

# A Rietveld Refinement of NaCl-type $\text{Ca}_5\text{Y}_4\text{S}_{11}$

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The crystal structure of  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  [ $a = 6.942(1)$  Å,  $\alpha = 33.380(5)^\circ$ , space group  $R3m$ , No. 166,  $Z = \frac{1}{2}$ ,  $D_x = 3.042$  g  $\text{cm}^{-3}$ ] was determined using Rietveld refinement of X-ray powder diffraction data collected with  $\text{CuK}\alpha_1$  radiation using a Guinier–Hägg camera.  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  is one end-member composition ( $x = \frac{2}{3}$ ) of the solid-solution  $(1-x)\text{CaS} \cdot x\text{Y}_2\text{S}_3$ , which can be considered as a modulated NaCl-type structure with modulation wave-vector  $\mathbf{q} = \frac{1}{2}(111)^*$ . The sulfur sublattice is fully occupied but the metal sublattice contains  $\frac{1}{3}$  vacancies on average. The refinement showed that the additional observed satellite reflections were almost entirely due to metal atom/vacancy ordering rather than sulfur atom displacement. Large anisotropic thermal parameters on both the sulfur and metal atoms were consistent with disordered displacement of these atoms by 0.2–0.4 Å normal to [111]. The chemical plausibility of the refined structure and the implication of this result for other substoichiometric NaCl-type solid solutions are discussed. © 1995 Academic Press, Inc.

## INTRODUCTION

$\text{Ca}_5\text{Y}_4\text{S}_{11}$  is one end-member composition ( $x = \frac{2}{3}$ ) of the solid-solution  $(1-x)\text{CaS} \cdot x\text{Y}_2\text{S}_3$  which is known to have, on average, the NaCl (B1) structure type (1–3). As discussed in our recent TEM study of the  $x = \frac{2}{3}$  member (4), this solid-solution is representative of the large family of substoichiometric solid solutions with this structure type, which includes early transition metal sulfides and selenides, calcium lanthanide sulfides and selenides, and transition metal carbides and nitrides (see references cited in Ref. (4)). In general, compositional and/or vacancy ordering in these phases leads to formation of superstructures of the NaCl type, and in some cases the observation of spectacular diffuse intensity distributions is indicative of short-range order even when long-range order, *i.e.*, a superstructure, is not observed. However, the chemical

driving force of this ordering, either short- or long-range, is not well understood.

In the solid solution which forms the subject of the present study, namely  $(1-x)\text{CaS} \cdot x\text{Y}_2\text{S}_3$ , the sulfur sublattice sites are fully occupied but, apart from the end-member, CaS, the metal sublattice necessarily contains vacant sites. For  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  the NaCl-type parent structure ( $Fm3m$ ,  $a \approx 5.66$  Å) distorts to give a  $2 \times$  superstructure with rhombohedral symmetry ( $R3m$ ,  $a = 6.942(1)$  Å,  $\alpha = 33.380(5)^\circ$ ).

In our earlier work (4) we preferred to describe  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  in terms of an  $Fm3m$  NaCl-type parent structure modulated by a single  $\mathbf{q} = \frac{1}{2}[111]^*$  modulation. One of the advantages of such a modulation wave description is that it more readily defines the structural degrees of freedom. Assuming that the modulation was driven by cation vacancy ordering and that the structural relaxation was associated with that ordering, it was shown that there were only two additional degrees of freedom. The first,  $\delta f_M$ , allows neighboring (111) metal atom planes to alternate in average occupancy between  $(f_M + \delta f_M)$  to  $(f_M - \delta f_M)$ , where  $f_M = \frac{1}{11}(5f_{\text{Ca}} + 4f_{\text{Y}})$ . The second is an associated [111] shift of the (111) planes of S atoms (see Fig. 6 of (4)).

The object of the present study has been to model the structure of  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  by refinement using X-ray powder diffraction (XRD) data leading to an understanding of the crystal chemical driving force for the formation of such substoichiometric NaCl-type solid solutions.

## EXPERIMENTAL

The synthesis of the  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  specimen used in this study is described elsewhere (4).

XRD data were collected using a Guinier–Hägg camera with  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.5406$  Å). Numerical intensities were obtained by measuring the Guinier–Hägg film with a densitometer with a nominal resolution of  $0.02^\circ\theta$ .

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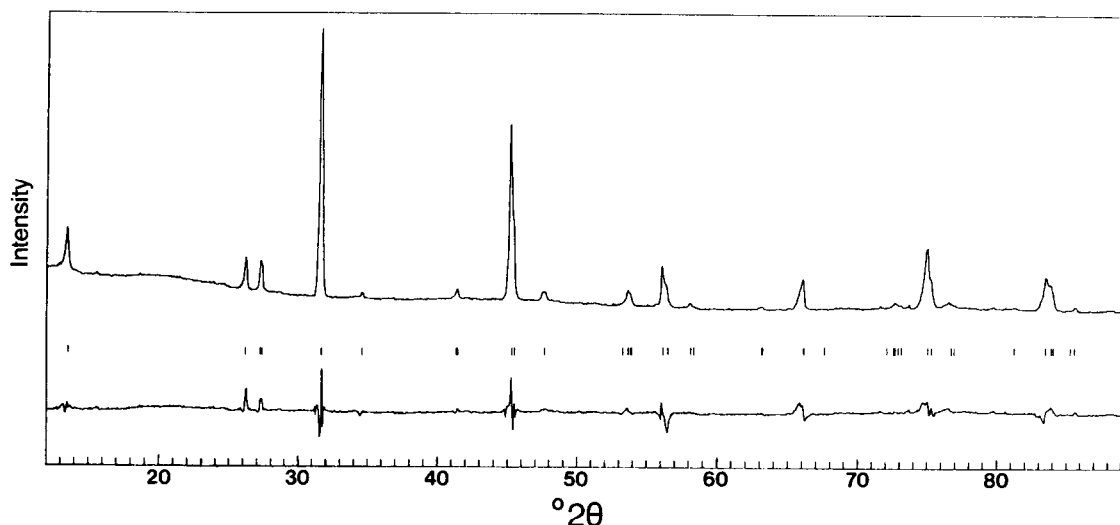


FIG. 1. XRD data ( $\lambda = 1.5406 \text{ \AA}$ ) for  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  showing the observed profile and the difference profiles ( $I_{\text{obs}} - I_{\text{calc}}$ ) together with reflection markers. The final refinement statistics were  $R_p = 7.8\%$ ,  $R_{\text{wp}} = 10.6\%$ , and  $R_{\text{Bragg}} = 4.5\%$ .

In practice the resolution of the densitometer trace was significantly reduced compared with the original film such that the rhombohedral splitting of parent structure lines was easily observed at low angle on the film but is only observable at high angle in the densitometer trace (see Fig. 1).

Data were corrected for the geometric factor associated with use of a Guinier-Hägg camera ( $G = 1/\cos(2\theta - \phi)$ , where  $\phi = 30^\circ$ ) (5) prior to refinement. Refinement was performed using the program DBW3.2 (6).

## RESULTS AND DISCUSSION

Refinement was performed using the Rietveld method for all data from  $12.7^\circ$  to  $90.2^\circ$   $2\theta$ . The non-atomic variables refined were zero correction, scale factor, pseudo-Voigt peak profile and width as a function of  $2\theta$ , a peak asymmetry parameter, and unit cell parameters. The profile background was interpolated between 11 points across the  $2\theta$  range.

The starting model for refinement of  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  placed a statistical distribution of Ca and Y on each of the two inequivalent metal sites with all the vacancies located on one of the two inequivalent sites. It was necessary to assume that all the vacancies were located in alternate metal layers as it is not possible to refine both the vacancy distribution and the Ca/Y ordering. As it is generally accepted that the modulation in such NaCl-type superstructures is driven by cation vacancy ordering, this assumption seemed chemically reasonable. Comparative refinement of various Ca/Y ordering schemes, some of which are listed in Table 1, indicated that there was some preference for Y over Ca on the fully occupied metal site.

A refinement minimum was achieved with 59% Y and 41% Ca on the fully occupied site and 14% Y, 50% Ca, and 36% vacancies on the partially occupied site. To check for uniqueness of the refinement minimum the sulfur atom was displaced to either side of the parent position.

During initial refinement cycles using independent isotropic thermal parameters it became clear that the sulfur atom displacement was relatively small. The refined positional parameters for the model using isotropic thermal parameters are given in Table 2.

TABLE 1  
Refinement Statistics for Various Models<sup>a,b</sup>

	$R_p(\%)$	$R_{\text{wp}}(\%)$	$R_{\text{Bragg}}(\%)$
Isotropic atom model			
Statistical Ca/Y distribution	9.6	12.9	5.0
Intermediate <sup>c</sup>	9.2	12.4	4.8
All Y on 3a site	9.3	12.8	6.5
Anisotropic atom models			
Statistical Ca/Y distribution	8.4	11.1	5.5
Intermediate <sup>c</sup>	7.9	10.5	4.7
All Y on 3a site	8.4	11.0	5.8
Disordered atom models			
Statistical Ca/Y distribution	8.4	11.3	5.0
Intermediate <sup>c</sup>	7.8	10.6	4.5
All Y on 3a site	8.3	11.0	5.2

Note:  $R_p = 100\sum|y_i - y_{ci}|/\sum|y_i|$ .  $R_{\text{wp}} = 100\sum w(y_i - y_{ci})^2/\sum w y_i^2$ .  $R_{\text{Bragg}} = 100\sum|I - I_c|/\sum I$ .

<sup>a</sup> All models locate  $\frac{4}{3}$  vacancies on the 3b site.

<sup>b</sup> Site symbols correspond to the hexagonal setting of  $R3m$ , No. 161 (refer to "International Tables for Crystallography," Vol. A).

<sup>c</sup> Site occupancies intermediate between statistical Ca/Y distribution and having all Y on the 3a site.

TABLE 2  
Refined Atomic Parameters<sup>a</sup>

Site	Multiplicity	$x/a$	$y/b$	$z/c$	$B$	Occupancy
Isotropic atom model						
M1	3a	0	0	0	0.4(1)	$\frac{1}{3}$ Ca $\frac{2}{3}$ Y
M2	3b	0	0	$\frac{1}{2}$	-0.5(1)	$\frac{1}{3}$ Ca $\frac{2}{3}$ Y
S	6c	0	0	0.252(1)	1.1(2)	1
Anisotropic atom model						
M1	3a	0	0	0	—	$\frac{1}{3}$ Ca $\frac{2}{3}$ Y
M2	3b	0	0	$\frac{1}{2}$	—	$\frac{1}{3}$ Ca $\frac{2}{3}$ Y
S	6c	0	0	0.253(1)	—	1
Site	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
M1	0.045(10)	0.045(10)	-0.001(1)	0.022(5)	—	—
M2	0.070(17)	0.070(17)	-0.004(1)	0.035(8)	—	—
S	0.101(13)	0.101(13)	-0.002(0)	0.051(6)	—	—
Disordered atom model						
Site	Multiplicity	$x/a$	$y/b$	$z/c$	$B$	Occupancy
M1	18f	0.075(7)	0	0	-2.3(6)	$\frac{1}{18}$ Ca $\frac{17}{18}$ Y
M2	18g	0.106(6)	0	$\frac{1}{2}$	-6.0(8)	$\frac{1}{18}$ Ca $\frac{17}{18}$ Y
S	18h	0.054(3)	-0.054(3)	0.252(1)	-3.1(5)	$\frac{1}{18}$ Ca $\frac{17}{18}$ Y

<sup>a</sup> Hexagonal setting, origin at center.  $a = 3.987(1)$ ,  $c = 19.651(5)$  Å.  
Intermediate Ca/Y distribution (see Table 1).

Using anisotropic thermal parameters the refinement improved;  $R_p$  dropped from 9.2 to 7.9%,  $R_{wp}$  dropped from 12.4 to 10.5%, and  $R_{Bragg}$  from 4.8 to 4.7%. The two metal atom sites and the sulfur atom showed highly anisotropic displacement normal to [111], that is, in the (111) atom planes. The fully occupied metal atom site showed the least displacement. Again comparative refinement of alternative Ca/Y ordering schemes was tested but the "intermediate" distribution still gave the best result (see Table 1). The refined model using the intermediate Ca/Y distribution on the two metal atom sites is listed in Table 2.

As large thermal motion in such a structure is improbable it was concluded that the large anisotropic thermal parameters were simply serving to model a disordered atomic distribution. The magnitudes of the  $\beta_{11}$  components implied a displacement of atoms of 0.2–0.4 Å from their average positions normal to [111]. The small negative values for the  $\beta_{33}$  components of the anisotropic thermal parameters is further symptomatic of inadequate modeling of the electron density by single atoms. Local displacements from average positions would be expected for such

a substoichiometric structure to allow for minimization of nonbonded interactions and to satisfy the bonding requirements of individual atoms.

It was decided to use a split atom model in which fractional isotropic atoms were displaced from their average positions normal to [111]. While this split isotropic atom model used the same number of variables as before, the refinement improved slightly.  $R_p$  dropped to 7.8%,  $R_{wp}$  increased to 10.6%, and  $R_{Bragg}$  dropped to 4.5% (see Table 1). The final refined split atom model with intermediate Ca/Y distribution is listed in Table 2. Figure 1 shows the observed XRD profile and the difference profile following the final cycle. It is evident from inspection of the difference plot that the peak profile is imperfectly modeled, but that the refined model provides a reasonable fit to the data using only seven atom-based variables out of a total of 17 free variables.

Unlike for the structural model using anisotropic thermal parameters the mean atomic displacements obtained from the split atom model will not be affected by absorption. There is a direct correlation between absorption and thermal parameters because their functional dependence

upon  $2\theta$  is very similar in the present case. The negative isotropic thermal parameters observed for the isotropic atom and split atoms models (Table 2) suggested that there was a problem with absorption. Absorption effects on intensity measurements would be expected for our data ( $\text{Ca}_5\text{Y}_4\text{S}_{11}$  has a linear absorption coefficient of  $362.5 \text{ cm}^{-1}$  for  $\text{CuK}\alpha_1$  (7)), but they could not easily be modeled. Therefore, although the isotropic thermal parameters derived from the split atom model may be unreliable the mean displacement of atoms from their average positions given by this model are quite reliable. However, as data were only collected to  $\sim 90^\circ 2\theta$  ( $\sin \theta/\lambda \approx 0.46$ ) it would not be possible to distinguish the six fractionally-occupied isotropic atoms from an annulus of electron density of the same radius.

The strong diffuse intensity distribution observed by electron diffraction (4) for  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  implies that the above structure refinement is only half of the story. The intensity and sharpness of the non-Bragg features implies that there is significant correlation of the vacancy distribution and associated atomic displacements. The refined model based on the Bragg reflections suggests that the major component of these atomic displacements is normal to [111]. To obtain further information about the local chemical environment of Ca, Y, and S atoms beyond what the present refinement has provided would require complete modeling of the diffuse intensity as well as the Bragg reflections.

Bond-valence sums (8, 9), or apparent valences (AVs), were calculated for atoms in the  $Fm\bar{3}m$  parent structure where each metal atom is surrounded by six sulfur atoms and each sulfur atom is surrounded by four, five, or six metal atoms depending on the location of metal site vacancies (see Table 3). The composition  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  requires that the average coordination environment for S atoms is 4.9. The AVs presented in Table 3 for the parent structure suggest that the bonding requirement of S is best satisfied by 5 coordination and that Ca and Y are slightly overbonded and significantly underbonded, respectively. The 5-coordinate environment predicted for this system is in agreement with the 5-coordinate environment for the transition metal ions in metalloid-deficient transition metal carbides, as derived from Monte Carlo simulation of the observed diffuse intensity distribution in these latter systems (9, 10).

Similar AV calculations for the refined anisotropic atom model, which does not allow for the  $0.2\text{--}0.4 \text{ \AA}$  displacements normal to  $[001]_{\text{hexagonal}}$  of atoms from their mean positions, show that the chemical environments of the two metal sites are now resolved due to the small S atom displacement. Without taking into account the  $0.2\text{--}0.4 \text{ \AA}$  displacements normal to  $[001]_{\text{hexagonal}}$  it is clear that Y would prefer to occupy the  $3a$  site while Ca would prefer

TABLE 3  
Bond Valence Sums for Parent and Refined  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  Structures

Atom	Coordination			
	4	5	6	Expected
Parent Structure, $Fm\bar{3}m$ , $a \approx 5.66 \text{ \AA}$				
S (all Ca)	1.43	1.79	2.15	2.0
S (all Y)	1.55	1.94	2.33	2.0
S (statistical distribution)	1.48	1.85	2.23	2.0
Ca			2.15	2.0
Y			2.33	3.0
Refined structure, $R\bar{3}m$ , $a = 6.942(1) \text{ \AA}$ , $\alpha = 33.380(5)^\circ$				
S ("intermediate" distribution)	1.44–1.59	1.86–1.94	2.28	2.0
Ca ( $3a$ site)			2.39	2.0
Y ( $3a$ site)			2.59	3.0
Ca ( $3b$ site)			1.98	2.0
Y ( $3b$ site)			2.15	3.0

Note:  $R_0(\text{Ca-S}) = 2.45 \text{ \AA}$ ,  $R_0(\text{Y-S}) = 2.48 \text{ \AA}$  (Brese and O'Keeffe, 1991).

the  $3b$  site. This is in agreement with the partitioning of Y and Ca obtained from the comparative refinements of metal site occupancy.

Using AV calculations it is possible to place chemical constraints on the local atomic displacements. If a Ca–S or an Y–S bond length were to shrink by  $0.2 \text{ \AA}$ , the corresponding bond valence would increase by  $\sim 0.27$  valence units. Given that sulfur is only slightly underbonded in a 5-coordinate parent structure environment (see Table 3) it follows that the average distance to the five metal atoms surrounding any particular sulfur atom must remain approximately unchanged.

On the other hand each metal atom is coordinated by six sulfur atoms. Given that in the parent structure Ca is slightly overbonded and Y is significantly underbonded, Ca–S bond lengths would tend to increase by  $0.03 \text{ \AA}$  on average, whereas Y–S bond lengths would need to decrease on average by  $0.1 \text{ \AA}$ . However, given the bonding requirements of the sulfur this would suggest that each sulfur atom would prefer to be coordinated by an approximately equal mixture of the two metal atoms, that is, either three Ca and two Y atoms, or two Ca and three Y atoms. In general, this coordination environment is generated by the  $\mathbf{q} = \frac{1}{2}\{111\}^*$  compositional modulation responsible for the observed superstructure. (See Fig. 2.)

The importance of this refinement is that it suggests that local bonding requirements of the constituent atoms play a major role, not only in the short-range ordering but also in the formation of the superstructure itself. This principle may well be applicable to other substoichiome-

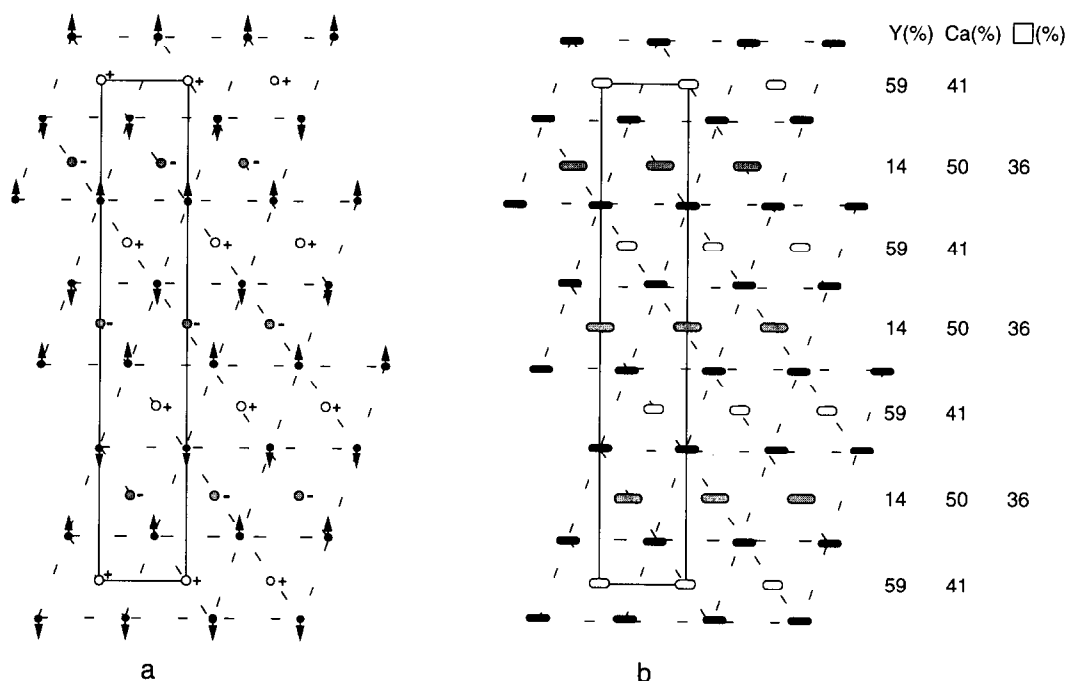


FIG. 2. (a) A  $[100]_{\text{hexagonal}}$  projection of  $\text{Ca}_5\text{Y}_4\text{S}_{11}$  showing the allowed degrees of freedom associated with the  $\mathbf{q} = \frac{1}{2}(111)^*$  modulation of the parent NaCl-type. (b) The refined split atom model showing the magnitude of the displacements of the metal and sulfur atoms to scale. The atoms are represented schematically as annuli of electron density of radius equal to the refined displacements normal to  $[100]_{\text{hexagonal}}$  for the split atom model.

tric NaCl-type solid solutions, particularly those observed in ternary systems.

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