JOURNAL OF SOLID STATE CHEMISTRY **30**, 79–82 (1979)

Lattice Parameters and Ionic Radii of the Oxide and Fluoride Garnets

RICHARD H. LANGLEY AND GEORGE D. STURGEON

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

Received March 11, 1978; in revised form November 20, 1978

An equation relating ionic radii and lattice parameters for compounds with the garnet structure has been fit to over 330 representative formulations. The radii of the anions, together with the radii and lattice sites of cations, are taken into account. This mathematical relationship can be used to test data, to assist in the assignment of cations to symmetry sites, to predict lattice parameters of unknown compositions, and to suggest the feasibility of preparing compounds with specific compositions. Previously unreported cationic radii for eight-coordinate Cu(I) and four-coordinate Co(III) and Fe(IV) as well as the radii of vacancies in the garnet structure are discussed.

Substances with the general formula $A_3B_2C_3X_{12}$ possessing the garnet structure continue to attract the interest of many scientists because of the numerous minerals which exhibit this structure, the important physical properties of both natural and synthetic compounds in this class, and the architectural nuances of this highly symmetric structure and large unit cell with a variety of symmetry sites to accomodate cations of different sizes and charges. The number of members of this class has been greatly enlarged by chemical synthesis. Efforts to impose some order within the class have become both more necessary and more promising of success.

Recently, both Saxena (*1*) and Cantor (*2*) have indicated the usefulness of molar volume in providing a means for estimating the molar entropies of silicate garnets. By comparison to the known entropy of a similar compound, the entropy of an unmeasured, or unknown, compound may be calculated from the molar volume (which requires only the lattice parameter), and the addition of a magnetic term for transition metal ions, if any.

A mathematical equation relating the length of the cubic unit-cell edge for silicate garnets to the radii of the cations in the silicate was reported by Novak and Gibbs (*3*). Their equation is:

$$a_0 \text{ (in angstroms)} = 1.61[r(A)]+1.89[r(B)]+9.04, \quad (1)$$

in which $r(A)$ is the ionic radius of the cation located in the *24c*, eight-coordinate, dodecahedral sites of space group $O_h^{10}-Ia3d$; $r(B)$ is the radius of the ion in the *16a*, octahedral sites. Employing the ionic radii reported by Shannon and Prewitt (*4*), unit cell parameters reasonably close to those determined experimentally were calculated.

At about the same time, Hrichova and Feixova (*5*) presented a similar equation based upon Ahrens radii and applied to both silicates and germanates:

$$a_0(\text{Å}) = 1.286[r(A)]+1.524[r(B)] + 2.100[r(C)]+8.940. \quad (2)$$

Here, $r(C)$ represents the radius of the ion in the *24d*, tetrahedral sites.

0022-4596/79/100079-04 $02.00/0

Later, Novak and Colville (*6*) revised Eq. (1), giving:

$$a_0(\text{Å}) = 1.7[r(A)] + 1.78[r(B)] + 2.17[r(C)] + 8.44 \quad (3)$$

Equation (3) was to be applied to both natural and synthetic garnets, including nonsilicate types. Instead of basing this equation on an external set of ionic radii, the apparent design is to use this equation to generate a self-consistent set of radii which will be specific for the oxide garnets as a class.

Initially unaware of Refs. (*5*) and (*6*), and interested in the heretofore ignored class of fluoride garnets, we considered a selected group of garnets involving either oxide ions (*7–20*) or fluoride ions, or both (*21–24*) with cations in the different sites for which reports were found. We chose to base our analysis on a standard and encompassing set of radii, namely, that of Shannon (*25*).

We considered 333 compositions involving 52 elements, 58 variations of element–oxidation state, and 87 combinations of element–oxidation state–lattice site. Specifically, the species represented in the formula $A_3B_2C_3X_{12}$ are shown in Table I.

TABLE I

IONS USED FOR LATTICE PARAMETER EQUATION (FORMULA: $A_3B_2C_3X_{12}$)

A	M^+:	Li, Na, K, Ag, Tl		
	M^{2+}:	Mg, Ca, Sr, Mn, Fe, Co, Cd, Pb		
	M^{3+}:	Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, In, Bi		
	M^{4+}:	Zr, Hf		
B	M^+:	Li, Na		
	M^{2+}:	Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd		
	M^{3+}:	Sc, Y, Dy, Ho, Er, Tm, Yb, Lu, Ti, V, Cr, Mn, Fe, Co, Ni, Rh, Al, Ga, In		
	M^{4+}:	Ti, Zr, Hf, Ru, Sn		
	M^{5+}:	Nb, Ta, Sb		
	M^{6+}:	Te		
C	M^+:	Li	M^{2+}:	Co, Zn, Cd
	M^{3+}:	Fe, Al, Ga	M^{4+}:	Ti, Si, Ge, Sn
	M^{5+}:	V, Nb, As		
X	O^{2-}:	F^-		

Our analysis of the lattice parameters and compositions generated the relationship:

$$a_0(\text{Å}) = 1.750[r(A)] + 1.653[r(B)] + 1.904[r(C)] + 6.225[r(X)]. \quad (4)$$

Here, the radius of the anion, $r(X)$, is introduced for the oxide and fluoride ions; 1.38 and 1.31 Å, respectively, were used. When more than one ion occupies a particular site, the weighted average of the respective radii is used.

The coefficients of the radii in Eq. (4) were determined using multiple regression analysis. Within our desire to include the maximum number of combinations of metal/oxidation state/coordination site, with no additional selectivity, the calculated coefficient of multiple determination (R^2) is 0.974. This can be improved by eliminating five compounds which lie outside four standard deviations, giving $R^2 = 0.997$. Repeating the process by eliminating three more compounds from the surviving list gives $R^2 = 1.001$.

Of the 333 compositions, 328 lie inside four standard deviations (SD), 327 within three SD, 323 within two SD, and 271 within one SD.

We have no basis other than large deviation from Eq. (4) for eliminating any compounds from the full list, but it is clear that certain compositions and lattice parameters are called into question. These are: $Mn_3NbZnFeGe_2O_{12}$ (12.49, 12.22); $Nd_3Ho_2Ga_3O_{12}$ (12.652, 12.916); $Nd_3Dy_2Ga_3O_{12}$ (12.510, 12.934); $Ca_3Zr_{1.65}Co_{0.35}Ge_{2.35}Co_{0.65}O_{12}$ (12.625, 12.980); and $Ca_3Zr_{1.8}Zn_{0.2}Ge_{2.2}Zn_{0.8}O_{12}$ (12.64, 13.02), where the reported and calculated lattice parameters, in angstroms, respectively follow the listed compositions. Some of these deviations may trace simply to problems in precise ascertation of stoichiometry. In some other cases, there is the question of whether high-spin or low-spin radii should be used in the calculation. The best fit will suggest correct electronic states in the absence of magnetic measurements.

Discussion

In Eq. (4) the coefficient of the anion radius is by far the largest, rightly reflecting the dominance of the anion in determining unit-cell size. All of the equations present coefficients for the cationic radii which emphasize the sensitivity to the tetrahedral site occupant. The coefficients assigned respectively to the octahedral and dodecahedral sites are closer together in all the equations, but only Eq. (4) slightly emphasizes the dodecahedral compared to octahedral sites. This remains true even if we eliminate data until the $R^2 = 1.001$ level is reached.

There are several reported garnet compositions which would include ions in coordination sites for which Shannon's compilation contains no radii. Using Eq. (4) it is possible to back-calculated from the lattice parameter to obtain calculated radii for such species. Ronniger and Mill' (*19*) listed a series of compounds of general formula $CuCa_2M_2V_3O_{12}$ (M = Mg, Mn, Co, Ni, and Zn) with lattice edges of 12.425 ± 3, 12.551 ± 5, 12.423 ± 3, 12.362 ± 3, and 12.449 ± 4 Å, respectively. These lead to calculated radii for eight-coordinate Cu(I) ranging from 1.04 to 1.13 and averaging 1.09 Å. This appears to be rather large when compared with Shannon's estimated values of 0.60 and 0.77 Å, respectively, for four-coordinate and six-coordinate Cu(I).

The four-coordinate Fe(IV) ion in $Y_{2.9}Ga_{0.1}Fe_2Fe(III)_{2.9}Fe(IV)_{0.1}O_{12}$ with a lattice parameter of 12.378 Å (*7*) leads to a value of 0.48 Å for the ionic radius of Fe(IV). In Shannon's list, this may be compared with 0.63 for high-spin Fe(II), 0.49 for Fe(III), 0.39 for Mn(IV), and 0.40 for Co(IV).

Similarly, a lattice parameter of 12.518 Å for $Ca_3Sc_{1.8}Zr_{0.2}Co_{0.2}Ga_{2.8}O_{12}$ (*7*) gives an ionic radius for four-coordinate Co(III) ion of 0.37 Å. This may be compared with 0.49 for Fe(III) and 0.58 for Co(II) in four-coordinate sites.

Finally, a lattice parameter of 12.475 Å for a compound tentatively reported to have the composition $CuGd_2Mn_2Ge_3O_{12}$ (*7*) leads to an eight-coordinate radius for Cu(II) ion of 1.442 Å. This value is clearly nonsensical. Reformulation of this compound as $(Gd_2Mn)(MnCu)Ge_3O_{12}$, however, causes it to agree nicely with Eq. (4). This illustrates one of the utilities of the equation.

We have also considered the hydrogarnets, using data reported by Ito (*26,27*). Of course, these are not truly of the garnet structure, since the cation on the tetrahedral site is missing. The apparent radius of the tetrahedral vacancies in these garnets is calculated to be 0.80 Å for the strontium series and between 0.71 and 0.78 Å for the calcium compounds. These radii lead to cation site/anion radius as high as 0.575. However, protons from the hydroxide ions are very likely located, at least to some extent, in or about these tetrahedral positions.

Similar attempts to determine sizes for octahedral and dodecahedral vacancies were unsatisfactorily contradictory and tenuous, being based on very limited data. In the case of the dodecahedral holes, the calculated size depends upon the radius assigned to the tetrahedral holes which are also present in the same compositions.

It is straightforward to predict that the lanthanon metal ions should be accomodated in the octahedral sites of the fluoride garnets. We have tentatively confirmed this prediction with at least one composition and are attempting to extend this one example to a more complete series.

The use of the unit-cell equation thus provides for the estimation of hypothetical garnet compositions and cation site distributions. It tests the reasonableness of proposed garnet formulations and reported lattice parameters. Its predictive power has already been effectively used. It can suggest electronic states of cations based upon differing radii of the states.

The known garnets have lattice parameters falling between 11.459 and 13.241 Å. If these limits are really effective, they in turn place obvious restrictions on the potential occupation by cations in the various cationic sites. One can speculate as to the possibility of using larger anions, but the restrictions of observed cases to fluorides, oxides, and hydroxides probably has less to do with ionic radii than with the chemical nature, including slight polarizability, of these anions.

Acknowledgments

We are pleased to acknowledge the assistance of Dr. Don Knittel and Mr. Thomas L. Groy in the analysis of our data. The support of the University of Nebraska Research Council is also gratefully noted.

References

1. S. K. Saxena, *Science* **193**, 1241–1243 (1976).
2. S. Cantor, *Science* **198**, 206–207 (1977).
3. G. A. Novak and G. V. Gibbs, *Amer. Mineral.* **56**, 791–825 (1971).
4. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B* **25**, 925–926 (1969).
5. R. Hrichova and J. Feixova, *Sb. Vys. Sk. Chem. Technol. Praze Mineral* **13**, 29–50 (1971); *Chem. Abstr.* **76**, 18879x (1972).
6. G. A. Novak and A. A. Colville. *in* "Abstr. Cordilleran Sect., Southwest Geol. Soc: Amer. Annu. Presentations, 1975"
7. S. Geller, *Z. Kristallogr.* **125**, 1–47 (1967).
8. L. Suchow, M. Kokta, and V. Flynn, *J. Solid State Chem.* **2**, 137–143 (1970).
9. L. Suchow and M. Kokta, *J. Solid State Chem.* **5**, 85–92 (1972).
10. L. Suchow and M. Kokta, *J. Solid State Chem.* **5**, 329–333 (1972).
11. M. Kokta and M. Grasso, *J. Solid State Chem.* **8**, 357–359 (1973).
12. D. Reinen, *Struct. Bonding (Berlin)* **7**, 114–184 (1970).
13. W. White and V. Keramides, *J. Amer. Ceram. Soc.* **54**, 472–473 (1971).
14. H. Nishizawa and M. Kuizumi, *Amer. Mineral.* **60**, 84–87 (1975).
15. S. Naka, Y. Suwa and S. Ito, *Kogyo Kagaka Zasshi*, **72**, 1480–1483 (1969).
16. G. Ronniger and B. Mill', *Kristallografiya* **16**, 1035–1036 (1971).
17. B. Mill' and G. Ronniger, *Kristallografiya* **18** 126–132 (1973).
18. G. Ronniger and B. Mill', *Kristallografiya* **18**, 303–307 (1973).
19. G. Ronniger and B. Mill', *Kristallografiya* **18**, 539–543 (1973).
20. J. Chassaing, *Rev. Chim. Miner.* **5**, 1115–1154 (1968).
21. R. J. de Pape, J. Portier, G. Gauther, and P. Hagenmuller, *C. R. Acad. Sci.* **265**, 1244–1246 (1967).
22. R. J. de Pape. J. Portier, J. Grannec, and P. Hagenmuller, *C. R. Acad. Sci.* **269**, 1120–1122 (1967).
23. A. Morell, B. Tanguy, J. Portier, and P. Hagenmuller, *J. Fluorine Chem.* **3**, 351–359 (1973/4).
24. R. Langley, Ph. D. dissertation, University of Nebraska, Lincoln (1977).
25. R. Shannon, *Acta Crystallogr. Sect. A* **32**, 751–767 (1976).
26. J. Ito and C. Frondel, *Amer. Mineral.* **52**, 1105–1109 (1967).
27. J. Ito, *Amer. Mineral.* **53**, 1663–1673 (1968).