(8) Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., Van Nostrand, New York, 1946.
(9) Hammett, L.P., *Chem. Revs.* **17**, 125 (1935).
(10) Hammett, L.P., "Introduction to the Study of Physical Chemistry," p. 323, McGraw-Hill, New York, 1952.
(11) Jaffé, H.H., *Chem. Revs.* **53**, 191 (1953).
(12) King, E.J., "Acid-Base Equilibria," Chap. 7 and 8, Pergamon Press, New York, 1955.
(13) Sprengling, G.R., Lewis, C.W., *J. Am. Chem. Soc.* **75**, 5709 (1953).
(14) Somers, B.G., Gutowsky, H.S., *Ibid.*, **85**, 3065 (1963).

RECEIVED for review February 10, 1966. Accepted September 12, 1966.

Preparation and Single-Crystal Growth of Anhydrous $RbMnCl_3$ and $CsMnCl_3$

M. KESTIGIAN, W. J. CROFT, and F. D. LEIPZIGER
Sperry Rand Research Center, Sudbury, Mass.

The formation of anhydrous $RbMnCl_3$ and $CsMnCl_3$ was confirmed by chemical analysis. Large, optical-quality single crystals were prepared by the temperature gradient and vertical Bridgman methods by utilization of an evacuated sealed ampoule technique. X-ray powder diffraction data obtained at room temperature indicate $RbMnCl_3$ and $CsMnCl_3$ to exhibit hexagonal symmetry with $a = 7.164$, $c = 17.79_8$, and $a = 7.288$, $c = 27.44$ A., respectively.

THE existence of $RbMnCl_3$ was first reported by Natsvlishvili and Bergman (*3*), who examined the liquidus line of the $RbCl$-$MnCl_2$ system. Gramakov (*1*) investigated the $RbCl$-$MnCl_2$ system and presented data that did not agree with the previous research. A more recent study of the $RbCl$-$MnCl_2$ and $CsCl$-$MnCl_2$ systems reports the formation of compounds of molar ratios 1:1, 2:1, and 3:2; and 1:1, 2:1, 3:1, and 1:4, respectively (*2*). The single-crystal growth and characterization of the anhydrous compounds $RbMnCl_3$ and $CsMnCl_3$ have not been reported previously.

EXPERIMENTAL

Anhydrous $RbMnCl_3$ and $CsMnCl_3$ were prepared by heating an intimate equimolar mixture of the respective alkali metal chloride and manganous chloride tetrahydrate in an atmosphere of dry hydrogen chloride transported by purified argon carrier gas. The sample, contained in a platinum vessel, was heated slowly to above its melting point and the temperature maintained for 2 hours. Single crystals were prepared by the vertical Bridgman and temperature gradient methods utilizing an evacuated sealed ampoule technique. Nominally a 100° C. temperature gradient between the hot and cool temperature zone and a travel rate of 1.5 mm. per hour were used. The single crystals were program cooled 20° per hour to room temperature to eliminate or minimize thermal shock effects.

ANALYSIS

Samples were weighed and dissolved in water. The chlorine was precipitated as $AgCl$, dried at 110° C., and weighed. The alkali metal cations were precipitated with tetraphenylboron, dried, and weighed. The manganese was determined titrimetrically with permanganate. Analysis. Calculated for $RbMnCl_3$: Rb, 34.6; Mn, 22.2; Cl, 43.2. Found: Rb, 35.1; Mn, 22.3; Cl, 43.4. Calculated for $CsMnCl_3$: Cs, 45.1; Mn, 18.7; Cl, 36.2. Found: Cs, 44.7; Mn, 19.1; Cl, 36.2.

CRYSTALLOGRAPHY

Because of the extremely hygroscopic nature of these materials, x-ray diffraction data were obtained by loading the powdered sample into a capillary which was then sealed with paraffin. The powdered samples were prepared by carefully grinding single crystalline material. These procedures were carried out in a purified nitrogen dry box. The preliminary x-ray powder diffraction patterns were obtained using $CuK\alpha$ radiation and a 114.6-mm. Debye camera. The final data were taken with a Norelco high-angle diffractometer. The x-ray powder pattern for $RbMnCl_3$ was indexed on the basis of a hexagonal unit cell with $a = 7.164$ A. and $c = 17.79_8$ A. ($c/a = 2.484$). The density was measured in toluene on a modified Berman balance and found to be 3.10. The theoretical density of a hexagonal unit containing six units of $RbMnCl_3$ was calculated to be 3.107. The hexagonal unit cell parameters for $CsMnCl_3$ are: $a = 7.288$ A. and $c = 27.44$ A.

The density was measured to be 3.48 grams per cc., which agrees with the calculated density for 9 $CsMnCl_3$ units in the provisional cell. The x-ray powder diffraction data for $RbMnCl_3$ and $CsMnCl_3$ are presented in Table I. The data were indexed on the basis of the two proposed unit cells. These crystallographic results are tentative and require further investigation.

Melting point determinations were made by use of a polarizing microscope equipped with a heating stage. The heating chamber was flushed continuously with helium that had passed through a trap cooled with liquid nitrogen. Small (0.1-mm.) single crystalline samples were rested directly on a transparent fused silica disk which was heated from below by a platinum coil. A Pt-Pt-13% Rh thermocouple was placed in direct contact with the disk and was calibrated against substances of known melting points. A melting point of 571° ±5° C. was determined for $RbMnCl_3$, and a melting point of 617° ±5° C. was found for $CsMnCl_3$. These values are somewhat higher than the corresponding values reported by Markov and Chernov (*2*). A possible explanation of the higher melting points observed in this investigation is the purity of the respective alkali metal chlorides. The starting materials and final products were analyzed spectroscopically and found to be at least 99.9% pure. When small amounts of one alkali metal cation were substituted for another, the melting point of the product was lower than that observed for the pure compound. These experiments, together with the fact that the alkali metal raw materials obtained from several suppliers were analyzed and rejected because of the presence

Table I. X-Ray Data for $RbMnCl_3$ and $CsMnCl_3$

(CuK_α = 1.5405 A.)

$RbMnCl_3$		$CsMnCl_3$	
$d_{obsd.}$, A.	I/I_0	$d_{obsd.}$, A.	I/I_0
5.86	9	4.65	19
4.28	11	4.137	47
3.613	25	3.645	100
3.578	62	3.326	8
3.087	10	3.138	19
3.053	21	3.076	17
2.966	18	3.048	19
2.929	28	3.011	10
2.747	47	2.869	71
2.543	100	2.736	83
2.352	11	2.514	8
2.338	28	2.458	20
2.097	4	2.321	25
2.074	17	2.255	5
2.069	16	2.189	17
1.967	14	2.105	39
1.958	9	2.071	15
1.807	12	2.039	5
1.791	22	2.000	3
1.723	4	1.958	8
1.667	8	1.870	2
		1.823	45
		1.800	7

of extraneous alkali metal cations, would appear to confirm this explanation.

Optical studies revealed both compounds to be uniaxial positive. Refractive indices were determined to be: $RbMnCl_3$, n_ϵ 1.700, n_ω 1.688; $CsMnCl_3$, n_ϵ 1.720, n_ω 1.692, as measured by the immersion method. Under microscopic examination, crystals of both compounds are colorless. The bulk color of the cesium compound is red, while that of the rubidium compound is orange.

ACKNOWLEDGMENT

The authors thank R. E. England and F. G. Garabedian, who assisted in the single-crystal growth, and R. J. Guidoboni, who assisted in the chemical analysis.

LITERATURE CITED

(1) Gramakov, S.D., *Zhur. Fiz. Khim.* **24**, 641 (1950).
(2) Markov, B.F., Chernov, R.V., *Ukrain. Khim. Zhur.* **24**, 139–42, 143–5 (1958).
(3) Natsvlishvili, E.R., Bergman, A.G., *J. Gen. Chem. (USSR)* **9**, 642 (1939); Landolt-Börnstein, II-3, pp. 105, 186, 267.

RECEIVED for review March 3, 1966. Accepted September 1, 1966.

High Temperature Heat Contents of Three Alpha Brass Alloys

Y. A. CHANG[1] AND R. HULTGREN
Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Mineral Technology, College of Engineering, University of California, Berkeley, Calif.

High temperature heat contents of three alpha brass alloys containing 19.8, 29.1, and 34.2 atom % zinc were measured from 300° to 810° K., using a diphenyl ether drop calorimeter. The results show that C_p measurements of Kussmann and Wollenberger are much too high but do not contradict the small anomalies they found. Tables of heat capacities and heat contents were prepared which show anomalies of approximately the same size, agree with the present heat contents, and extrapolate to the low-temperature values.

DATA on heat contents above room temperature of alpha brass alloys are contradictory. C_p measurements of Kussmann and Wollenberger (*6*) show small, well-defined anomalies near 500° K. which they interpret as being due to disordering processes. However, their values are too high to join smoothly with Huffstutler's (*2*) low-temperature measurements, and integration of their C_p values gives heat contents higher than those determined by Ruer and Kremers (*7*). In each case, the discrepancy is large—approximately 8%. Measurements of an alpha brass containing 9.7 atomic % zinc by the present authors (*1*) agreed with Huffstutler and disagreed with Kussmann and Wollenberger. It was decided to extend the measurements to higher zinc alpha brasses.

EXPERIMENTAL

Chemical analyses of the three alpha brass samples are shown in Table I. Metallographic examination showed the presence of a single well-annealed alpha phase.

Heat contents (300° to 800° K.) above room temperature were determined in a diphenyl ether drop calorimeter described elsewhere (*3*, *5*). Samples consisting of single pieces weighing about 0.7 gram were wrapped in platinum foil so that the heat loss during the drop would be uniform and correctible. Heat given off during cooling in the calorimeter melted some of the diphenyl ether at its melting point, 300° K. The amount melted was determined by the expan-

Table I. Chemical Analyses of Alpha Brass Alloys, Wt. %

	Alloy No.		
	1	2	3
Cu	79.75	70.42	65.18
Sn	0.00	0.045	0.000
Pb	0.003	0.05	0.001
Fe	0.015	0.02	0.002
Ni	0.01	0.02	0.002
Bi	. . .	0.000	0.000
Zn	20.22	29.445	34.815

---

[1] Present address: Materials Research Laboratory, Aerojet-General Corp., Sacramento, Calif.