Lattice parameter and stoichiometric variations in CdSe

Compound semiconductors and careful characterization of their properties as a function of variations of composition are major concerns of the solid-state technologist. Lattice parameter measurements provide one means of detecting large variations of stoichiometry.

Lattice parameters of synthetic cadmoselite have been measured by many workers as shown in Table I. Since thermodynamic studies [11. 12] indicate a relatively narrow range of stoichiometry (significantly less than 1%) one would not expect such widely varying results for what should be an accurate parameter. Because of the pioneering work in experimental methods as initiated by Straumanis and Ievins [13] accurate data can be routinely recorded for the subsequent calculation of the lattice parameters. In an attempt to clarify the differences found for the lattice parameters of CdSe, I have applied the Bradley–Jay method of parameter calculations as well as varied the chemical stoichiometry of the CdSe samples. Since the parameter of silicon has been accurately determined it is a good material for a secondary test of the calculation methods.

Fine powder of Eagle-Picher ultrapure 99.99+% CdSe was placed in a transparent fused-silica capsule. Two additional capsules were filled with similar CdSe and 0.005 mole excess zone-refined cadmium and CdSe plus 0.005 mole excess 99.995% pure selenium respectively. Two fused silica plugs, $\frac{1}{2}$ in. long, were inserted in each capsule and each capsule was then sealed at the top plug under vacuum after purging twice with cp argon. The capsules were heated at 622–3° C for 500 h and water quenched. The material was sieved through a 325 mesh screen without mortaring. The silicon used had less than 200 parts per million total impurities. Analysis of all materials made independently after heat-treatment revealed no significant changes in impurity concentrations.

TABLE I Room temperature lattice parameters of cadmoselite

a_0 (Å)	c_0 (Å)	Temperature (° C)	References
4.31(1)	7.02(2)	RT	[1]
4.31	7.03	RT	[2]
4.299	7.010	25	[3]
4.28	7.00	RT	[4]
4.285	6.993	RT	[5]
4.308 6	7.024	RT	[6]
4.291(1)	7.03(3)	RT	[7]
4.309	7.034	RT	[8]
4.297 2(3)	7.006 5(50)	RT	[9]
4.305 52	7.025 3	RT	[10]
4.299 9(10)*	7.010 9(15)*	24	This work

*Three standard deviations.

Copper $K\alpha$ X-rays ($K\alpha_1 = 1.540\,50$ Å, $K\alpha_2 = 1.544\,34$ Å) and cobalt $K\alpha$ X-rays ($K\alpha_1 = 1.788\,96$ Å, $K\alpha_2 = 1.792\,79$ Å) with two standard 114.5 mm diameter Debye-Scherrer cameras and a 340 mm diameter Van Arkel camera were used in the experiments. The 340 mm diameter camera was found useful for the resolution and correct indexing of the complicated back-reflection region of CdSe.

During the X-ray exposures, camera temperatures were monitored at short intervals using attached laboratory thermometers. The temperature was constant within 1° C for all nine CdSe exposures.

Bradley and Jay [14] have illustrated refinement calculations in their comprehensive paper concerned with lattice parameters and the various errors associated with their calculation. A similar method with least-squares refinement was programmed on an IBM 7094 computer for earlier work [15, 16] and for these results.

Lattice parameters for CdSe as shown in Table I are in good agreement with the results of Swanson *et al.* [3]. Reasonable agreement is also found with earlier workers [1, 2]. Earlier results would be expected to be of lower accuracy as back-reflection profiles were not utilized. Cook [17] has indicated that his sample contained a 2.7% sulphur impurity. This would account for the smaller lattice parameters obtained in his study.

In this work, the relatively long heat-treatment plus the fact that excess constituents were found in their respective capsules after heat-treatment would indicate that equilibrium in a closed system was obtained at 622° C. This temperature is in the range where deviations from stoichiometry are most significant [11]. Table II illustrates the lattice parameters of samples with varying composition. These parameters, within their accuracy of measurement, $\sigma_a = 0.0003$ Å and $\sigma_c = 0.0005$ Å, point to a very narrow range of stoichiometry as indicated

TABLE II Lattice parameters of cadmoselite

a_0 (Å)	c_0 (Å)	Temperature (° C)	Composition before heat-treatment
4.2999	7.0110	24	CdSe + 0.005M excess Cd
4.2999	7.0115	24	CdSe + 0.005M excess Se
4.3000	7.0100	24	CdSe no excess

by thermodynamic studies [11, 12]. The divergent results of other workers can then most probably be explained by impurities such as sulphur, a possible mis-indexing of the very complicated back-reflection region, or possibly effects of polytypism and stacking faults introduced by sample grinding. Yu and Gielisse [18] have indicated that such effects can occur in CdSe after pressure treatment.

The silicon result, the average of four films corrected for thermal expansion to 25° C [19], of 5.430 60 Å [18] is in excellent agreement with other workers [19, 20].

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ROBERT R. REEBER
Institut fur Kristallographie,
Rhein.–Westf. Techn. Hochschule Aachen,
51 Aachen, Germany

* Present address: c/o A. Gross, 3379 South Stafford St., Arlington, Va 22206, USA.