ISOMORPHISM AND CRYSTALLINE SOLUBILITY IN THE GARNET FAMILY*

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Abstract

Several dozen compositions have been reacted "dry" and under high water pressures in order to determine the extent, and explain the reason for, the solubility among the three garnet groups: ugrandite, pyralspite and the rare earth garnets.

Ionic radius is shown to be the dominant variable, although a charge correction must be applied to the ions of different charges. At low pressure very little binary solubility is found between representatives of the pyralspite and ugrandite groups. However, complete crystalline miscibility exists between the rare earth garnets and each of the natural garnet groups. Moreover, $3CdO \cdot Al_2O_3 \cdot 3SiO_2$ also forms a garnet structure completely miscible with both spessartite and uvarovite. Very little Fe^{3+} was admitted into the $12CaO \cdot 7Al_2O_3$ garnet, and attempt at substitution of substantial amounts of OH^- and F^- in most garnets was unsuccessful.

Introduction

The garnet mineral family stands as one of the two most important silicate families based on a structure containing independent SiO_4 tetrahedra. To mineralogists the garnets have provided a fruitful field for the investigation of the influence of ionic substitution on properties. Moreover, with ions in the four, six and eight-fold coordinated positions this structure provides an excellent model for crystal chemical studies. The existence in nature of two essentially separate groups of garnets, the so-called pyralspite and ugrandite groups, has called for an explanation. In petrology the presence of various garnets has been used as a p-t indicator and experimental data on the actual conditions necessary for their formation have always been desired. However, the impetus for nearly all the recent synthesis work in garnets came from the discovery by Bertaut, *et al.* (1957) of ferrimagnetism in the Fe_2O_3-rare-earth compounds with the garnet structure.

The problem of immediate concern is the nature and extent of crystalline solubility among different garnet "groups." Thus, one may inquire whether or not it is conclusively established that there is no solubility between the pyralspite and ugrandite groups. Actually there is no reliable experimental evidence on this point, neither at high pressures nor even at low pressures. What is the controlling variable which controls mutual intersolubility here? Likewise does the rare earth garnet group dissolve either or both of these former groups? What factors limit the ions which

can be admitted into the rare earth garnets? Is there any anion solubility? What other types of crystalline solubility are possible? Thus Keith and Roy (1954) who first described the preparation of the rare earth ferrites with a garnet structure postulated the existence of solid solution leading to a structure of the type formula: $Y_3^{VIII}YAl^{VI}(AlO_4)_3$ equivalent to $YAlO_3$; while even earlier Yoder and Keith (1951) had shown continuous solubility from spessartite to $Y_3Al_5O_{12}$.

A study of the crystalline solubility in the rare earth garnets would also indicate the directions in which the magnetic properties can be varied by introduction of either diamagnetic or paramagnetic ions in the desired coordination.

EXPERIMENTAL PROCEDURE

Samples were prepared mostly as powders by the grinding and mixing in alcohol of stoichiometric proportions of the oxide, nitrate, or carbonate of the cation with silicic acid. Germanium oxide (GeO_2) was used in all cases for the Ge^{4+} substitutions. The samples were then dried and placed in platinum crucibles. They were heated at 750° C. in most cases for at least four hours. This temperature varied somewhat with the materials used since it had to be high enough to effect decomposition of the compounds used without causing any volatilization. After this heating, the samples were re-ground and re-mixed either in an agate mortar and pestle or in a Wig-l-bug type mixer.

Some samples were prepared as gels by dissolving the required amounts of the element nitrate in distilled water, adding colloidal silica (as ammonium-stabilized "Ludox") and heating on a steam bath until a gel-like solid is formed. The gel is then heated overnight at 750° C., and then re-ground and mixed. Chemicals used in the preparation of samples were of reagent grade except for the rare earth compounds which were at least 99 per cent pure, and in many cases 99.9 per cent pure. (Manufacturer's analysis is found to be fairly reliable by x-ray fluorescence.)

The "dry" runs were made mostly by suspending a platinum foil envelope containing the sample in a kanthal-wound or platinum-wound furnace. Some runs were made in sealed gold or platinum tubes, especially where losses of one of the components due to volatilization was previously noted. For the hydrothermal runs, the samples were placed in gold foil envelopes or in sealed gold tubes which, in turn, were placed in a "test-tube" bomb and heated in a kanthal-wound furnace. In those cases where water was desired as a component, only gold foil envelopes were used and temperatures were held at approximately 250° C. Uniaxial high pressure devices were used for runs involving pressures of 20,000 to 50,000 atmospheres.

All experimental work was carried on in a sub-solidus temperature range. The optimum temperature for reaction was determined empirically in most cases. All runs were made for a period of at least 20 hours. Increased time increased the crystallinity of the final product in most cases. After completion of the run, the samples were examined by powder diffraction methods using a Norelco wide-range diffractometer. Scanning was at a rate of two degrees (2θ) per minute. The petrographic microscope was used in some cases to determine the presence of more than one phase. Unit cell measurements were derived from diffractometer patterns run at $\frac{1}{4}°$ (2θ) per minute.

Each composition was reacted under the chosen set of conditions and examined petrographically and by x-ray diffraction for the phases present. Some 300 runs were made. Where the product was essentially monophasic, it was presumed that the total original composition was in that phase: care was exercised in the case of GeO_2 or of fluorides in using this argument only if sealed tubes had been used. If the product showed two garnet phases the system was presumed to be binary and the composition assumed to be on the join. Arguments for slight changes in stoichiometry are not advanced since no special attempt was made to determine the presence of very small amounts of additional phases. The only data listed (see Table I) are the cell dimensions of some of the garnets prepared.

Results and Discussion

I. Isomorphism

Substitutions in garnet structures were attempted in the eight, six and four coordination positions. Coupled substitutions in two, three and all four positions (including the anion) were also tried.

Substitution in the Eight Coordinated Position

In the formula $3XO \cdot Al_2O_3 \cdot 3SiO_2$, which may be regarded as the type formula, the following ions were introduced for X: Mg, Ni, Mn, Cd, Ca, Sr, Ba. In the past only the manganese garnet has been formed at atmospheric pressure. It was found that a Cd-garnet could also be synthesized easily "dry." At elevated pressures the Mg-garnet pyrope was synthesized first by Coes and details of the synthesis of the anhydrous Ca-garnet, grossularite, are given by Roy and Roy, 1957. Outside of these none of the others yielded garnets. Quite clearly calcium was near the upper end of the "structure field" and Sr^{2+} was too large. However, a $3CdO \cdot Fe_2O_3 \cdot 3SiO_2$ composition did not form a garnet structure at atmospheric pressure.

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TABLE I. DATA ON PREPARATION AND UNIT CELLS OF SOME SYNTHETIC GARNETS

Garnet synthesized	Starting materials	Conditions of formation			Unit cell a_0 (Å)
		T° C.	P (atm.)	t(hrs.)	
$3CdO \cdot Al_2O_3 \cdot 3SiO_2$	$Cd(NO_3)_2 \cdot 4H_2O$ $Al(NO_3)_3 \cdot 9H_2O$ Silicic Acid	880	1	70	11.82 ± 0.02
$3MnO \cdot Al_2O_3 \cdot 3SiO_2$	$MnCO_3$ $Al(NO_3)_3 \cdot 9H_2O$ Silicic Acid	1100	1	21	11.64 ± 0.01
$3CaO \cdot Cr_2O_3 \cdot 3SiO_2$	$CaCO_3$ $Cr(NO_3)_3 \cdot 9H_2O$ Silicic Acid	1200	1	24	11.974 ± 0.003[1]
$3MnO \cdot Al_2O_3 \cdot 3GeO_2$	$MnCO_3$ $Al(NO_3)_3 \cdot 9H_2O$ GeO_2	1200	1	24	11.91 ± 0.01
$3Y_2O_3 \cdot 5Al_2O_3$	Y_2O_3 $Al(NO_3)_3 \cdot 9H_2O$	1200	1	36	12.01 ± 0.02[2]
$3Gd_2O_3 \cdot 5Al_2O_3$	$Gd(NO_3)_3 \cdot 6H_2O$ $Al(NO_3)_3 \cdot 9H_2O$	1200	1	36	12.12 ± 0.01
$3CaO \cdot Fe_2O_3 \cdot 3GeO_2$	$CaCO_3$ Fe_2O_3 GeO_2	1000	1	82	12.34 ± 0.01
$3Gd_2O_3 \cdot 5Fe_2O_3$	$Gd(NO_3)_3 \cdot 6H_2O$ Fe_2O_3	1200	1	24	12.44 ± 0.01

[1] Crystal Data, Ed. Eonnay and Nowacki.
[2] Keith and Roy (1954).

Substitutions in the Octahedral Site Alone

In the type formula $3CaO \cdot X_2O_3 \cdot 3SiO_2$ the number of ions likely to enter the X position is small, Al, Cr, Fe, Ga are the obvious choices. All these have been successfully introduced. However, only Cr_2O_3, which never appears in four coordination forms the garnet uvarovite at atmospheric pressure (Hummel, 1950).

## Substitutions in the Tetrahedral Site Alone

Only one tetravalent ion can possibly substitute for Si^{4+} and these Ge^{4+} substitutions enhance the case of formation of many garnets at atmos-

pheric pressure as was first shown by Tauber, Banks, and Kedesdy (1958). Both the germanium analogue $(3MnO \cdot Al_2O_3 \cdot 3GeO_2)$ of spessartite (which can be prepared at atmospheric pressure) and the germanium analogue $(3CaO \cdot Fe_2O_3 \cdot 3GeO_2)$ of andradite (which cannot be so made) were easily prepared. It was fully expected that $3MgO \cdot Al_2O_3 \cdot 3GeO_3$ would yield a garnet at atmospheric or low pressures. However, not even at 40,000 atmospheres and 500° C. could we get a garnet, showing that the requirement for pressure in pyrope synthesis to put Mg in eight and Al in six coordination is unaffected by the size of the tetrahedral cation. The failure to synthesize a Ge-grossularite $3CaO \cdot Al_2O_3 \cdot 3GeO_2$ is ascribed to too large a total of ionic sizes.

VIII–IV Coupled Substitutions

This is the main substitution yielding the rare earth garnet. In the type formula $3CaO \cdot Fe_2O_3 \cdot 3SiO_2$ the trivalent ions from Nd to Lu can be combined in the Ca position with Fe^{3+} in the Si position. All the Fe^{3+} can be replaced in most cases by Al or Ga but never by Cr^{3+}. Nothing new was added in this study to the extensive work by Bertaut and his coworkers and the Bell Telephone Laboratories group.

Attempts to leave the rare earth ion and the sixfold Fe^{3+} in the magnetic garnet structure and replace the tetrahedral iron only gave negative results in the following cases:

$$3Y_2O_3 \cdot 2Fe_2O_3 \cdot 3B_2O_3$$
$$3Gd_2O_3 \cdot 2Fe_2O_3 \cdot 3B_2O_3$$
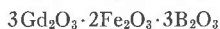
Al_2O_3 will of course replace Fe_2O_3 in these garnets but it can be distributed over both four and six coordination sites. The B_2O_3 which can only accept four-fold sites does not seem to substitute easily nor does Cr^{3+} (which will only accept six fold sites) in $3Gd_2O_3 \cdot 2Cr_2O_3 \cdot 3Fe_2O_3$, although this latter phase will definitely enter partially into solid solution with other garnet phases such as $3CaO \cdot Fe_2O_3 \cdot 3GeO_2$ (*vide infra*).

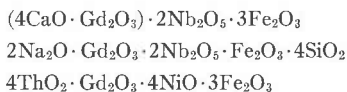### *VIII-VI-IV Substitutions*

One entirely different group of garnets based on the "$12CaO \cdot 7Al_2O_3$"* structure was considered. This compound is known to have the garnet structure presumably with all the eight-fold sites occupied by Ca, the four fold by Al and the six fold by both. This composition must of course be "defective" in some way, or conceivably the exact formula may be more complex, but this need not concern us here. Attempts were made to introduce Fe^{3+} for Al^{3+} in the hope that ferrimagnetic phases could be made. At the compositions $12CaO \cdot (6Al \cdot 1Fe)_2O_3$ and $12CaO \cdot (4Al \cdot 3Fe)_2O_3$

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* The composition of this compound has earlier been given as $5CaO \cdot 3Al_2O_3$. For a discussion of the structure see Büssem and Eitel (1936); Majumdar and R. Roy (1956).

strongly magnetic mixtures of phases were obtained. However, a careful study showed that the garnet phase was not affected and took in very little Fe^{3+} in solid solution and that the magnetic phase was the dicalcium ferrite solid solution $2CaO \cdot (FeAl)_2O_3$.

The following combinations which would have made available a wide range of ions for substitution were all unsuccessful:

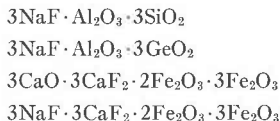$$(4CaO \cdot Gd_2O_3) \cdot 2Nb_2O_5 \cdot 3Fe_2O_3$$
$$2Na_2O \cdot Gd_2O_3 \cdot 2Nb_2O_5 \cdot Fe_2O_3 \cdot 4SiO_2$$
$$4ThO_2 \cdot Gd_2O_3 \cdot 4NiO \cdot 3Fe_2O_3$$

Likewise in $3Y_2O_3 \cdot 2Ni_2O_3 \cdot 3Ni_2O_3$ which was run up to 700° C. at 200 atmospheres of oxygen the nickel could not be maintained in the trivalent oxidation state and no garnet was formed.

Coupled Substitutions Involving the Anions

A garnet structure is known for the phases: $3CaO \cdot Al_2O_3 \cdot 3SiO_2$ and $3CaO \cdot Al_2O_3 \cdot 6H_2O$, in which one may regard the $3Si^{4+}$ ions $+ 12(O^{2-})$ ions as being replaced by three vacancies $+ 12(OH^-)$ ions. Furthermore, a virtually complete though probably metastable series of solid solutions exists between the two end members. Thus it was reasoned that Fe^{3+} ions could be substituted in these phases and that similar anion substitutions could be made in other garnets.

By hydrothermal reaction at 250° C. or lower no definite garnet phase could be obtained from the $3CaO \cdot Fe_2O_3 \cdot 6H_2O$ composition, but the temperatures used are probably above the maximum stability of this phase. The composition $Gd_3Al_5O_{12}$ was run at various low temperatures and pressures in the hope that a hydroxyl garnet might form and throw the excess Al^{3+} out as a hydroxide. This did not happen. Partial solid solution was obtained successfully along the join $3CaO \cdot Al_2O_3$ $\cdot 3SiO_2 - Ca_3Fe_2(OH)_{12}$. No fluoride substitutions were successful although such oxyfluoride phases may have been easier to grow as single crystals. The following were tried both at atmospheric pressure and up to 4000 atmospheres in sealed gold tubes:

$$3NaF \cdot Al_2O_3 \cdot 3SiO_2$$
$$3NaF \cdot Al_2O_3 \cdot 3GeO_2$$
$$3CaO \cdot 3CaF_2 \cdot 2Fe_2O_3 \cdot 3Fe_2O_3$$
$$3NaF \cdot 3CaF_2 \cdot 2Fe_2O_3 \cdot 3Fe_2O_3$$

II. CRYSTALLINE SOLUBILITY

Two or three mixtures only were prepared in each system to be checked for the presence of solid (more accurately crystalline) solution. The dangers and limitations of such a preliminary study are obvious. In general, however, if the two mixtures at say $\frac{1}{3}$ and $\frac{2}{3}$ mole fraction across the

TABLE II. TYPICAL DATA ON PREPARATION AND UNIT CELLS OF
SOME SOLID SOLUTIONS

System	Starting materials	Conditions of formation			Unit cell (Å)
		T° C.	P (atm.)	t (hrs.)	
$3CaO \cdot Al_2O_3 \cdot 3SiO_2$ $3CdO \cdot Al_2O_3 \cdot 3SiO_2$	$CaCO_3$ $Cd(NO_3)_2 \cdot 4H_2O$ $Al(NO_3)_3 \cdot 9H_2O$ Silicic Acid	750	1000	66	50% Cd $= 11.82 \pm .01$
$3MnO \cdot Al_2O_3 \cdot 3SiO_2$ $3CdO \cdot Al_2O_3 \cdot 3SiO_2$	$MnCO_3$ $Cd(NO_3)_2 \cdot 4H_2O$ $Al(NO_3)_3 \cdot 9H_2O$ Silicic Acid	880	1	70	50% Cd $= 11.79 \pm .01$
$3CaO \cdot Al_2O_3 \cdot 3SiO_2$ $3CaO \cdot Cr_2O_3 \cdot 3SiO_2$	$CaCO_3$ $Al(NO_3)_3 \cdot 9H_2O$ $Cr(NO_3)_3 \cdot 9H_2O$ Silicic Acid	1150	1	66	33% Ca $= 11.93 \pm .01$
$3MnO \cdot Al_2O_3 \cdot 3SiO_2$ $3MnO \cdot Al_2O_3 \cdot 3GeO_2$	$MnCO_3$ $Al(NO_3)_3 \cdot 9H_2O$ GeO_2 Silicic Acid	1200	1	28	50% Ge $= 11.78 \pm .02$
$3CaO \cdot Al_2O_3 \cdot 3SiO_2$ $3Y_2O_3 \cdot 5Al_2O_3$	$CaCO_3$ Y_2O_3 $Al(NO_3)_3 \cdot 9H_2O$ Silicic Acid	750	1000	90	50% Y $= 11.95 \pm .02$
$3CaO \cdot Fe_2O_3 \cdot 3SiO_2$ $3CaO \cdot Fe_2O_3 \cdot 3GeO_2$	$CaCO_3$ Fe_2O_3 GeO_2 Silicic Acid	1200	1	80	50% Ge $= 12.23 \pm .02$
$3CaO \cdot Cr_2O_3 \cdot 3SiO_2$ $3Gd_2O_3 \cdot 5Fe_2O_3$	$CaCO_3$ $Cr(NO_3)_3 \cdot 9H_2O$ Gd_2O_3 Fe_2O_3 Silicic Acid	1150	1	21	50% Gd $= 12.22 \pm .01$
$3CaO \cdot Fe_2O_3 \cdot 3GeO_2$ $3Gd_2O_3 \cdot 5Fe_2O_3$	$CaCO_3$ Fe_2O_3 GeO_2 $Gd(NO_3)_3 \cdot 6H_2O$	1200	1	24	33% Gd $= 12.38 \pm .01$

TABLE II (*Continued*)

System	Starting materials	Conditions of formation			Unit cell (Å)
		T°C.	P (atm.)	t (hrs.)	
$3Gd_2O_3 \cdot 5Al_2O_3$ $3Gd_2O_3 \cdot 5Fe_2O_3$	$Gd(NO_3)_3 \cdot 6H_2O$ $Al(NO_3)_3 \cdot 9H_2O$ Fe_2O_3	1200	1	24	33% Fe=12.21 ± .01 50% Fe=12.30 ± .01
$3Gd_2O_3 \cdot 5Fe_2O_3$ $3Y_2O_3 \cdot 5Fe_2O_3$	$Gd(NO_3)_3 \cdot 6H_2O$ $Y(NO_3)_3 \cdot 4H_2O$ Fe_2O_3	1200	1	67	33% Y_2O_3=12.42 ± .01
$3CaO \cdot Fe_2O_3 \cdot 3SiO_2$ $3Gd_2O_3 \cdot 5Fe_2O_3$	$CaCO_3$ Gd_2O_3 Fe_2O_3 Silicic Acid	1200	1	24	50% Gd=12.20 ± .03
$3Y_2O_3 \cdot 5Al_2O_3$ $3Y_2O_3 \cdot 5Fe_2O_3$	$Y(NO_3)_3 \cdot 4H_2O$ $Al(NO_3)_3 \cdot 9H_2O$ Fe_2O_3	1200	1	80	50% Fe=12.22 ± .04
$Ca_3Al_2(OH)_{12}$ $3CaO \cdot Fe_2O_3 \cdot 3SiO_2$	$CaCO_3$ $Al(NO_3)_3 \cdot 9H_2O$ Silicic Acid	260	1000	72	50% Fe=12.13 ± .03

binary system both give single phase garnets with spacings intermediate between the end members, the results are reported as complete solid solution. Naturally such a cursory examination is also limited with respect to the influence of pressure and temperature on solubility. Hence, in the following reports only the "*p*" and "*t*" of preparation are reported, although no drastic changes in extent of solubility should be expected with a few hundred degrees rise in temperature or a few thousand atmospheres fall in pressure.

The solid solubility results may be grouped into several logical divisions:

1. *Solubility Among Members of Ugrandite Group*

The complete mutual solubility of grossularite and andradite is thoroughly established in natural minerals. The only pair studied here was the pair uvarovite-grossularite, in which within our crude precision complete solubility was found to exist. In addition, complete solubility was found in the system $3CaO \cdot Cr_2O_3 \cdot 3SiO_2 - 3CaO \cdot Fe_2O_3 \cdot 3GeO_2$ demon-
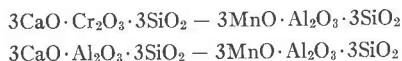
strating the virtual certainty of complete solubility in the uvarovite-andradite $(3CaO \cdot Fe_2O_3 \cdot 3SiO_2)$ join.

2. *Solubility Among Members of the Pyralspite Group*

From natural analyses there is good evidence for complete solubility along the joins almandine-pyrope and spessartite-almandine. Attempts were made to study the third binary join spessartite-pyrope. Since spessartite can be made at atmospheric pressure, it was hoped that partial solid solutions towards the magnesium member would form even at atmospheric pressure. However, no evidence for appreciable solid solution in the spessartite was obtained in runs from one to 40,000 atmospheres. Since a thorough study was not made of each system our failure to get solubility should not be taken as conclusive evidence of the absence of such solubility, especially in view of the fact that in these runs no pyrope phase crystallized.

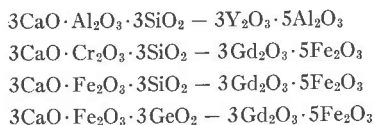## 3. *Solubility Between Pyralspite and Ugrandite Groups*

In standard mineralogical text books (*e.g.* Winchell) there is usually shown about 20 per cent solubility of each group in the other. However, in very few analyses of natural garnets do we encounter binary solid solution but instead very complex multicomponent situations. The following binary joins were chosen as both *typical*, and most likely to give the maximum solubility:

$$3CaO \cdot Cr_2O_3 \cdot 3SiO_2 - 3MnO \cdot Al_2O_3 \cdot 3SiO_2$$
$$3CaO \cdot Al_2O_3 \cdot 3SiO_2 - 3MnO \cdot Al_2O_3 \cdot 3SiO_2$$

Intuitively the latter case would be expected by most experienced crystal chemists to be almost certain to give extensive solid solution. Experimentally practically no solid solution was found in either system.

4. *Rare Earth Garnets—Ugrandite Solubility*

All three members of the ugrandite group were studied separately with one of the rare earth garnets: In all the following cases the evidence for complete solubility was clear (although andradite was not made at atmospheric pressure the $\frac{2}{3}$ mole andradite member could be so made):

$$3CaO \cdot Al_2O_3 \cdot 3SiO_2 - 3Y_2O_3 \cdot 5Al_2O_3$$
$$3CaO \cdot Cr_2O_3 \cdot 3SiO_2 - 3Gd_2O_3 \cdot 5Fe_2O_3$$
$$3CaO \cdot Fe_2O_3 \cdot 3SiO_2 - 3Gd_2O_3 \cdot 5Fe_2O_3$$
$$3CaO \cdot Fe_2O_3 \cdot 3GeO_2 - 3Gd_2O_3 \cdot 5Fe_2O_3$$

This demonstrates that in some garnets not only are Al^{3+} and Si^{4+} completely interchangeable (as shown first by Yoder and Keith, 1951) but likewise Fe^{3+} and Si^{4+}. It was to be expected that the Si^{4+} could also be
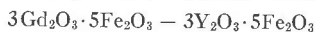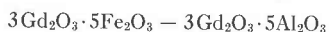
continuously replaced by Ge^{4+}; this was proved in the case $3CaO \cdot Fe_2O_3 \cdot 3SiO_2 - 3CaO \cdot Fe_2O_3 \cdot 3GeO_2$.

5. Rare Earth Garnets—Pyralspite Solubility

Yoder and Keith (loc. cit.) have already established such solubility for the pair: $3MnO \cdot Al_2O_3 \cdot 3SiO_2 - 3Y_2O_3 \cdot 5Al_2O_3$. Our attempt to study the join $3FeO \cdot Al_2O_3 \cdot 3SiO_2 - 3Y_2O_3 \cdot 5Al_2O_3$ cannot be regarded as experimentally successful enough to prove the absence or presence of solubility in the system. Considerable difficulty was experienced in keeping the iron all divalent in the high pressure apparatus.

6. Solubility Among Rare Earth Garnets

It was expected of course that Al^{3+} and Fe^{3+} will replace each other easily, and likewise it was thought probable that Gd^{3+} and Y^{3+} would substitute completely for each other. In the systems:

$$3Gd_2O_3 \cdot 5Fe_2O_3 - 3Gd_2O_3 \cdot 5Al_2O_3$$
$$3Gd_2O_3 \cdot 5Fe_2O_3 - 3Y_2O_3 \cdot 5Fe_2O_3$$
$$3Y_2O_3 \cdot 5Al_2O_3 - 3Y_2O_3 \cdot 5Fe_2O_3$$

this expectation was experimentally demonstrated.

7. Other Solubility Relations Showing the Dominance of the Ionic Radius Variable

By and large the data bear out the principle that the size of the ions is the important variable in determining solubility. However, considerable interpretation of the data needs to be made in order to show this.

Thus, it is easy enough to understand complete solubility of grossularite, uvarovite and andradite since octahedral Cr^{3+}, Al^{3+} and Fe^{3+} usually show such solubility at high temperatures. It is possible to explain the failure to obtain solubility between spessartite and pyrope by showing that the ionic radii (0.91 and 0.78) are different enough to prevent it. Likewise the failure to obtain a spessartite-grossularite solid solution may be laid to the differences in size of Mn^{2+} and Ca^{2+}—especially in eight-coordination. In six-coordinated positions as in tephroite and rhodonite there is considerable solubility.

Difficulties arise when we consider the case of solubility of the rare earth garnets with both the entire ugrandite group and at least spessartite of the other group. This can be brought into line if we apply a Pauling-type charge correction* to the radii of the rare earths, thus making them intermediate between Ca^{2+} and Mn^{2+}, Fe^{2+}, etc. rather than larger

* $R_{z',z''} = \dfrac{R_{1,1}}{n-1 R_{z',z''}}$

even than Ca^{2+}. The Goldschmidt radii are of course given for the rare earth ions in the trivalent six-coordinated state, and the justification for applying the charge correction is purely empirical, *i.e.* a trivalent ion occupying a site "normally" occupied by a divalent one appears to act as though it were smaller than usual. Without experimental data a case could be made for the opposite effect.

Some final data lend additional weight to the importance of size. The only other divalent ion of size intermediate between Ca^{2+} and Mn^{2+} is Cd^{2+} and $3CdO \cdot Al_2O_3 \cdot 3SiO_2$ shows complete solubility with both $3MnO \cdot Al_2O_3 \cdot 3SiO_2$ and $3CaO \cdot Al_2O_3 \cdot 3SiO_2$ type members of the pyralspite and ugrandite groups. Again, although complete solid solution existed between the Cd^{2+} and Mn^{2+} virtually no solid solution could be detected of Mg^{2+} in the Cd^{2+} phase.

The fact that the system $3CdO \cdot Al_2O_3 \cdot 3SiO_2 - 3Y_2O_3 \cdot 5Fe_2O_3$ showed considerable solid solution in each member but a distinct gap shows again that no generalization can escape exception.

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