 1990; Krygowski & Woźniak, 1991) of the four variables (a - h , d - h , c - h_{sh} and c - h_l) defining the structure of garnets are shown in Table 8.



(a)



(b)



(c)

Fig. 8. Linear relationships for $\{A\}_3Al_5O_{12}$, $\{A\}_3Fe_5O_{12}$ and $\{A\}_3Ga_5O_{12}$ compounds: (a) $c-h_{sh}$ versus r_{Ef} ; (b) $c-h_l$ versus r_{Ef} ; (c) u.c.p. versus r_{Ef} . Confidence intervals for slopes and tolerance intervals are all at the significance level $\alpha = 0.05$.

Table 6. Results of principal component analysis

a_1 , a_2 , a_3 and a_4 represent loadings of linear combination of variables for the first component

$$\text{Factor (1)} = a_1(a-h) + a_2(d-h) + a_3(c-h_{sh}) + a_4(c-h_l).$$

Sample	a_1	a_2	a_3	a_4	% variation
Total	0.9	0.8	1.0	0.9	80
$\{A\}_3Al_5O_{12}$	-0.4	0.9	1.0	1.0	63
$\{A\}_3Fe_5O_{12}$	0.4	0.9	1.0	1.0	66
$\{A\}_3Ga_5O_{12}$	0.2	1.0	1.0	1.0	70
$Y_3X_5O_{12}$	1.0	1.0	1.0	0.4	73

In the simplest case of three variables X_1 , X_2 and X_3 , the partial correlation coefficient $r_{12.3}$ describes the power of correlation between residuals of regressions of pairs of variables (X_1 , X_3) and (X_2 , X_3). This means that the influence of variable X_3 on variables X_1 and X_2 , replaced by residuals, are correlated. In the case of four variables when any two of them are correlated the other two are controlled. For example, correlation coefficient $r_{a-h, d-h, c-h_{sh}, c-h_l}$ gives us an estimate of the correlation between $a-h$ and $d-h$, while variables $c-h_{sh}$ and $c-h_l$ are controlled.

It appears that the highest partial correlation exists between $c-h_{sh}$ and $c-h_l$ parameters (partial correlation coefficients for the total sample and all subsamples with the exception of subsample $Y_3[(B)]_5O_{12}$ are larger than 0.9). Of course, in the case of the $Y_3[(B)]_5O_{12}$ subsample, there is no doping at dodecahedral sites and the changes of these parameters have a secondary character being a reaction to doping at the other sites. In

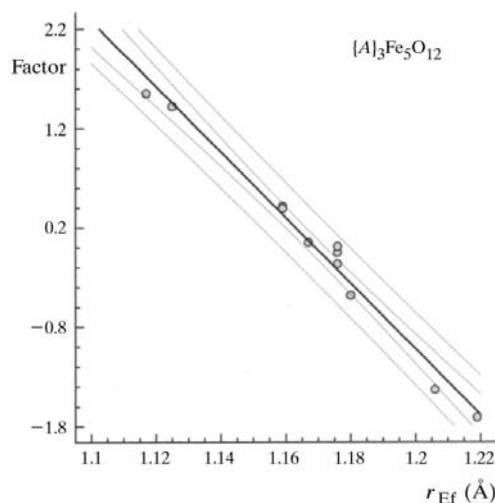


Fig. 9. Linear relationship between component 1 and r_{Ef} for the $\{A\}_3Fe_5O_{12}$ subsample. All values are given in Å. The confidence interval for slope and the tolerance interval are both at the significance level $\alpha = 0.05$.

Table 7. Simple regressions of the first components (a_1) versus dopant radius or effective dopant radius

		Correlation coefficient	Slope	Intercept
$X_3Al_5O_{12}$	a_1 versus r_{Ef}	-0.95 (34)	-51 (5)	60 (6)
$X_3Al_5O_{12}$, $X = 100\%$ of one element	a_1 versus r_S	-0.96 (31)	-38 (5)	43 (5)
$X_3Fe_5O_{12}$	a_1 versus r_{Ef}	-0.99 (15)	-33 (2)	39 (2)
$X_3Fe_5O_{12}$, $X = 100\%$ of one element	a_1 versus r_S	-0.99 (14)	-28 (1)	33 (2)
$X_3Ga_5O_{12}$	a_1 versus r_S	0.99 (14)	28 (2)	-33 (2)

Table 8. Partial correlation coefficients

	All data	$\{A\}_3Al_5O_{12}$	$\{A\}_3Fe_5O_{12}$	$Y_3X_5O_{12}$
Number of data points	140	15	9	10
$a-h$ versus $d-h$	-	-	-	0.722
$a-h$ versus $c-h_{sh}$	0.726	-	-	-
$a-h$ versus $c-h_l$	-0.531	-	-	-
$d-h$ versus $c-h_{sh}$	0.803	-	0.899	0.847
$d-h$ versus $c-h_l$	-0.772	-	-0.834	-
$c-h_{sh}$ versus $c-h_l$	0.945	0.903	0.984	-

consequence, one cannot expect a strong correlation between these two parameters. However, because strong partial correlation exists for relations $a-h$ versus $d-h$ and $a-h$ versus $c-h_l$ (when the other two structural variables are controlled), it can easily be confirmed that these are the octahedral sites which are doped for this subsample.

For all data, most partial correlation coefficients are significant and some of them have negative signs ($a-h$ versus $c-h_l$ and $d-h$ versus $c-h_l$). These two regressions, however, have positive 'normal' correlation coefficients. It can be concluded, then, that for these two relations the influence of correlation with the other variables is so strong that it can even change the signs of slopes, as in the relations between $a-h$ and $c-h_l$ and also $d-h$ and $c-h_l$. When the data with the partial doping are excluded the partial correlation becomes even stronger.

3. Conclusions

We emphasize that most of the structural parameters describing garnet structure are correlated and that the type and degree of correlation depends on the doping site and the type of garnet. Structural parameters are not equally sensitive to doping. When the dodecahedral sites are doped the shortest dodecahedral parameter is the most sensitive one (except the unit-cell parameter). The effective ion radius can help to establish the unknown concentration of doping ions only on the basis of known

unit-cell parameters or other distances (known from X-ray or neutron diffraction). According to the PCA results, the first component explains most of the variation of structural data and it is geometric in nature. This component correlates with the effective ion radius related to ionic radius and concentration of doping ions. Partial correlation helps to identify the strongest relations between pairs of variables when the influence of the other structural variables on them is controlled. The strongest relationships between structural parameters can hide the weaker ones (change the sign of their slopes), while comparing the results of the partial and standard correlation analyses.

References

- Armbruster, T. & Geiger, C. A. (1993). *Eur. J. Mineral.* **5**, 59–71.
- Bergerhoff, G., Hundt, R., Sievers, R. & Brown, I. D. (1983). *J. Chem. Inf. Comput. Sci.* **23**, 66–69.
- Bergerhoff, G. & Sievers, R. (1989). *Nachr. Dok.* **40**, 27–31.
- Czerwiński, J., Iwasiewicz, A., Paszek, Z. & Sikorski, A. (1990). *Statistical Methods in Applied Chemistry*. Amsterdam: PWN, Elsevier.
- Espinosa, G. P. (1962). *J. Chem. Phys.* **37**, 2344–2347.
- Geller, S. (1967). *Z. Kristallogr.* **125**, 1–47.
- Hazen, R. M. (1976). *Am. Mineral.* **61**, 266–271.
- Hazen, R. M. & Finger, L. W. (1978). *Am. Mineral.* **63**, 297–303.
- Krygowski, T. M. & Woźniak, K. (1991). *Similarity Models in Organic Chemistry, Biochemistry and Related Fields*, edited by R. I. Zalewski, T. M. Krygowski and J. Shorter, ch. 1, pp. 1–76. Amsterdam: Elsevier.
- Meagher, E. P. (1975). *Am. Mineral.* **60**, 218–228.
- Pawlak, D. A., Frukacz, Z., Mierczyk, Z., Suchocki, A. & Zachara, J. (1998). *J. Alloys Comput.* **275–277**, 361–364.
- Rodić, D., Tellgren, R. & Guillot, M. (1991). *J. Magn. Magn. Mater.* **94**, 260–266.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–762.
- Spiegel, M. R. (1961). *Schaum's Outline Series Theory and Problems of Statistics*. New York: McGraw-Hill Book Co.