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High-Pressure Phase Transformation Studies of $M_{1-x}Rh_xSe_2$ (M = Pd, Pt)

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Members of the system $Pd_{1-x}Rh_xSe_2$, prepared at ambient pressure, consisted of mixtures of $PdSe_2$ and $RhSe_2$. Compositions with $x \geq 0.3$, subjected to a pressure of 50 kbar and 1000 °C, gave a single-phase region crystallizing with the pyrite structure. For the system $Pt_{1-x}Rh_xSe_2$ ($x \leq 0.4$) sample preparation at 1000 °C and ambient pressure yielded a solid solution crystallizing with a CdI_2 structure. A high-pressure phase transformation was not observed for this system at 50-kbar pressure and 1000 °C.

Introduction

A number of transition-metal ditellurides may be induced to undergo a high-pressure phase transformation from a cadmium iodide structure to a pyrite structure by chemical substitution. Among the systems which have been studied are $Ni_{1-x}Fe_xTe_2$[1] and $Pd_{1-x}Rh_xTe_2$.[2] Although $NiTe_2$ undergoes only a partial transformation from a cadmium iodide structure to a pyrite structure at 89 kbar,[3] a single-phase pyrite region may be obtained for the system $Ni_{1-x}Fe_xTe_2$ ($0.4 \leq x \leq 0.8$) at 60-kbar pressure.[1] $PdTe_2$ also crystallizes with the cadmium iodide structure at ambient pressure. However, at 60-kbar pressure a complete transformation to a pyrite phase was obtained for $Pd_{1-x}Rh_xTe_2$ ($x \geq 0.6$).[2]

At ambient pressure $PdSe_2$ crystallizes with a layer structure (space group *Pbca*; a = 5.741 Å, b = 5.866 Å, c = 7.691 Å). Grønvold and Røst[4] have indicated that $PdSe_2$ may be described in terms of an elongated pyrite structure. At pressures as high as 65 kbar, Bither[5] observed only a compression of the structure in the interlayer direction but he did not report a transformation to the pyrite structure. He also noted that high-pressure synthesis of rhodium-substituted $PdSe_2$ yielded a mixture containing a $PdSe_2$ high-pressure orthorhombic phase and a pyrite phase ($a \sim$ 6.12 Å). $RhSe_2$ has been reported to adopt either an orthorhombic $IrSe_2$ structure[6] (*Pnam* with a = 20.91 Å, b = 5.951 Å, c = 3.709 Å) at room temperature or a pyrite structure ($a \sim$ 6.01 Å, extrapolated value) at high temperature.[7] Comparison of the cell constants for these two pyrite phases indicates that the pyrite phase obtained by Bither[5] for rhodium-substituted $PdSe_2$ contains rhodium.

$PtSe_2$ crystallizes with the CdI_2 structure (space group $P\bar{3}m1$; a = 3.724 Å, c = 5.062 Å). High-pressure phase transformations for $PtSe_2$ have not been reported.

The systems $M_{1-x}Rh_xSe_2$ (M = Pd, Pt) were investigated both at ambient pressure and under high pressure in order to determine the extent of solid solution and the effect of the rhodium substitution for palladium and platinum on the existence of high-pressure phases.

Table I. Lattice Constants and Densities for $Pd_{1-x}Rh_xSe_2$ Phases Obtained at 50-kbar Pressure and 1000 °C

phase	a_0, Å	ρ_{exptl}, g/cm^3	ρ_{calcd}, g/cm^3
$Pd_{0.7}Rh_{0.3}Se_2$	6.123 (2)	7.5 (1)	7.62
$Pd_{0.6}Rh_{0.4}Se_2$	6.109 (2)	7.6 (1)	7.66
$Pd_{0.4}Rh_{0.6}Se_2$	6.076 (2)	7.7 (1)	7.76
$Pd_{0.2}Rh_{0.8}Se_2$	6.048 (2)	7.8 (1)	7.85
$RhSe_2$	6.018 (2)	7.9 (1)	7.95

Experimental Section

All polycrystalline samples were prepared by reacting stoichiometric quantities of the elements in evacuated silica tubes. The samples were heated for 1 week with several intermittent grindings. At the end of each heat treatment the samples were cooled to room temperature at the rate of 100 °C/h.

The reacted polycrystalline samples were subjected to 1000 °C and 50-kbar pressure for $1^1/_2$ h in a belt apparatus described by Hall.[8] Reactions were not carried out at higher temperatures in order to avoid decomposition of the products. At the end of each experiment, the sample was allowed to cool for 15 min and the pressure was then reduced to 1 atm (ambient pressure).

The phases present in each sample were identified from powder patterns obtained with a Norelco diffractometer equipped with a high-intensity copper source and a graphite monochromator (λ(Cu Kα) 1.5418 Å) located in the diffracted beam. Lattice parameters were calculated from a least-squares refinement using 2θ angles corrected relative to a KCl internal standard. Densities were measured by the hydrostatic technique described by Adams.[9] Perfluoro(1-methyldecalin) served as the density fluid which was calibrated with a high-purity silicon crystal (ρ = 2.33 g/cm^3 at 25 °C).

Results

Ambient Pressure. For the system $Pd_{1-x}Rh_xSe_2$ ($0.1 \leq x \leq 0.9$) the products obtained at 750 °C and ambient pressure contained three structure types, namely, $PdSe_2$, $RhSe_2$ ($IrSe_2$ structure), and $RhSe_2$ (pyrite structure).

For the system $Pt_{1-x}Rh_xSe_2$ ($x \leq 0.4$) sample preparation at 1000 °C yielded a single-phase region with the CdI_2

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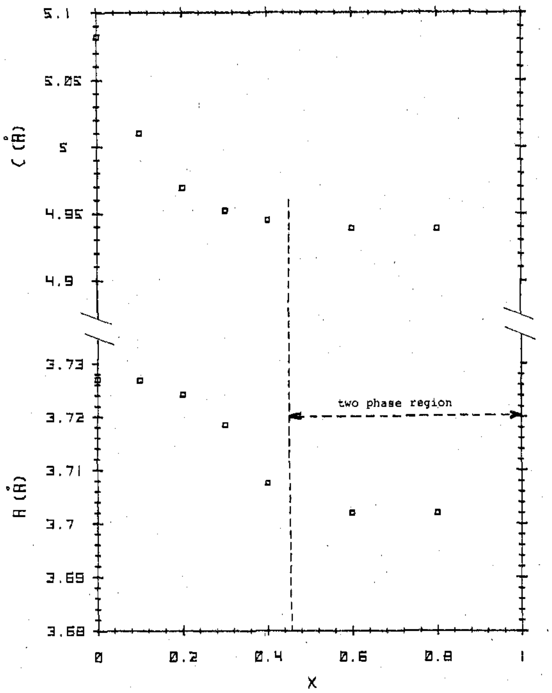

Figure 1. Variation in cell edge with composition for the ambient-pressure $Pt_{1-x}Rh_xSe_2$ hexagonal system.

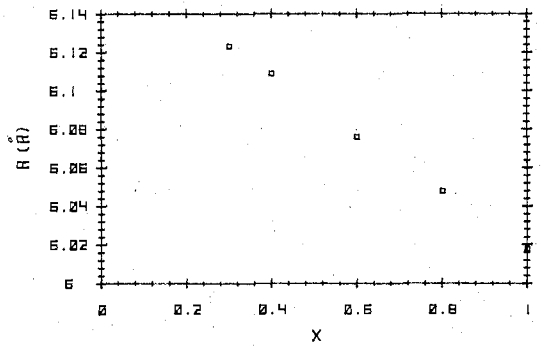

Figure 2. Variation in cell edge with composition for the high-pressure $Pd_{1-x}Rh_xSe_2$ cubic system.

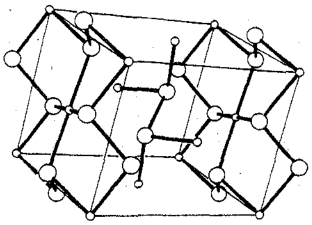

Figure 3. The $PdSe_2$ structure.

structure. Cell constants are plotted as a function of composition in Figure 1. In addition to this solid solution, a $RhSe_2$ pyrite phase appeared for compositions where x is somewhat greater than 0.4.

High Pressure. When subjected to 50-kbar pressure and 1000 °C, $PdSe_2$ retained an orthorhombic structure with $a = 5.758$ Å, $b = 5.858$ Å, and $c = 7.628$ Å. The cell volume of 257.3 Å^3 for this product is smaller than 259.0 Å^3 reported by Grønvold and Røst for $PdSe_2$ prepared at ambient pressure. For the composition $Pd_{0.8}Rh_{0.2}Se_2$, a mixture of the orthorhombic and pyrite phases was obtained. However, for $x \geq 0.3$ a solid solution resulted with the pyrite structure. Lattice constants and densities are listed in Table I. The lattice constants are plotted as a function of composition in Figure 2. For the system $Pt_{1-x}Rh_xSe_2$, all samples subjected to high pressure consisted of two phases: $PtSe_2$ (CdI_2 structure) and $RhSe_2$ (pyrite structure).

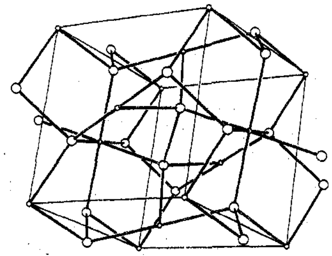

Figure 4. The pyrite structure.

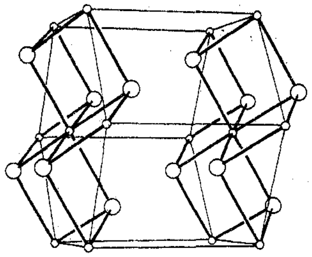

Figure 5. The CdI_2 structure.

Table II. Structure Types for Ni, Pd, and Pt Dichalcogenides[a]

	chalcogen		
metal	S	Se	Te
Ni	pyrite	pyrite	CdI_2[b] → pyrite
Pd	$PdSe_2$	$PdSe_2$ → pyrite	CdI_2[c] → pyrite
Pt	CdI_2	CdI_2	CdI_2

[a] An arrow indicates a reported high-pressure phase transformation to the pyrite structure with chemical substitution. References: NiS_2, $NiSe_2$, and PtX_2 (X = S, Se, Te), ref 10; $NiTe_2$, ref 1; $PdSe_2$, this work; $PdTe_2$, ref 3. [b] System $Ni_{1-x}Fe_xTe_2$. [c] System $Pd_{1-x}Rh_xTe_2$.

Discussion

$PdSe_2$ has a layer structure (Figure 3) which can be derived from an elongation of the anion octahedra of the pyrite structure (Figure 4). This elongation generates square-planar coordination for the 4d^8 Pd. In both structures anions are found as Se_2^{2-} pairs. In the CdI_2 structure (Figure 5) in which the platinum dichalcogenides crystallize, the 5d^6 Pt species occupy octahedral sites between alternate anion layers.

Transformations from the $PdSe_2$ and CdI_2 structures to the more dense pyrite structure are favored by high pressure. Although such a phase transformation was not observed at 50-kbar pressure for $PdSe_2$, chemical substitution of rhodium for palladium did induce a transformation to the pyrite structure. For such a transformation there is no change in the electronic structure of Pd since (d^8) Pd is present in both phases. For $PtSe_2$ a phase transformation could not be promoted via rhodium chemical substitution under the same experimental conditions used for the transformation of a Rh-substituted $PdSe_2$.

In Table II structure types and known phase transformations to the pyrite structure are given for the Ni, Pd, and Pt dichalcogenides with chemical substitutions. A pyrite phase is listed for each of the Ni dichalcogenides and for $PdSe_2$ and $PdTe_2$. Chemical substitution should promote a phase transformation to the pyrite structure for PdS_2 as observed here for $PdSe_2$. Phase transformations for the Pt dichalcogenides have not been reported. Indeed, attempts to induce a transformation for $PtSe_2$ with rhodium chemical substitution at 50-kbar pressure were unsuccessful. Comparison of the solid-state chemistry of Ni, Pd, and Pt, indicates that $5d^8$ Pt cannot occupy an octahedral site, whereas d^8 Ni and d^8 Pd are known to occupy octahedral sites. This is consistent with the failure to observe a phase transition for rhodium-substituted platinum diselenide.

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Registry No. $PdSe_2$, 60672-19-7; $RhSe_2$, 12038-76-5; $PtSe_2$, 12038-26-5.

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Chloro Complexes in Molten Salts. 6. Potentiometric and Vapor Pressure Study of the System $KCl–AlCl_3$ in the Temperature Range 275–350 °C

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By potentiometric measurements with chlorine/chloride electrodes (and aluminum electrodes) the solubility of KCl in $KCl–AlCl_3$ melts was examined in the temperature range 275–350 °C. A plot of $-pK_s$ (where K_s is the solubility product of K^+ and Cl^- in molar concentrations) vs. the inverse absolute temperature in the above temperature range gave an almost linear plot. From this plot $\Delta S°$ and $\Delta H°$ (for dissolution of KCl in $KAlCl_4$) were calculated to be 46.8 (11) J/(deg mol) and 19.7 (6) kJ/(mol), respectively. It was furthermore found that for up to a mole fraction of $AlCl_3$ of 0.524 62 in the temperature range from 275 to 350 °C, the potentiometric results were best explained by a combination of two reactions: $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$ and $Al_2Cl_7^- \rightleftarrows Al_2Cl_6 + Cl^-$ (model 1) or $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$ and $3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$ (model 2). However, combined potentiometric and vapor pressure measurements could better be explained by three reactions (model 3): (i) $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$, (ii) $3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$, and (iii) $2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6 + 2Cl^-$. The p*K* values (based on molar concentrations) for reaction (i) were found to be 8.15 (1), 7.80 (2), 7.47 (2), and 7.15 (3) at 275, 300, 325, and 350 °C, respectively. Possible values for reaction (ii) were found to be 7.6 (4), 7.3 (6), 7.1 (7), and 7.1 (11) and for reaction (iii) 15.4, no value found, 14.0, and 12.1 at 275, 300, 325, and 350 °C, respectively. From the temperature dependence of reaction (i) it was found that in the temperature range 275–350 °C the values of $\Delta S°$ and $\Delta H°$ were 0.9 (22) J/(deg mol) and 86.0 (12) kJ/mol, respectively.

Introduction

An exact value for the equilibrium constants for the acid–base reactions in molten chloroaluminates at different temperatures is of the utmost importance when one is dealing with examination of chloro complexes of dilute metal salts dissolved in these melts. Very accurate values of the equilibrium constants for the solvents are necessary in order to get the correct values for the dilute systems.

In the present paper a more detailed examination than performed earlier[1] for the $KCl–AlCl_3$ system is presented. In a fairly small range around 50–50 mol % $KCl–AlCl_3$ one equilibrium (i.e., $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$) is sufficient to explain the acid–base reactions of the melt itself reasonably well.[1,2] However, if very accurate measurements are performed or if a larger range is examined, the above model is quite inadequate.

The closely related system $NaCl–AlCl_3$ has been examined potentiometrically by several authors.[3-5] The measurements have been performed mostly by use of aluminum electrodes but also chlorine/chloride electrodes in an open system have been used.[3] Boxall et al.[5] examined the potentiometric measurements for this system over a fairly large compositional range (50–70 mol % $AlCl_3$) in terms of the species Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, and Al_2Cl_6. In order to obtain agreement between the calculated and measured values at high $AlCl_3$ composition, the activity coefficients were adjusted to vary as required by a regular solution. Fannin et al.[4] did not take the change in activity coefficients into consideration even when they were working in a large compositional range; on the other hand, they included on the acidic side the existence of $Al_3Cl_{10}^-$ in order to obtain better agreement between measured and calculated values. The existence of a higher polymeric aluminum species than $Al_2Cl_7^-$ and Al_2Cl_6 in $KCl–AlCl_3$ (and in $NaCl–AlCl_3$) is supported by Raman spectroscopic evidence.[6-8] The existence of $AlCl_4^-$ and $Al_2Cl_7^-$ is well supported by the Raman spectra as is the existence of Al_2Cl_6. However, at higher contents of $AlCl_3$, the bands which cannot be ascribed to any of the above species appear.

Experimental Section

The chemicals in the present work were prepared in the same way as in previous work dealing with $KCl–AlCl_3$ solvents.[1,9] Similarly, the experimental technique concerning the potentiometric measurements was the same as described in previous work.[1,9,10] A concentration cell made of Pyrex glass (without a pressure equilibrium connecton tube between the two chambers[10]) was used for the potentiometric measurements. The electrode material was either glassy carbon (V10 from Carbone Lorraine) for the chlorine/chloride electrodes or pure aluminum (99.999%, Atomergic Chemetals Corp.) for the aluminum electrodes.

The furnace and its regulation have been described in detail in connection with a method for determination of densities of molten

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