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Structure and Physical Properties of YSe_{1.83}

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Received February 13, 1995

YSe_{1.83} was synthesized by vapor transport technique and its crystal structure was determined. The structure was isostructure of LaTe_{2-x}, which was layered structure consisting of two-atom thick layers of YSe with distorted NaCl-type structure and one-atom thick layer of Se. The substructure of YSe_{1.83} was tetragonal with space group of P4/nmm and $a=4.011(2)$ and $c=8.261(3)$ Å with final $R/R_w=6.4/6.9\%$. The superstructure with $a_{super}=2a$, $b_{super}=6b$ and $c_{super}=2c$ was found. The measurements of electronic and magnetic properties of this compound indicate that it is an electronic insulator and diamagnet.

Introduction

Layered transition-metal dichalcogenides have been extensively studied for their interesting low-dimensionality and resulting anisotropic properties.^{1,2} Many phases of layered structures lead to rich intercalation chemistry with many potential applications. The electronic and magnetic properties of some dichalcogenide MX₂ (M=V, Nb, Ta, X=chalcogen), especially d^1 compounds, are closely related to structural transitions. It has been known that the structural transition in d^1 transition metal dichalcogenides is related with CDW (Charge Density Wave) instability and the single d -electron coupled with two-dimensional character was found to be the driving force for CDW.^{3,4}

However, rare earth compounds such as DySe₂ and GdSe₂ are inverse analogies of d^1 transition metal dichalcogenides, since there is one hole in Se p -band. Many rare earth diselenides and ditellurides display nonstoichiometry owing to deficiencies of chalcogen sites. Some supercells⁵ due to the ordering of chalcogen vacancies in this nonstoichiometric compounds were also reported. In a previous study, an incommensurate superstructure in DySe_{1.83} was found and it was assigned to be the CDW type.⁶

During the investigation of YSe system to find new low-dimensional compounds, a new phase, YSe_{1.83}, was found. The structure of YSe_{1.83} is closely related to LaTe₂ and NdTe₃.⁷ The structure of NdTe₃ can be described as consisting of two-atom thick layers of NdTe with distorted NaCl-type and

two-atom thick layers of Te with sequence of layers along the c axis being ... Te NdTe, NdTe, Te, Te, NdTe, NdTe, Te However, the LaTe₂ structure consists of the sequence of layers, ... Te LaTe, LaTe, Te, LaTe, LaTe, Te It has been known that the LaTe₂ phase displays a solid solution region up to near LaTe_{1.7} and that there is the tellurium deficiency resulted from the removal of Te from pure tellurium layers.

In the Weissenberg and rotation photographs of the titled compound, superstructure reflections were indicated, but these reflections were not strong enough to refine structure. Thus, only the substructure is reported in this work. The electronic and magnetic properties are also reported.

Experimental

Sample of overall composition Se/Y=1.83 was prepared directly from elemental yttrium (99.9% Strem Chemicals) and selenium (99.999% Aldrich chemicals). The mixture of two elements was sealed in a evacuated quartz tube and heated at 800 °C for two weeks. The product obtained was homogeneous platelike polycrystals with reddish metal luster.

Single crystals of YSe_{1.83} were grown by chemical vapor transport technique with iodine. The starting elements, yttrium and selenium with the ratio of Se/Y=2.0, and iodine (~1 mg/cm³) were sealed in a evacuated quartz tube, which then were placed in a two-zone furnace with temperature gradient of 30 °C. The starting materials were placed at high

temperature end. The sample was heated at 800 °C for 2 weeks and then cooled to 400 °C with the rate of 2 °C/hr. Rotation and Weissenberg (Cu K α radiation) photographs were taken to check the crystallinity, lattice type and cell parameters of superstructure. All the measurements for the structural refinement were made on a Enraf-Nonius CAD4 X-ray diffractometer with graphite monochromated Mo K α 1 radiation ($\lambda_1=0.7093$ Å). Data collection and structural refinement were performed with the aid of SHELEX-93 crystallographic software package. And the cell parameter was determined by the least-square type analysis using reflections observed in 2θ range of 30°-50°.

Powder X-ray diffractometer data were taken using a Siemens X-ray diffractometer and Fe filtered Co K α radiation. Diffraction data were analysed using Rietveld-type full profile refinement technique.⁸ Electrical resistivity measurements were made for single crystals and pressed pellets of bulk YSe_{1.83} using standard four-probe technique.

Electrical contacts to the sample were made with indium for the pellets and silver paste for the single crystals. The magnetic susceptibility was measured at room temperature using Guoy balance.

Combustion analysis was carried out at 800 °C by oxidizing YSe_{1.83} and weighing the final product Y₂O₃.

Results and Discussion

A plate shaped crystal having dimensions of 0.235×0.250×0.023 mm³ was mounted on a glass fiber with epoxy cement. Weissenberg and rotation photographs indicated a very weak superstructure reflections corresponding to $a_{super}=2a$, $b_{super}=6c$ and $c_{super}=2c$. The cell parameters and orientation matrix for data collection obtained from the least-square method in the range of 30°< 2θ <50°, corresponded to a tetragonal unit cell with $a=4.011(2)$ and $c=8.261(3)$ Å. The reflections from superstructure were too weak to determine the structure, thus only substructure was determined here.

A data set was collected on the tetragonal subcell by using $\omega-2\theta$ reflections with 3°< 2θ <60°. Based on the obtained systematic absences ($h+k$: $h+k=2n+1$ absent), the space group was determined and found to be P4/nmm. Atomic scattering factors for neutral atoms were taken from "International table of x-ray crystallography". An empirical absorption correction was applied on the basis of ψ scans. Intensities of standard reflections did not decay throughout data correction. Yttrium and selenium atoms were located using direct methods. Previously reported DySe_{1.85} structure was used in devising structural models for refinement.⁷ Details of X-ray data collection and information about the structure determination are given in Table 1.

The isothermal parameters of selenium and yttrium atom in the distorted NaCl-layer were acceptable values and the occupation factors did not deviate from unity within standard deviation, thus its value was fixed at unity. The anomalously large isothermal parameters were found for Se(2) atoms in the square sheets, and refinement reached to 83% occupancy with minimum R_w value. The anisotropic thermal ellipsoids of Y(1) and Se(1) in the distorted NaCl-layers were found to be elongated along the c -direction. However, the thermal ellipsoid of Se(2) in Se sheets was flattened in the c -direction (Figure 1). Of the several possible distortions from ideal $\bar{4}m\bar{2}$

Table 1. Summary of the Structure of YSe_{1.83} Crystal Data, Intensity Collection and Refinement

Crystal shape	Flat plate
Crystal volume (mm ³)	0.235×0.250×0.023
Radiation	Mo K α_1 ($\lambda=0.7093$ Å)
Determination of cell parameters	
no. of reflections used	20
θ range (degree)	1.5-30.0
Cell parameters at room temp.(Å)	$a=4.011(2)$ $c=8.261(3)$
Space group	P4/nmm
Z	2
Calculated density (g/cm ³)	6.168
Intensity data collection	
Scan mode	$\omega-2\theta$
Standard reflections	110, $\bar{1}10$, 112, $\bar{1}\bar{1}2$
Unique reflections ($F>2\sigma(F)$)	212
Linear absorption coeff. (cm ⁻¹)	490.7
Transmission	0.142-0.770
Structure refinement	
no. of parameters refined	12
R	0.064
R_w	0.069

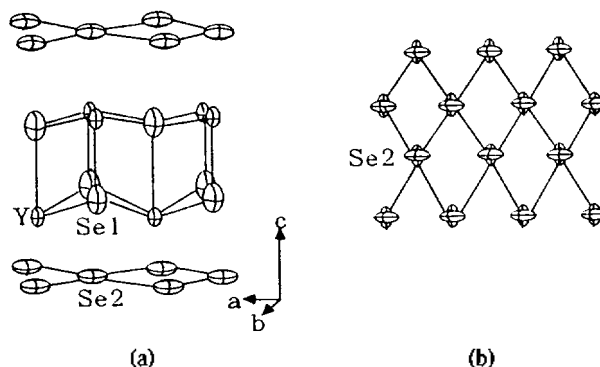


Figure 1. (a) The substructure of YSe_{1.83}. (b) Single sheet of Se(2). In (a), for clarity, the Se(2) atoms are drawn as flattened thermal ellipsoids, in (b) the reported thermal ellipsoids are shown.

symmetry site, the thermal ellipsoid of Se(2) in Se square sheets was found to be distorted along either a or b direction and this result was consistent with the previous report on DySe_{1.85}.⁶ Such distortions indicate a shift of Se position away from any Se-Se bonds, thus this feature excludes the possibility of Se-Se dimerization in Se square sheets as previously observed in some rare earth dichalcogenides.

There are two types of Se and one type of Y (Table 2). Each Se(1) has five nearest neighbors, at 2.945(4Y) and at 2.945 Å (1Y). Each Y is surrounded by nine nearest neighbors at 2.945 Å (4Se(1)), 2.970 Å (1Se(1)) and 3.014 Å (4Se(2)). The seleniums contacting the basal plane are considerably shorter than the other Se-Se distances and this indicates that these seleniums have considerably strong metallic-covalent character (Table 3). If the ionic radius for Se²⁻ is taken as 2.2 Å and the metallic radius is taken as 1.4

Table 2. Refined Atomic Positions, Fractional Occupancies and Thermal Parameters (\AA^2) of $YSe_{1.83}$

Atom	Position	x	y	z	Occupancy	U_{11}	U_{22}	U_{33}
Y	2c	0.25	0.25	0.7277(4)	1.00	0.0056(9)	0.0056(9)	0.036(2)
Se1	2c	0.25	0.25	0.3682(3)	1.00	0.0056(8)	0.0056(8)	0.021(4)
Se2	2a	0.25	0.75	0.00	0.415(1)	0.16(1)	0.027(4)	0.010(2)
Se2'	2a	0.25	0.75	0.00	0.415(1)	0.027(4)	0.16(1)	0.010(2)

Table 3. Interatomic Distances of $YSe_{1.83}$ (\AA)

Y-1Se(1)	2.970(4)
Y-4Se(1)	2.945(3)
Y-4Se(2)	3.014(2)
Se(2)-4Se(2)	2.836(2)
Se(1)-4Se(2)	3.644(2)

Table 4. Summary of the Structure of $YSe_{1.83}$ from Powder X-ray Diffraction Data Refinement by Rietveld Analysis

		Atomic position	% Occupancy
Y(1)	2c	(1/4, 1/4, 0.3713(7))	84
Y(2)	2c	(1/4, 1/4, 0.8571(5))	100
Se(1)-1	2c	(1/4, 1/4, 0.1809(7))	84
Se(1)-2	2c	(1/4, 1/4, 0.6888(5))	100
Se(2)-1	2a	(1/4, 3/4, 0)	80
Se(2)-2	2b	(1/4, 3/4, 1/2)	53
Temperature factor (\AA^2)			0.3009

$R_w=3.55\%$, $R=2.66\%$, space group: $P4/nmm$, cell parameters (\AA): $a=4.011(2)$, $c=16.485(5)$

\AA , the bonding can be considered as about 70% metallic-covalent.⁵ These results are consistent with the results of the $LaSe_2$ and $ErSe_2$ -type compounds. It has been known that infinite chalcogen sheets play an important role in these materials. Previously, the selenium dimers, Se^{2-}_2 in $RuSe_2$ were observed in Raman experiments.⁹ In the disulfides such as LaS_2 and pyrite, the sulfur sheets are distorted to form insulating S^{2-}_2 dimers.¹⁰ In ditellurides metallic structures are generally built up from cubes or square sheets of Te atoms, and such tellurim sheets are not distorted and their electrical properties are metallic.¹¹ It has been known that the resistivity of $LaTe_3$ is 0.3-0.7 of $LaTe_2$, rationalizing the metallic properties originated from Te sheets.⁷ The square sheets of Se atoms found in $DySe_{1.85}$ are expected to have compromised properties between distorted insulating dimers and undistorted metallic infinite sheets.

Starting with the substructural information obtained above, the powder patterns were analysed using Rietveld-type refinement technique. The powder diffraction pattern for this phase could be indexed with tetragonal unit cell of $a=4.0121$ \AA $c=16.485$ \AA . The superstructure reflections indicated doubled unit cell c . The space group $P4/nmm$ was also valid in the powder pattern. In this refinement, scale factor, zero point, back ground parameters, cell parameters and atomic positions were the variables (Table 4). The result of powder X-ray analysis on site occupancies was different from that

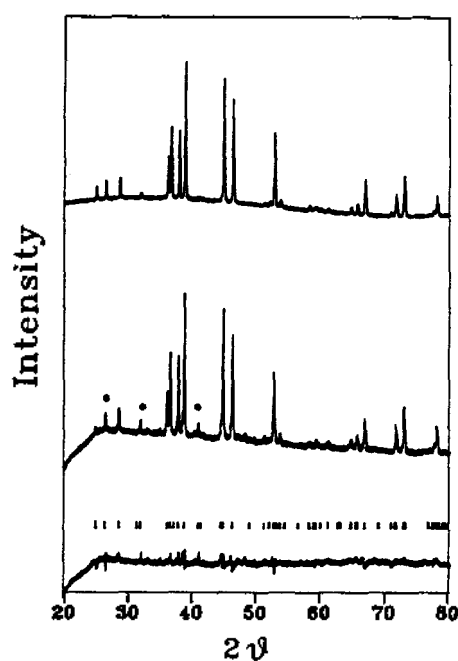


Figure 2. The Rietveld refinement results for $YSe_{1.83}$. Comparison of the calculated pattern (top) and the observed pattern (below). Vertical strokes indicate calculated Bragg peak positions. Bottom lines indicate the difference between the observed and calculated patterns. $R_w=4.5\%$, $a=4.011(2)$ and $c=16.485(5)$ \AA , space group= $P4/nmm$. Star marks represent the superstructure reflections.

obtained from the single crystal analysis. The occupancies in two repeating Se layers in the unit cell appear to be a little different, and also partial occupancies on Y and Se in YSe layers were revealed (Figure 2). Star marks in Figure 2. represent the superstructure reflections and the peak at 26.5° (2θ) was especially sensitive to the concentration of the vacancies on the YSe layers. The composition calculated from powder X-ray refinement result was in good agreement with the composition obtained from the combustion analysis ($YSe_{1.76 \pm 0.03}$ vs. $YSe_{1.77 \pm 0.02}$).

The resistivity measurement was carried out for single crystal and the property of this material was found to be an insulator. The magnetic susceptibility measurements showed diamagnetism ($\chi = -4.3 \times 10^{-7}$ emu/g). The insulating property seems to be originated from the ordering in defect Se sheet.

In summary, single crystal of $YSe_{1.83}$ was prepared by vapor transport technique and its crystal structure was determined. The structure was isostructural of $LaTe_{2.4}$, which is a layered structure consisting of two-atom thick distorted

NaCl-type layers of YSe and one atom thick layer of Se. The substructure of $\text{YSe}_{1.83}$ is tetragonal with $P4/nmm$ symmetry with $a=4.011(2)$ and $c=8.261(3)$ Å with final $R/R_w=6.4/6.9\%$. The superstructure with $a_{\text{super}}=2a$, $b_{\text{super}}=6b$ and $c_{\text{super}}=2c$ was found. The complicated superstructure reflections observed in Weissenberg photograph suggested the further ordering within Se layers.

In the powder X-ray diffraction analysis, the superstructure with $a_{\text{super}}=a$, $b_{\text{super}}=b$ and $c_{\text{super}}=2c$ was found and the occupancies in two repeating Se layers in the unit cell appear to be a little different, and also partial occupancies on Y and Se in YSe layers were revealed. The measurements of electronic and magnetic property indicate that this compound is an electronic insulator and diamagnet.

Acknowledgment. The present study was supported by the Korean Science and Engineering Foundation (92-25-00-02) and in part by the Basic Science Research Institute Program, Ministry of Education, BSRI-94-3413. We thank professors Young-Ja Park and Soon-Won Lee for helping with X-ray single crystal experiments.

Supplementary Material Available. Tables of observed and calculated structure factors for $\text{YSe}_{1.83}$ (2 pages) will be sent, when they are requested to the author.

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Template Synthesis of New Nickel(II) Complexes of 14-Membered Pentaaza Macrocyclic Ligands: Effects of C-Alkyl and N-Hydroxyalkyl Pendant Arms on the Solution Behaviors of the Complexes

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Received February 17, 1995

New square planar nickel(II) complexes with various 1-alkyl (**4a-4c**) and 1-hydroxyalkyl (**4d-4f**) derivatives of the 14-membered pentaaza macrocycle 8-ethyl-8-nitro-1,3,6,10,13-pentaazacyclotetradecane have been synthesized by two-step metal template condensation reactions of ethylenediamine, nitroethane, formaldehyde, and appropriate primary amines. The nitro group and/or hydroxyl group of **4a-4f** are not directly involved in the coordination. The nickel(II) complexes exist in coordinating solvents such as MeCN, Me_2SO , and H_2O as equilibrium mixtures of the square planar $[\text{Ni}(\text{L})]^{2+}$ ($\text{L}=\mathbf{4a-4f}$) and octahedral species $[\text{Ni}(\text{L})\text{S}_2]^{2+}$ ($\text{S}=\text{solvent molecule}$). Although the ligand field strength and redox potentials of the complexes are not affected by the nature of the substituents, the formation of octahedral species for **4d-4f** in MeCN is strongly restricted by the hydroxyl group. Synthesis, characterization, and solution behaviors of the nickel(II) complexes are described.

Introduction

Since properties of polyaza macrocyclic ligands and complexes are closely correlated with their structural characteristics, a variety of research has concerned the synthesis of

new types of such compounds. Especially, macrocyclic compounds with functional pendant arms such as hydroxyalkyl group have received much attention, because the introduction of a functional group into a macrocyclic compound often causes a considerable change in chemical properties.¹⁻⁶