literature.[11] Although this ion is often found to be asymmetric, the present structure requires crystallographic $2/m$ site symmetry. It is possible that there is some disorder in the lattice at the triiodide sites, concomitant with the disorder observed for the cation. As noted in the Experimental Section, the final difference Fourier map showed residual electron density in that region. Trial refinements in both centric and acentric space groups were unable to establish this possibility, however.

As discussed previously,[1] the $\mathrm{Mo{=}O}$ stretching bands in the solid-state infrared spectra of $[\mathrm{MoOCl(CNCH_3)_4}](\mathrm{I_3})$ and related compounds are split, a result that was ascribed to nonequivalent site symmetries. The present structure is consistent with (but does not prove) that explanation since random disorder of the oxygen and chlorine atoms in the lattice could produce different local environments for the $\mathrm{Mo{=}O}$ oscillator. If the structure were ordered in Im, only one $\mathrm{Mo{=}O}$ stretching frequency would be expected.

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Registry No. $[\mathrm{MoOCl(CNCH_3)_4}](\mathrm{I_3})$, 50432-36-5.

Supplementary Material Available: Table S1 listing observed and calculated structure factor amplitudes and Table S2 giving root-mean-square amplitudes of thermal vibration (6 pages). Ordering information is given on any current masthead page.

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Two New Compounds in the Ternary System Germanium–Arsenic–Selenium[1]

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In the framework of investigations about crystallization of melts in the ternary system Ge–As–Se we became interested in the preparation of ternary compounds. Vinogradova et al.[2] obtained two crystalline phases by annealing glasses with compositions near Ge:As:Se = 1:1:1. Dta measurements indicated that one was a defined compound at or near the 1:1:1 composition. However, no single-crystal work was reported, probably because it is difficult to prepare crystals of ternary compounds from their melts.

Results and Discussion

Single crystals of GeAsSe and $\mathrm{GeAs_4Se}$ (the stoichiometric formulas were determined by electron microprobe analyses) were prepared by a solid–vapor phase reaction of GeSe and As, sealed in evacuated silica ampules, at temperatures between 580 and 600 °C.

When GeSe and As were heated with a 1:1 stoichiometry at 580 °C for 2 h, we obtained only crystals of GeAsSe as reaction product. Two different compounds, GeAsSe and $\mathrm{GeAs_4Se}$, resulted when excess arsenic was present in the reaction ampule. Finally, a reaction of GeSe and As with a 1:4 stoichiometry at a temperature of 600 °C for at least 12 h yielded mainly $\mathrm{GeAs_4Se}$.

Powder patterns of both compounds were taken. Neither one agreed with those reported by Vinogradova et al.[2] although their data from differential thermal analysis were in agreement with those we took from GeAsSe. Our thermogram of GeAsSe shows a beginning of the melting at a temperature of 617 °C. On cooling (10 °C/min) no exothermic peak due to crystalline solidification was observed. By reheating, a glass transformation step appeared at a temperature of about 400 °C. On further heating, no recrystallization or melting peaks were observed. The thermogram taken of $\mathrm{GeAs_4Se}$ shows an endothermic peak beginning at 645 °C (solidus temperature) and a second one ending at 747 °C (liquidus temperature).

Weissenberg and Buerger precession photographs of both compounds were taken. The diffraction symmetry was mmm for GeAsSe, and the systematic absences were $0kl$, $k + l = 2n + 1$, $h0l$, $h + 1 = 2n + 1$, and $hk0$, $h = 2n + 1$, consistent with the space group $Pnna$ (No. 52). The cell parameters, obtained from x-ray photographs, were $a = 5.07$ Å, $b = 10.12$ Å, and $c = 11.69$ Å with $Z = 8$. For $\mathrm{GeAs_4Se}$ the diffraction symmetry was $2/m$ and the systematic absences were $00l$, $l = 2n + 1$, indicating the space groups $P2_1$ (No. 4) or $P2_1/m$ (No. 11). The cell parameters, also obtained from film data, were $a = 12.37$ Å, $b = 6.57$ Å, $c = 3.59$ Å, and $\gamma = 101°$ with $Z = 2$.

The compound GeAsSe seems to have a marked tendency to twin which made it difficult to find single crystals of a quality suitable for x-ray measurements. Another difficulty arises from the mechanical properties of both compounds. GeAsSe crystallizes as platelets, which show a distinct sheet splitting. These platelets are highly sensitive to mechanical deformations, and when touched, they very easily bend plastically. $\mathrm{GeAs_4Se}$ crystallizes as thin "laths", which show an extreme fiber splitting when stressed.

The optical properties also help to distinguish the two compounds. $\mathrm{GeAs_4Se}$ is opaque and a grayish and has a metallic shine in reflecting light. GeAsSe also has a metallic luster in reflecting light but appears red in transmitting light. If polarized light is transmitted perpendicularly to the plane of the platelet, the optical properties of GeAsSe are in agreement with the symmetry proposed.

Registry No. GeSe, 12065-10-0; As, 7440-38-2; GeAsSe, 12344-64-8; $\mathrm{GeAs_4Se}$, 58228-76-5.

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