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Characterization of the $CaCl_2$–YbI_2 System by X-Ray Powder Diffraction

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The $CaCl_2$–YbI_2 system was investigated over the entire composition range by X-ray powder diffraction methods. It is characterized by a complicated mixture of phases, each of which extends over wide composition limits. The solid solution regions observed in the system, expressed in terms of mole percent $CaCl_2$, and the structure types present in these regions are as follows: 0 to 55, CdI_2 type; ~25 to ~65, 6-R CdI_2 polytype; ~35 to 85, unknown type; ~85 to 100, α-PbO_2 type; and ~35 to 100, $CaCl_2$, pseudo-rutile type. The latter two modifications are common to pure $CaCl_2$. The ideal composition of the uncharacterized phase is probably $Ca_3YbCl_6I_2$ ($MCl_{1.5}I_{0.5}$).

Introduction

A 6-R polytypic modification of YbI_2 which exhibited extensive solid solution was observed in the $YbCl_2$–YbI_2 system (*1*). Even though YbI_2 has the CdI_2-type structure, polytypes have not been reported from preparations which involved either melted or sublimed pure YbI_2 (*2*). It thus seemed probable that this polytypism, observed in specimens prepared under high-temperature conditions that usually yield the 2-H form, resulted because the chloride anion behaved like an impurity anion and caused stacking disorders (*3*). In the $YbCl_2$–YbI_2 system a 6-R modification which could not be obtained pure extended from 10 to ~85 mole% YbI_2. We investigated another MCl_2–YbI_2 system in which the M cation size was similar to that of Yb^{2+} to explore this polytypism further. From ionic radius considerations $M = Ca^{2+}$ appeared a logical choice (*4*).

The $CaCl_2$–$YbCl_2$ and $CaCl_2$–$YbCl_3$ systems have been investigated by X-ray powder diffraction techniques (*5*). Even though the cation sizes (with coordination number VIII) are almost identical (*4*), 1.28 Å for Yb^{2+} vs 1.26 Å for Ca^{2+}, the behavior of the calcium ion in these systems differs from that of the Yb^{2+} ion. It was thought that in an iodide-containing system this difference might be deemphasized because the larger, "softer" iodide anion could potentially accommodate slight cation differences and might accentuate the similarities between Ca^{2+} and Yb^{2+}. We thus undertook a study of the $CaCl_2$–YbI_2 system.

Experimental

Ytterbium diiodide was prepared from the metal (99%, Research Chemicals, Phoe-

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nix, AZ) and excess HgI_2, as described previously (*1*). Anhydrous $CaCl_2$ (Mallinckrodt, St. Louis, MO) was melted under vacuum prior to use. All sample manipulations were effected in an argon-filled glovebox whose atmosphere was continuously purged to both water (molecular sieves) and oxygen (heated BASF catalyst).

The $CaCl_2$–YbI_2 samples, ground in stoichiometric proportions in an agate mortar, were confined in previously outgassed quartz tubes. They were melted carefully under Ar with a hand torch and quenched in air.

The pulverized products were examined by the Guinier X-ray diffraction technique with Cu$K\alpha_1$ radiation; NBS certified Si [a = 5.43082(3) Å] served as the internal standard. X-ray powder diffraction sets that could not be indexed by inspection were submitted to the indexing program ITO9 (*6*) or TREOR (*7*). Lattice parameters were refined by the program APPLEMAN (*8*); X-ray intensity calculations were performed with the program POWD12 (*9*). All calculations were effected on a VAX 11/750 computer.

Results and Discussion

Lattice parameters and corresponding cell volumes are presented as a function of the mixed composition in Table I. Phases observed in this system, together with their composition ranges, where appropriate, are presented schematically as a function of both mole percent $CaCl_2$ and mole percent YbI_2 in Fig. 1. In some YbI_2-rich specimens traces of YbOI (as evidenced by the presence of a 9.36 Å X-ray reflection) were observed. Since it was not clear whether YbOI formed during synthesis or during X-ray examination, experiments in which more than traces of oxide iodide were found were either repeated or deleted from consideration.

TABLE I

LATTICE PARAMETERS AND VOLUME/CATION DATA AT SELECTED COMPOSITIONS IN THE $CaCl_2$–YbI_2 SYSTEM

Mole% YbI_2	Phase(s) observed	Lattice parameters					Vol./cation (Å^3)	Ref.[a]
		a (Å)	b (Å)	c (Å)	β (°)[b]	γ (°)		
0	$CaCl_2$	6.253(2)	6.434(3)	4.167(2)	—	—		
15	$CaCl_2$	6.249(3)	6.441(2)	4.175(2)	—	—		
25	$CaCl_2$	6.26(1)	6.466(5)	4.177(2)	—	—		
	A	13.662(3)	11.325(2)	4.549(1)	91.52(2)	—	58.63	
35	$CaCl_2$	6.262(3)	6.458(4)	4.174(2)	—	—		
	A	13.633(5)	11.305(5)	4.549(1)	91.48(3)	—	58.42	
	Poly	4.433(1)	—	20.86(1)	—	120.	59.15	
60	$CaCl_2$	6.295(3)	6.448(6)	4.183(2)	—	—		
	A	13.659(5)	11.332(4)	4.547(2)	91.45(3)	—	58.63	
	Poly	4.453(6)	—	20.8(1)	—	120.	59.62	
	YbI_2	4.504(4)	—	7.01(1)	—	120.	61.58	
85	YbI_2	4.484(2)	—	6.967(3)	—	120.	60.66	
100	YbI_2	4.503(1)	—	6.970(3)	—	120.	61.20	
	YbI_2	4.503	—	6.972	—	120.		(*3*)

Note. Observed structure types are $CaCl_2$ (*Pnnm*); YbI_2 ($P\bar{3}m1$), CdI_2 type.

[a] This work, except as noted.

[b] 90°, unless indicated otherwise.

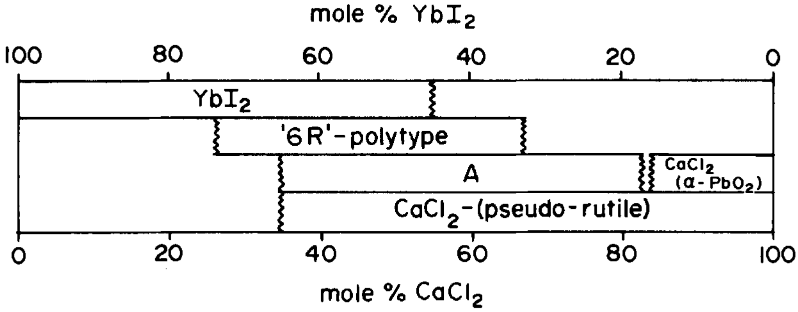

FIG. 1. A schematic representation of the $CaCl_2$–YbI_2 system. The bands indicate the regions over which the various phases are observed. The α-PbO_2 and pseudo-rutile forms are common to $CaCl_2$. The structure type of the phase designated A could not be determined.

Only one single-phase solid solution region was observed. It spanned 0 to ~25 mole% $CaCl_2$ and exhibited the CdI_2-type structure common to YbI_2. At the other end of the system from 85 to 100 mole% $CaCl_2$ the two polymorphic modifications common to $CaCl_2$, the pseudo-rutile and α-PbO_2 structure types, were present. Because the ionic radii of these ions are similar, cell volumes may not reflect cation substitution. Reflections of α-PbO_2-type $CaCl_2$ are not observed beyond about 15 mole% YbI_2; those of the pseudo-rutile $CaCl_2$ structure type can be found in samples that contain 65 mole% YbI_2.

In the $CaCl_2$–$SrCl_2$ system (*10*), just as in this system, with increasing concentration of the larger ion, whether Sr^{2+} in that system or I^- in this one, the α-PbO_2 modification appears to be the less stable polymorph, even though in both $CaCl_2$ polymorphic modifications interatomic distances and coordination polyhedra are almost identical. This observation may be explained on the basis on the higher density of the α-PbO_2-type modification; with increasingly larger ion content (Sr^{2+} or I^-), the concomitant substitution for Ca^{2+} or Cl^- ions in the $CaCl_2$ lattice causes the less densely packed modification to survive longer. On the basis of the lattice parameters the solubility limit of YbI_2 in the pseudo-rutile lattice appears to be about 15 mole%, but if the cations are not randomly distributed between the phases the actual solubility could be much different from this. On the other hand, although the exact solubility limit in the α-PbO_2-type structure is uncertain because the number of observed reflections is small, it is clear that only very limited YbI_2 solubility prevails. This behavior is consistent with that observed in the $YbCl_2$–YbI_2 system (*1*).

In the region 35–85 mole% $CaCl_2$, a new unknown phase is observed. This phase, designated $Ca_3YbCl_6I_2$ (i.e., $MCl_{1.5}I_{0.5}$) and labeled A in Fig. 1, is a major component of the sample that contains 75 mole% of $CaCl_2$. Its diffraction pattern is indexed by the programs TREOR (*7*) and ITO9 (*6*) as monoclinic with a small distortion from orthogonality. Lattice parameters of the 25 mole% YbI_2 composition specimen are a = 13.662(3), b = 11.325(2), c = 4.549(1) Å, and β = 91.53(2)° with a unit cell volume of 703.6 Å^3; the figure-of-merit (*11*) is 11.3. On the basis of cell volume, z = 8. Observed interplanar d-spacings (in Å) and intensities are: 8.712(w$^+$), 6.804(w), 5.655(vvw), 4.355(m$^-$), 4.225(m), 4.066(w), 3.993(w), 3.639(w$^+$), 3.444(w$^+$), 3.412(w$^+$), 3.160 (vw), 3.064(s), 2.904(w$^+$), 2.825(vw), 2.768 (w), 2.691(vw), 2.654(vw), 2.3652(m$^+$), 2.2742(w$^-$), 2.2339(w$^-$), 2.2140(w), 2.1903 (w), 2.1367(w), 2.1120(vvw), 2.0307(vw), 1.8950(w).

Searches of the Crystal Data Determinative Tables (*12*) and the CRYSTDAT computer data file (*13*) for Cl^- and I^--containing species with lattice parameters consistent with those observed for the $MCl_{1.5}I_{0.5}$ compound were unsuccessful. Furthermore, a similar pattern could not be identified in the ASTM Powder Diffraction File (*14*), so this compound may represent a new structural group. Because under the preparatory conditions used it could be obtained only as one component of a mixture and only as a microcrystalline specimen, neither detailed analytical nor structural data are available. It is interesting to note that the volume of the elementary cell of this compound is four times larger than that of the pseudo-rutile $CaCl_2$ form, and the indexing program's metric symmetry test suggests the possibility of pseudo-cubic symmetry.

In the region 25–70 mole% $CaCl_2$ another phase with a sequence of reflections similar to those observed in the 6-R YbI_2 polytype modification was identified (*1*). Hexagonal lattice parameters of this compound at the 65 mole% $CaCl_2$ composition, together with the cell volume were a = 4.433(1), c = 20.86(1) Å, V = 354.9(3) $Å^3$. These lattice parameters compare favorably with those observed in the $YbCl_2$–YbI_2 system at the 50 mole% composition, a = 4.455(2) and c = 20.870(5) Å, particularly when compositional differences between the samples are considered.

The intensity of the polytype X-ray diffraction reflections varied as a function of initial mixture composition. Some reflection intensity variations can be readily understood. Since the ionic radii of the cations are similar (*5*), substitution should be facile. On the assumption that the anionic composition remained invariant at $MCl_{1.5}I_{0.5}$, a series of theoretical X-ray powder diffraction patterns was calculated with the positional and thermal parameters described in (*1*). These calculations explained most but not all of the observed intensity variations. For example, the intensity of reflection (104), which was the strongest reflection in the 6-R "YbClI" polytype (*1*), was less than the calculations indicated it should be. In the $YbCl_2$–YbI_2 system the polytype X-ray diffraction intensities were very sensitive to halide ion positional parameters. Such sensitivity also probably prevails in this system, and agreement between observed and calculated intensities might be improved by varying these positional parameters. However, the limited number of unique reflections precludes the precise experimental determination of the halide positional parameters that was done in (*1*).

These polytype intensity variations could also be the result of a different polytype modification, but it is difficult to justify such a hypothesis in view of both the limited number of unique reflections and the good agreement of the reflection positions with those observed in the YbI_2–$YbCl_2$ system. Further investigation, e.g., different heat treatment conditions, another system, or a single crystal X-ray diffraction study if crystals can be prepared, is necessary to definitively resolve this problem.

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