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# The Structure of $Ca_{0.3}Sr_{0.7}Cl_2$ and $Ca_{0.46}Sr_{0.54}Cl_2$ by the X-Ray Rietveld Refinement Procedure

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The structures of tetragonal $Ca_{0.3}Sr_{0.7}Cl_2$ and orthorhombic $Ca_{0.46}Sr_{0.54}Cl_2$ were determined from X-ray powder diffraction data by the Reitveld line-profile fitting procedure. The tetragonal phase crystallizes in space group $P4/n$ ($SrBr_2$-type structure) with $a = 10.898(2)$ and $c = 6.744(2)$ Å. The cations are distributed randomly over the 8g and 2c sites. For this structure $R_f = 0.095$ and $R_{wp} = 0.168$. The orthorhombic phase crystallizes in space group $Pbca$ ($SrI_2$-type structure) with $a = 13.421(5)$, $b = 7.053(3)$, and $c = 6.817(2)$ Å. The $R_f$ and $R_{wp}$ factors are 0.081 and 0.164, respectively. Interatomic distances for both phases are reported and compared with those of related structures. The $CaCl_2$–$SrCl_2$ system is found to exhibit in the 0–25 mole% region the $CaCl_2$- and $\alpha$-$PbO_2$-type structures rather than the $CaCl_2$- and $SrI_2$-type structures reported previously.

## Introduction

A recent investigation of the $CaCl_2$-$MCl_2$ ($M$ = Sr, Eu) systems indicated in the region 65–80 mole% $SrCl_2$ and 65–85 mole% $EuCl_2$ a phase different from the parent structures and from either their metastable or high pressure modifications (*1*). The tetragonal lattice parameters indicated the phase to be of the $SrBr_2$-type. X-Ray powder diffraction intensities calculated with the program POWD12 (*2*) with positional parameters reported for $SrBr_2$ supported the correctness of this model (*3*). Agreement between the observed and calculated intensities suggested that the cations were randomly distributed over the two cation sites. However, in view of the anion ordering observed in related mixed-anion divalent cation systems, it seemed desirable to verify this hypothesis with a complete structural study.

A different phase with lattice parameters suggestive of the $SrI_2$-type structure was observed in both systems in the range 45–60 mole% $MCl_2$. The high-pressure modification of $CaCl_2$ also exhibits the $SrI_2$-type structure (*4*). Precise positional parameter data for neither the high-pressure modification of $CaCl_2$ nor the related mixed-anion phases which exhibit this structure type have been reported. It thus seemed desirable to also investigate this phase. When single crystals of a suitable size could not be grown, a Rietveld X-ray line profile examination was undertaken.

## Experimental

Anhydrous $CaCl_2$ (Mallinckrodt, St. Louis, MO) and $SrCl_2$ (AESAR, Johnson

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Matthey, Inc., Seabrook, NH) reactants were melted in vacuum prior to use. Purity was verified by X-ray powder diffraction analysis as described previously (*1*). All sample manipulations were effected in an argon-filled glove box whose recirculated atmosphere was purged of both water (molecular sieves) and oxygen (BASF catalyst).

Specimens were prepared by grinding stoichiometric quantities of the reactants in an agate mortar. The mixture was transferred to previously outgassed quartz tubes, blanketed with argon to atmospheric pressure, melted with a hand torch, and quenched. The pulverized product was mixed with NBS certified Si [$a$ = 5.43082(3) Å] and examined by the Guinier X-ray diffraction technique. Lattice parameters were determined with the program APPLEMAN (*5*).

Intensity data were collected with a Philips APD 3720 diffractometer system equipped with a sample spinner and $\theta$-compensating slit. The moisture-sensitive sample was covered initially with 0.009 mm Al foil and subsequently with a layer of paraffin oil to inhibit hydration during the long diffractometer measurement period. In addition, nitrogen dried by passage through a liquid $N_2$-trap was flowed through the sample chamber. Diffraction patterns obtained both before and after the measurement were identical, an indication of the absence of hydration during data collection. Details relevant to both data collection and the crystals are presented in Table I. Refinement was effected with the XRS82 system (*6*) on a VAX 11/750 computer.

The 0–55 mole% region of the $CaCl_2$–$SrCl_2$ system was reinvestigated by the Guinier X-ray powder diffraction technique. The procedures utilized have been described (*1*).

TABLE I

CRYSTALLOGRAPHIC AND RIETVELD REFINEMENT DATA FOR $Ca_{0.3}Sr_{0.7}Cl_2$ AND $Ca_{0.46}Sr_{0.54}Cl_2$

| | $Ca_{0.3}Sr_{0.7}Cl_2$ | $Ca_{0.46}Sr_{0.54}Cl_2$ |
|---|---|---|
| $2\theta$ range (°) | 10–80 | 10–65 |
| Step scan increment, $2\theta$ (°) | 0.02 | 0.02 |
| Count time (sec/step) | 15 | 15 |
| Standard peak; *hkl*, $2\theta$ | 121(211), 22.47 | 211, 22.40 |
| R for standard peak (%) | 2.2 | 2.6 |
| Space group | *P*4/*n* | *Pbca* |
| $a$ (Å) | 10.898(2) | 13.421(5) |
| $b$ (Å) | | 7.053(3) |
| $c$ (Å) | 6.744(2) | 6.817(2) |
| Number of observations | 3223 | 2477 |
| Number of structural parameters refined | 19 | 15 |
| Number of reflections | 237 | 103 |
| Number of profile parameters | 8 | 9 |
| $R_f = \Sigma\|F_o - F_c\|/\Sigma F_o$ | 0.095 | 0.081 |
| $R_i = \Sigma\|F_o^2 - F_c^2\|/\Sigma F_o^2$ | 0.136 | 0.110 |
| $R_{wp} = \{\Sigma w_i[y_i(0) - y_i(c)/c]^2/\Sigma w_i y_i(0)^2\}^{1/2}$ | 0.168 | 0.164 |
| $R_{exp}$ | 0.134 | 0.139 |
| Preferred-orientation vector and factor | 001, 0.67(3) | 010, 0.14(4) |
| Max shift/error | 0.003 | 0.08 |

## Structure Refinement

The Cu*Kα* component was stripped with the APD software which uses the procedure described in (*7*). The diffractometer data were also tested with this APD software for systematic errors, i.e., slight misalignment or displacement of the sample surface from the $\theta$-shaft axis, and coefficients determined by least-squares were applied by the program STEPCO (*6*) to the observed data. *D* values derived from the Guinier data were used as a reference pattern in this systematic error correction procedure. The measured intensity data were multiplied by the factor, $1/\sin\theta$ to correct for the $\theta$-compensating slit (*8*). A correction was also applied for beam absorption by the protective Al foil. If an Al layer with thickness "*t*" is situated parallel to the sample surface, then at any given Bragg angle, $\theta$, the diffracted beam is attenuated by $\exp[-2m_it/\sin\theta]$. In this equation $m_i$ is the Al linear absorption coefficient and the factor "2" reflects the fact that both entrance and exit beams pass through the foil.

The scale factor was refined initially, followed by the scale factor and cell parameters, then the scale and profile parameters. In succeeding steps positional parameters were included with an overall temperature factor. Finally, individual isotropic temperature factors were refined together with positional and profile parameters.

### $Ca_{0.3}Sr_{0.7}Cl_2$

Al foil served as the protective agent for the first data set. The $SrBr_2$ atomic parameters provided the structural model. Since in the $SrBr_2$ structure there are two cation positions, 8g and 2c, three cation distribution models were considered in subsequent calculations:

(a) cations distributed randomly,
(b) all Ca atoms in the 8g position, and
(c) Ca atoms completely occupying the 2c and part of the 8g positions.

The *R* factors for the model designated (c) were significantly larger than those for the other models, so this possibility was dismissed. Refinement of models (a) and (b) gave essentially identical discrepancy factors; neither model yielded superior positional or thermal parameter e.s.d.'s. Since preferred orientation and Al foil absorption effects could mask small differences, reflection intensities, which according to intensity calculations for both models should differ appreciably, were compared with the diffractometer and Guinier data. To facilitate this comparison a factor $R_m$, defined as

$$R_m = \Sigma_i|Io_i - Ir_i|/\Sigma_i(0.5)(Io_i + Ir_i), \quad (1)$$

was calculated. In Eq. (1) $Io_i$ and $Ir_i$ represent, respectively, the intensity calculated for the "*i*" reflection for the ordered and random models. By calculating $R_m$ for different $2\theta$ intervals, the angular range in which the greatest difference occurs between the models was identified: 10–22° $2\theta$. Comparison of observed intensities with those calculated for the two models suggested the random model to be correct. However, because of absorption by the Al foil, the signal/noise ratio in the critical 10–22° region was low (only weak and very weak reflections were present).

To confirm that the random model (a) was indeed the correct one, another data set was collected with a protective coating of paraffin oil rather than Al foil. These data yielded upon refinement all *R* parameter values for the random model smaller than those for the ordered model. In addition, a rather high-temperature factor for the Sr atom in position 2c in ordered model (b) suggested excessive electron density in that position and further called this model into question. According to the Hamilton test method (*9*), the hypothesis of cation ordering could be rejected at the 0.005 confidence level. ($R_{wp}$ for random and ordered models were 0.168 and 0.172; ordering was considered a one-dimensional hypothesis;

2637 observations.) No pronounced electron density maximum was found in the difference Fourier map in any position. During refinement composition was included as a variable, but was fixed at the mixed composition when it became apparent that refinement was converging to the mixed stoichiometry.

### *$Ca_{0.46}Sr_{0.54}Cl_2$*

Paraffin oil served as the protective agent for this sample. Positional parameters for $SrI_2$ (*10*) provided the structural model. In the final stages of refinement composition was allowed to vary. Because occupancy and thermal parameters were strongly correlated, they were refined in alternate cycles. According to the Hamilton test method (*9*), the stoichiometry refinement results can be accepted at the 0.005 confidence level ($R_{wp}$ ratio, 1.006; one-dimensional hypothesis, 2474 observations).

A vacancy model in which the occupancy of Cl-1 (the anion which exhibits the higher temperature factor) and the cation were simultaneously reduced from 1.00 to 0.85 in steps of ~0.025, while stoichiometry was maintained, was also tested.

## Results

Atomic positional parameters and $R$ values for both structures are presented in Tables I and II. Average bond distances for $Ca_{0.3}Sr_{0.7}Cl_2$ are compared with those of $SrBr_2$ in Table IIIA; average bond distances for $Ca_{0.46}Sr_{0.54}Cl_2$ are compared with those for $YbCl_2$ in Table IIIB. The observed, calculated, and difference patterns for both structures are presented in Figs. 1A and 1B, respectively.

Pure $CaCl_2$ could be prepared in the pseudo-rutile ($CaCl_2$-type) structure only with difficulty by heating the diphasic mixture in pyrolytic graphite boats at 750°C in an Ar atmosphere and subsequently cooling it moderately slowly. This observation is consistent with those of Anselment (*11*).

The $CaCl_2$–$SrCl_2$ system is reinterpreted as follows: From 0 to ~25 mole% $SrCl_2$ the pseudo-rutile ($CaCl_2$)- and the $\alpha$-$PbO_2$-type structures are present. While solid solution was readily apparent over this region in the X-ray reflections assignable to the $CaCl_2$-type structure, the $2\theta$ positions of the very few reflections attributable to the $\alpha$-$PbO_2$ structure remained invariant. The intensity of these latter reflections slowly faded such that none could be observed beyond the 25 mole% composition. From 25 to 45 mole% $SrCl_2$, a two-phase region with $SrI_2$- and $CaCl_2$-type structures prevailed; and from 45 to 60 mole% $SrCl_2$, $SrI_2$-type solid solution was observed. X-ray powder diffraction photographs of the $CaCl_2$–$EuCl_2$ system over the 0 to 45 mole% $EuCl_2$ region were also reexamined (*1*). The behavior of this system is identical to that of the $CaCl_2$–$SrCl_2$ system, with the same phases observed over similar composition limits. The remainder of the systems is as described previously (*1*).

TABLE II

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR $Ca_{0.3}Sr_{0.7}Cl_2$ AND $Ca_{0.46}Sr_{0.54}Cl_2$

| Atom | *x* | *y* | *z* | *U* | PP |
|---|---|---|---|---|---|
| | | (A) $Ca_{0.3}Sr_{0.7}Cl_2$ [origin at $\bar{4}$] | | | |
| Sr-1 | −0.142(1) | 0.831(1) | 0.252(3) | 0.025(3) | 0.7 |
| Sr-2 | 0 | 0.5000 | 0.841(4) | 0.023(8) | 0.7 |
| Ca-1 | −0.142(1) | 0.831(1) | 0.252(3) | 0.025(3) | 0.3 |
| Ca-2 | 0 | 0.5000 | 0.841(4) | 0.023(8) | 1.0 |
| Cl-1 | −0.096(6) | 0.714(4) | 0.630(5) | 0.06(2) | 1.0 |
| Cl-2 | 0.099(5) | 0.707(4) | 0.098(4) | 0.04(1) | 1.0 |
| Cl-3 | 0 | 0 | 0 | 0.02(2) | 1.0 |
| Cl-4 | 0 | 0 | 0.5000 | 0.04(2) | 1.0 |
| | | (B) $Ca_{0.46}Sr_{0.54}Cl_2$ | | | |
| Sr-1 | 0.1105(9) | 0.463(2) | 0.270(3) | 0.023(5) | 0.54(1) |
| Ca-1 | 0.1105(9) | 0.463(2) | 0.270(3) | 0.023(5) | 0.46(1) |
| Cl-1 | 0.216(3) | 0.114(5) | 0.141(5) | 0.06(1) | 1.0 |
| Cl-2 | −0.031(2) | 0.251(9) | −0.024(6) | 0.02(1) | 1.0 |

*Note*. PP is the population parameter. The temperature factor has the form $\exp(-T)$ where $T = 8\pi^2U(\sin\theta/\lambda)^2$ for isotropic atoms. The e.s.d. of the last significant digit is given in parentheses.

TABLE III

COMPARISON OF COORDINATION POLYHEDRA

| Atom | Coord. number and atom | Average bond distance (Å) | Atom | Coord. number and atom | Average bond distance (Å) |
|---|---|---|---|---|---|
| | | (A) $Ca_{0.3}Sr_{0.7}Cl_2$ vs $SrBr_2$ | | | |
| Sr(Ca)-1 | 7 × Cl | 2.96(4) | Sr-1 | 7 × Br | 3.156(7) |
| Sr(Ca)-2 | 4 × Cl-1 | 2.93(5) | Sr-2 | 4 × Br-1 | 3.115(8) |
| | 4 × Cl-2 | 3.05(4) | | 4 × Br-2 | 3.165(7) |
| Cl-1 | 3 × Sr(Ca) | 2.94(5) | Br-1 | 3 × Sr | 3.156(8) |
| Cl-2 | 4 × Sr(Ca) | 3.00(5) | Br-2 | 4 × Sr | 3.182(7) |
| Cl-3 | 4 × Sr(Ca) | 2.95(1) | Br-3 | 4 × Sr | 3.106(5) |
| Cl-4 | 4 × Sr(Ca) | 2.93(1) | Br-4 | 4 × Sr | 3.126(5) |
| | | (B) $Ca_{0.46}Sr_{0.54}Cl_2$ vs $YbCl_2$ | | | |
| Ca(Sr) | 3 × Cl-1 | 2.88(3) | Yb | 3 × Cl-1 | 2.802(5) |
| | 4 × Cl-2 | 2.91(5) | | 4 × Cl-2 | 2.874(4) |
| Cl-1 | 3 × Ca | 2.88(3) | Cl-1 | 3 × Yb | 2.802(5) |
| Cl-2 | 4 × Ca | 2.91(5) | Cl-2 | 4 × Yb | 2.874(4) |

## Discussion

### *General System Behavior*

Three $CaCl_2$ polymorphic modifications have been characterized (*11*). Two of these ($\alpha$-$PbO_2$ and $CaCl_2$) normally coexist when pure $CaCl_2$ is melted and subsequently quenched; the third with the $SrI_2$-type structure has been observed only in high-pressure experiments (*4*, *12*). The structures of the two former modifications are well known. In both structures cation coordination is octahedral while anion coordination is triangular. Interatomic distances in the coordination polyhedra are also similar. The volume per cation values in the pseudo-rutile and "$PbO_2$" modifications are 84.00 and 82.76 Å$^3$, respectively.

X-Ray powder diffraction studies of the $CaCl_2$–$SrCl_2$ system indicate that with increasing Sr content the $\alpha$-$PbO_2$ modification disappears first. The invariance of the observed $\alpha$-$PbO_2$ reflections in a solid solution region of $CaCl_2$-type structure is at first glance disconcerting. However, when along with this observation the unit cell volumes and the difficulty of preparing pure $CaCl_2$ in the pseudo-rutile form are considered, a reasonable explanation can be developed. The $\alpha$-$PbO_2$ modification appears to be stable only over the narrow composition range of 0 to <1–2 mole% $SrCl_2$, a range that appears invariant in our X-ray studies. Both structural forms would coexist. Because of its small volume, the $\alpha$-$PbO_2$-form seems to be near its limit of stability with a cation of the size of $Ca^{2+}$, and consequently is able to dissolve much less of the larger $Sr^{2+}$ ion than is the pseudo-rutile form. Under such circumstances, the same composition of $SrCl_2$-saturated $\alpha$-$PbO_2$-type phase would precipitate in each experiment, but in progressively decreasing quantities, as the melt became more Sr-rich and the cation size effectively increased. The ~2 to 25 mole% region would then appear to be a two-phase region.

Since the $\alpha$-$PbO_2$ modification disappears first, and the pseudo-rutile form persists to ~45 mole% $SrCl_2$, it appears that with increasing larger atom content the less densely packed structure is the more stable.

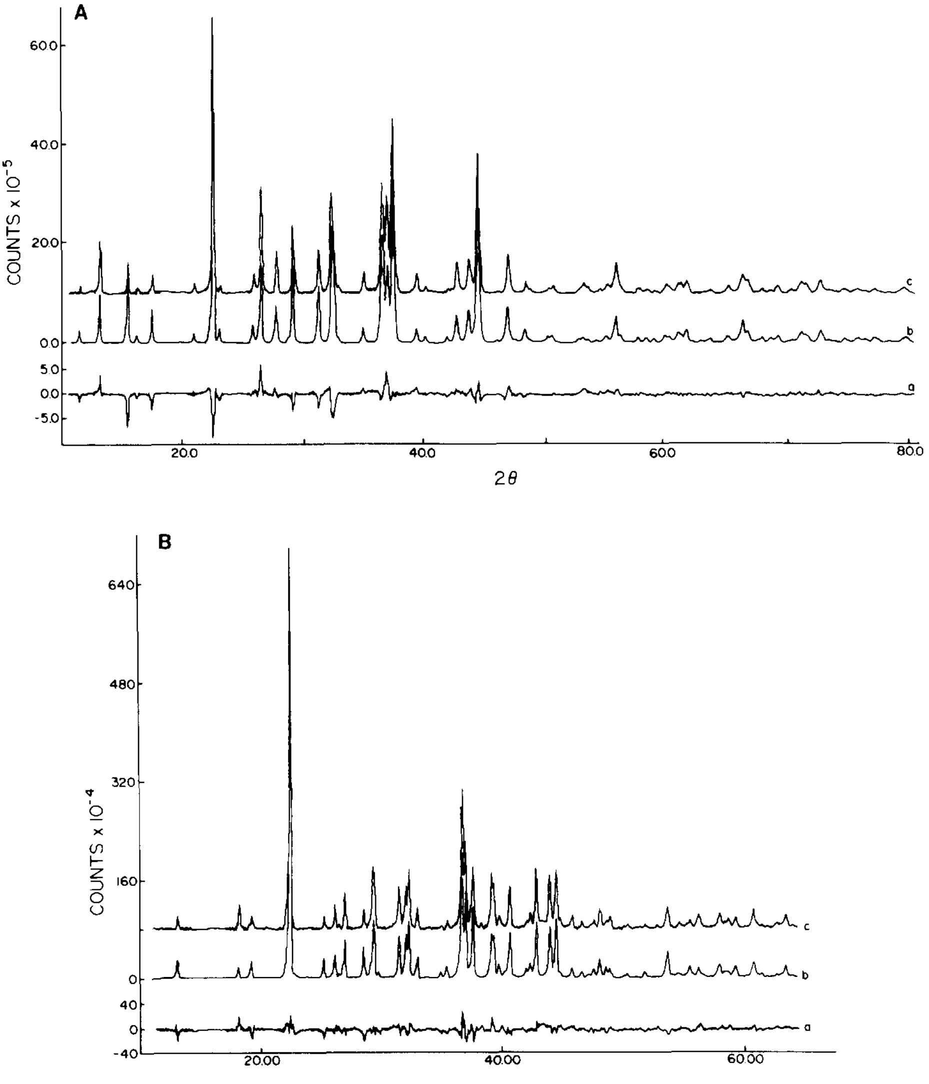

FIG. 1. Observed (c), calculated (b), and difference (a) diffraction patterns for $Ca_{0.3}Sr_{0.7}Cl_2$ (A) and $Ca_{0.46}Sr_{0.54}Cl_2$ (B).

*$Ca_{0.3}Sr_{0.7}Cl_2$*

Coordination is identical to that in $SrBr_2$ with the 2c cations eightfold coordinated (square antiprismatic) and the 8g cations sevenfold coordinated (monocapped severely distorted octahedral) with an eighth further-removed anion (which causes the distortion). Twelve of the anions are coordinated tetrahedrally and eight triangularly with the coordination distance of one of the latter three cations ~0.06 Å longer than that of the others. In the systems $MCl_2$–$CaCl_2$, $M$ = Sr and Eu, the coordination number of both the cations and the anions increases with increasing $M$ content (*1*).

Anion coordination changes from 3 in both of the $CaCl_2$ modifications to 3 and 4 in the $SrI_2$ and $SrBr_2$ types of structures, and then reaches 4 in the fluorite structure. The bond distances reported in Table III indicate consistent agreement between the two structures.

As is apparent in Fig. 1A, the very strong reflection at ~22° 2$\theta$ exhibits the greatest $Y_o-Y_c$ difference. An attempt to apply a secondary extinction correction to this peak failed to improve the refinement. Some of the other reflection differences, particularly those at ~32, 36, and 44° 2$\theta$, seem to result from a slight angular mismatch between the calculated and observed peak positions. Inclusion of data beyond 80° 2$\theta$ exacerbated this apparent angular error. Some differences may result from the rather high preferred orientation factor; it is possible that in a case of high preferred orientation the exponential formula exp($p$ cos (2$\sigma$)) (*6*) is inadequate, but no attempt was made to alter the XRS-82 code to allow a different formulation.

### $Ca_{0.46}Sr_{0.54}Cl_2$

Data were collected over the 2$\theta$ range 10–85°, but refinement was effected only through 65° because the peak profile parameters for the higher angle reflections appeared to differ from those of the lower angle region. Inclusion of the higher angle region not only produced larger discrepancy factors but also made refinement unstable. The refined occupancy parameters for Sr and Ca ions suggest that a melted equimolar mixture of $CaCl_2$ and $SrCl_2$ yields a phase somewhat more Sr rich than the mixed composition. This behavior may be caused by loss of one component during synthesis or by the presence of small amounts of unreacted $CaCl_2$ microcrystals, an amount too small to be detected in the X-ray powder photographs.

The vacancy model with occupancy factors of 0.975 for cations yielded results comparable to those obtained for the full occupancy model. The 0.95 model yielded slightly increased $R$ values; models with lower occupancy values produced significantly larger discrepancy indices. Since partial occupancy models fail to yield superior discrepancy factors, there is no justification to prefer a vacancy model.

Interatomic distances calculated by the program BONDLA (*6*) can be compared with those in the related $SrI_2$-type $YbCl_2$ (*12*). They are consistent with values expected for a structure in which the cation is of a size comparable to the average size of the cations in this mixture (*13*). The cations are sevenfold coordinated, but one (Sr, Ca)–Cl-2 distance, 3.13(5) Å, is longer than the corresponding $YbCl_2$ distance, 2.981(4) Å. Additionally, one Sr(Ca)–Cl-1 distance, 2.70(3) Å, is shorter than the $YbCl_2$ distance, 2.757(5) Å. The effect of these subtle changes as is evidenced in the Cl–Sr(Ca)–Cl angles is to make the coordination in this structure appear more octahedral than it does in $YbCl_2$. Half of the anions are coordinated by three cations. The remaining eight anions, which have smaller isotropic temperature factors, are coordinated by four cations in a distorted tetrahedral arrangement.

In summary, it would seem that if a larger sized ion is added to a compound which can exist in two polymorphic modifications, the less densely packed structural modification will prevail initially as the structure that can more easily accommodate the "increasing larger ion content" and provide a site for higher coordination. In like fashion, since high pressure also produces high coordination, the structure of mixed ion phases can be expected to be similar to those observed for the parent phases at high pressures.

## Acknowledgment

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