

Characterization of the $\text{CaCl}_2\text{-YbCl}_2$ and $\text{CaCl}_2\text{-YbCl}_3$ Systems by X-Ray Powder Diffraction

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The $\text{CaCl}_2\text{-YbCl}_2$ and $\text{CaCl}_2\text{-YbCl}_3$ systems were investigated by X-ray powder diffraction methods. The $\text{CaCl}_2\text{-YbCl}_2$ system exhibits two solid-solution regions: one spans 0-~15 and the other ~55-100 mole % YbCl_2 . The $\text{CaCl}_2\text{-YbCl}_3$ system, on the other hand, is best characterized by essentially total insolubility of the parent phrases. © 1990 Academic Press, Inc.

Introduction

Mixtures of nonisomorphous parent phases usually produce either eutectic structures or two solid-solution regions separated by one or more different structure-type phases (1). Isomorphous systems, on the other hand, typically exhibit only continuous solid-solution over the full composition range (1, 2). The CN VI crystal radii of Ca^{2+} and Yb^{2+} are almost identical, 1.14 vs. 1.16 Å, respectively, whereas that of Yb^{3+} is slightly smaller, 1.008 Å (3). The CN VII crystal radii of Ca^{2+} and Yb^{2+} are 1.20 and 1.22 Å, respectively. When pure CaCl_2 is melted and subsequently quenched, the coexisting (pseudo-rutile, *Pnnm*) CaCl_2 -type and (*Pbnm*) $\alpha\text{-PbO}_2$ -type structures typically result (4); a (*Pbca*) SrI_2 -type structure is observed under high pressure (5). The SrI_2 -type structure is also exhibited by YbCl_2 (6, 7). Since mixed

halide systems frequently exhibit a modification characteristic of the high pressure form of one of the parent phrases, an intermediate composition SrI_2 -type phase was expected in the $\text{CaCl}_2\text{-YbCl}_2$ system (8). The related $\text{CaCl}_2\text{-YbI}_2$ system was complicated. It evidenced two intermediate phases which extended over wide composition limits: a "6-R" CdI_2 -type polytype and a phase whose structure could not be characterized (9). These observations suggested that this $\text{CaCl}_2\text{-YbCl}_2$ system might be particularly interesting.

The divalent-trivalent system, on the other hand, appeared less likely to yield intermediate composition phases because of significant differences in structure types, Cl/M ratio, and ion sizes. Pure YbCl_3 exhibits the (*C2/m*) AlCl_3 -type structure (10). However, *C2/m* trivalent lanthanoid halides combine with divalent halides to form vernier-type structures, e.g., $\text{Yb}_6\text{Cl}_{13}$ and $\text{Yb}_5\text{ErCl}_{13}$ (11), and *C2/m* symmetry DyCl_3 combines with cubic SrCl_2 (12). No report of a calcium-lanthanum halide vernier-type phase could be found. Thus, an

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investigation of the CaCl₂-YbCl₃ system also seemed to be potentially of interest. The results of these studies are presented herein.

Experimental

Reactants YbCl₂ and YbCl₃ were synthesized from Yb₂O₃ (99.9%, Research Chemicals, Phoenix, AZ). The trihalide was prepared by the ammonium halide matrix procedure (13, 14) as described previously (15). The impure product, confined in a previously outgassed quartz tube, was purified by sublimation in a 10⁻⁶ Torr vacuum at ~920°C. YbCl₂ was prepared from a 2:1 YbCl₃:Yb (99.9%, Research Chemicals) mixture as described previously (16). Anhydrous CaCl₂ (reagent grade, Mallinckrodt, St. Louis, MO) was melted in vacuum prior to use. All halide manipulations were effected in an argon-filled glove box whose atmosphere was continuously purged of both H₂O (molecular sieves) and O₂ (heated BASF catalyst).

The CaCl₂-YbCl₂ specimens were prepared by grinding stoichiometric proportions of the reactants in an agate mortar, confining the mixtures in previously outgassed quartz tubes, heating them to melting under vacuum with a hand torch, and then air-quenching them. Selected specimens were resealed in quartz, heated to melting in a tube furnace and cooled to room temperature over a 48-hr period.

In the CaCl₂-YbCl₃ system 10, 20, 50, and 70 mole% YbCl₃ mixtures were examined. These preparations, mixed as described above, were confined in pyrolytic graphite crucibles and heated in a tube furnace under high vacuum at 400°C for an hour. The temperature was increased to 500°C, the assembly filled with prepurified Ar, and the temperature then elevated above the YbCl₃ melting point, 865°C (17), and maintained there for ~20 min. The heating assembly was then removed

quickly from the furnace to quench the molten specimen.

The pulverized products were examined in an evacuated 114.6-mm-diameter Guinier-Hägg X-ray camera with CuK α ₁ ($\lambda\alpha_1 = 1.54050 \text{ \AA}$) radiation; NBS certified Si ($a = 5.43082(4) \text{ \AA}$) was the internal standard. Reflection positions were determined as described previously (15). Lattice parameters calculated initially with a locally written least-squares program were refined with the program APPLEMAN (18). For selected compositions theoretical X-ray powder diffraction intensities were calculated on a VAX 11/750 computer with the program POWD12 (19); exponential scattering factors were used with estimated temperature factors of 1.5 \AA^2 for anions and 1.0 \AA^2 for cations.

Results and Discussion

The CaCl₂-YbCl₃ System

The phases C2/m YbCl₃ and Pnmm-type (pseudo-rutile) CaCl₂ were identified at the 10, 20, 50, and 70 mole % YbCl₃ compositions. Lattice parameters observed for YbCl₃, $a = 6.739(3) \text{ \AA}$, $b = 11.651(8) \text{ \AA}$, $c = 6.383(4) \text{ \AA}$, $\beta = 110.51(5)^\circ$, are in good agreement with literature values (15). Even 10 mole % YbCl₃ specimens exhibited readily detectable interplanar d -spacings assignable to YbCl₃. Lattice parameter data indicate no solubility whatsoever of CaCl₂ in YbCl₃; volume/cation data remain invariant within uncertainty limits. The observed Pnmm CaCl₂ lattice parameters, $a = 6.261(2) \text{ \AA}$, $b = 6.436(3) \text{ \AA}$, and $c = 4.166(2) \text{ \AA}$, agree well with literature values (9). However, the very small increase observed in the CaCl₂ lattice parameters at the 20 mole % composition, $a = 6.262(2) \text{ \AA}$, $b = 6.439(3) \text{ \AA}$, and $c = 4.171(1) \text{ \AA}$, may suggest minimal Yb³⁺ solubility in CaCl₂. Although the Yb³⁺ ion is smaller than that of Ca²⁺ (3), the need for charge balance would require

introduction of either cation vacancies or excess anions into the lattice. Both effects would lead to lattice expansion. The absence of appreciable YbCl_3 solubility suggests either that the rutile-type structure does not dissolve trivalent lanthanoid at all or that the lattice energy is so great it cannot tolerate the disorder that would be created by substitution of the higher charged Yb^{3+} cation.

We observed a similar absence of YbCl_3 solubility in SrCl_2 , a salt well-known for its ability to solubilize trivalent chlorides (20, 21) and to form vernier phases such as $(\text{Sr}, \text{Eu})\text{Cl}_{2+x}$ (12) and $(\text{Sr}, \text{Nd})\text{Cl}_{2+x}$ (22). The YbCl_3 insolubility in SrCl_2 suggests that the problem stems as much, if not more, from the unique properties of ytterbium salts as it does from those of calcium salts.

It is somewhat surprising that the $\alpha\text{-PbO}_2$ modification of CaCl_2 was not observed in this system since it was present in the $\text{CaCl}_2\text{-YbI}_2$ system (9). Its absence may result because an intermediate such as $(\text{Ca}, \text{Yb})\text{Cl}_{2+x}$ forms at elevated temperatures and decomposes as the mixture is cooled. A decomposition mechanism is suggested by the appearance of the X-ray powder diffraction films. YbCl_3 prepared by thermal decomposition of $(\text{NH}_4)_3\text{YbCl}_6$ (14) at $\sim 450^\circ\text{C}$ produces an X-ray powder diffraction pattern with a small number of broad reflections whose intensities differ significantly from those of previously melted YbCl_3 . The X-ray diffraction patterns of the YbCl_3 component in the melted $\text{CaCl}_2\text{-YbCl}_3$ specimens were similar to those of thermally decomposed $(\text{NH}_4)_3\text{YbCl}_6$. This observation suggests that a high temperature phase of intermediate composition decomposed at $\sim 450^\circ\text{C}$ to produce the characteristic YbCl_3 decomposition product, not the product expected from the quenching of a melted specimen. This decomposition may then lead to the pseudo-rutile form and to exclusion of the

$\alpha\text{-PbO}_2$ form. Unfortunately, the hypothesis can be verified only either by high temperature X-ray diffraction studies or through more rapid quenching than was achievable.

The $\text{CaCl}_2\text{-YbCl}_2$ System

Two solid-solution regions were observed. The first spans 0 to ~ 15 mole % YbCl_2 and exhibits the pseudo-rutile and $\alpha\text{-PbO}_2$ -type CaCl_2 polymorphic modifications (23). The second spans ~ 55 to 100 mole % YbCl_2 and exhibits the SrI_2 -type structure common to YbCl_2 .

Lattice parameters (and cell volume/cation data) presented in Table I for 10, 20, 30, 50, and 70 mole % YbCl_2 specimens as well as X-ray powder diffraction intensity variations substantiate these solubility limits. A comparison between observed and calculated X-ray powder diffraction intensities suggests a 10–20 mole % YbCl_2 solubility limit in both CaCl_2 lattice modifications. For example, the $Pnmm$ CaCl_2 (011) reflection is absent in pure CaCl_2 , but is observed in 10–30 mole % YbCl_2 specimens. Intensities calculated for this reflection are 1, 7, and 10 for 0, 10, and 20 mole % YbCl_2 specimens, respectively. Since X-ray powder diffraction patterns of 20 mole % YbCl_2 specimens also exhibit a few reflections assignable to YbCl_2 , the solubility limit in $Pnmm$ CaCl_2 is established at ~ 15 mole %. On the other hand, in the $\alpha\text{-PbO}_2$ -type structure the intensity of the (111), (121), and (221) reflections, which differ in pure CaCl_2 , were of nearly the same intensities in samples which contained from 10 to 40 mole % YbCl_2 , suggestive of an ~ 10 mole % YbCl_2 solubility limit. Other X-ray reflection intensity variations were consistent with this solubility limit. Since in both CaCl_2 polytypes there is only one cation position and since reflections suggestive of superstructure were not observed, a random cationic arrangement was assumed for these intensity calculations.

TABLE I
LATTICE PARAMETERS AND VOLUME/CATION DATA AT SELECTED COMPOSITIONS IN THE
CaCl₂-YbCl₂ SYSTEM

| Mole % YbCl ₂ | Phase(s) observed ^a | Lattice parameters | | | Vol/cation (Å ³) | Reference ^b |
|-----------------------------|-----------------------------------|--------------------|------------|------------|---------------------------------|------------------------|
| | | <i>a</i> Å | <i>b</i> Å | <i>c</i> Å | | |
| 0 | CaCl ₂ | 6.253 (2) | 6.434 (3) | 4.167 (2) | 83.82 | (9) |
| | | 6.261 (2) | 6.426 (2) | 4.167 (1) | 82.76 | |
| | α-PbO ₂ | 6.268 (1) | 7.619 (6) | 6.923 (4) | 82.65 | (4) |
| 6.280 (1) | | 7.620 (2) | 6.918 (2) | 82.76 | | |
| 6.263 (1) | | 6.441 (2) | 4.174 (1) | 84.27 | | |
| 10 | CaCl ₂ | 6.289 (7) | 7.65 (1) | 6.913 (6) | 83.12 | |
| | α-PbO ₂ | 6.268 (1) | 6.451 (2) | 4.180 (1) | 84.51 | |
| 20 | CaCl ₂ | 6.296 (1) | 7.642 (2) | 6.978 (1) | 83.33 | |
| | α-PbO ₂ | 6.279 (1) | 6.451 (1) | 4.181 (1) | 84.67 | |
| 30 | CaCl ₂ | 6.314 (3) | 7.627 (5) | 6.936 (3) | 83.50 | |
| | α-PbO ₂ | 13.114 (3) | 6.915 (2) | 6.682 (1) | 75.74 | |
| 50 | YbCl ₂ | 13.133 (2) | 6.935 (1) | 6.697 (1) | 76.24 | |
| 70 | YbCl ₂ | 13.143 (2) | 6.948 (1) | 6.698 (1) | 76.46 | |
| | | 13.15 (3) | 6.94 (2) | 6.69 (2) | 76.3 | (6) |

^a Observed structure types are CaCl₂, *Pbnm* α-PbO₂ and *Pnmm* pseudo-rutile; YbCl₂, *Pbca*.

^b This work, except as noted.

A solid-solution with the YbCl₂-type structure was observed in the ~55-100 mole % YbCl₂ region. Since both cations have nearly identical ionic radii, factors other than radii limit solubility. Possible factors include electronic configuration and coordination preference differences. The common Ca²⁺ coordination number in CaCl₂ is six (4); under high pressure it forms the seven coordinate SrI₂-type structure common to YbCl₂ (5). Unlike CaCl₂, YbCl₂ does not exhibit polymorphic modifications. Thus, the coordination number preferred by Ca²⁺ is six with seven possible, while that for Yb²⁺ is seven. In fact, Yb²⁺ in the vernier-type structures exhibits seven or higher coordination numbers (11). This coordination preference by ytterbium may limit the solubility of the Yb²⁺ cation in the CaCl₂-type structure. However, the CaCl₂-MCl₂ systems for *M* = Eu and Sr exhibit the seven coordinate SrI₂-type structure not common to either parent phase at the 40-60 mole % CaCl₂ composi-

tion (24). Thus formation of a seven coordinate SrI₂-type structure is possible for CaCl₂, and its absence in this system must relate more to the character of the combination than to that of either chloride.

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