ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2009, Vol. 54, No. 6, pp. 840–841. © Pleiades Publishing, Inc., 2009.
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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

X-Ray Diffraction Study of $CsZn_2Br_5$

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Received April 17, 2008

Abstract—$CsZn_2Br_5$ crystals are studied by X-ray diffraction. The compound crystallizes in the monoclinic system with the unit cell parameters a = 6.8880(12) Å, b = 10.4703(19) Å, c = 6.5197(9) Å, β = 108.25°, V = 446.55 Å^3, ρ_{calcd} = 4.960 g/cm^3. Refractive indices are n_p = 1.640 and n_p = 1.754.

DOI: 10.1134/S0036023609060047

The phase diagram of the $ZnBr_2$–CsBr system was studied in [1, 2], where three compounds were found to exist. Two of them (Cs_3ZnBr_5 and Cs_2ZnBr_4) melt congruently at 530°C and 560°C, respectively; $CsZn_2Br_5$ melts incongruently at 285°C and has two polymorphs with transition temperatures of 215°C at for $ZnBr_2$ percentages higher than 66.67 mol % and 225°C when $ZnBr_2$ percentages are equal to or higher than 66.67 mol %. The Cs_3ZnBr_5 compound crystallizes in the tetragonal system, and Cs_2ZnBr_4 in the orthorhombic system [2]. The $CsZn_2Br_5$ compound was prepared for the first time. There no data on the crystal structure of $CsZn_2Br_5$ in the literature. The aim of this work was to synthesize $CsZn_2Br_5$, grow single crystals of the compound, and determine its crystal structure by X-ray diffraction.

EXPERIMENTAL

The compound $CsZn_2Br_5$ was synthesized from purified cesium and zinc bromides taken in stoichiometric amounts. The $ZnBr_2$ compound was synthesized as described in [3] from zinc cuttings of high purity grade, aqueous hydrobromic acid of pure for analysis grade, and chemically pure grade bromine. $ZnBr_2$ crystals were recrystallized from diluted hydrobromic acid, collected on a glass filter, and dried at 200°C. The cream-colored $ZnBr_2$ crystals obtained were very hygroscopic; because of this, all operations with this compound were performed in a box filled with dry argon. The synthesized $ZnBr_2$ was purified by repeated (four–to sixfold) sublimation under vacuum at 480°C.

Cesium bromide of chemically pure grade was recrystallized from an aqueous solution, which was followed by filtration and dehydration. The impurity level in the purified zinc and cesium bromides was less than 1×10^{-3} wt % as determined by emission spectral analysis.

The synthesis of $CsZn_2Br_5$ was carried out in evacuated (to 10^{-1} Pa) and sealed quartz ampules at 640°C; the melt was stirred for 1 day and cooled with a furnace.

The crystals were grown by zone melting in cone-tipped quartz ampules (of the cone angle was 15°–18°). The temperature of the molten zone was 420°C; the zone movement velocity was 2.7 mm/h. Two passages were performed. As a result, a colorless, transparent block crystal of $CsZn_2Br_5$ was grown. $CsZn_2Br_5$ was a hygroscopic compound, and all operations with were performed in a box filled with dry argon.

The sample obtained was studied by differential thermal analysis (DTA) and X-ray powder diffraction; refractive indices were measured. Differential thermal analysis was performed on an NTR-64 pyrometer with a Pt–Pt/Rh thermocouple and calcined Al_2O_3 as a standard. The heating rate was 8–10 K/min; the error of peak temperature determination was ±5 K. X-ray powder diffraction studies crystals were performed for ground crystals on a DRON-1.0 diffractometer (CuK_α radiation, Ni filter, 2θ scan, 1°/min). The error of the X-ray diffraction measurements was ±3'. To protect hygroscopic $CsZn_2Br_5$ from air humidity, the powdered sample was placed in a Teflon cell covered with a Teflon film 0.01 mm thick. The refractive indices were determined with an MIN-4 polarizing microscope in transmitted nonpolarized light using 98 standard immersion liquids (whose refractive indices were from 1.408 to 1.780). The Becke method was used for comparison of the refractive indices of liquids and immersed grains.

RESULTS AND DISCUSSION

The DTA curve of $CsZn_2Br_5$ displays two peaks at 215 and 285°C. The first of them is assigned to the polymorphic transition in $CsZn_2Br_5$, and the second corresponds to incongruent melting [2].

Observed and calculated X-ray diffraction data for $CsZn_2Br_5$ (low-temperature phase)

Line no.	I, %	d, Å	$\sin^2\theta_{obs}$	$\sin^2\theta_{calcd}$	$\Delta = \sin^2\theta_{obs} - \sin^2\theta_{calcd}$	hkl
1	39	3.9230	0.03856	0.03852	0.00004	101
2	47	3.3590	0.05259	0.05259	0.00000	–201
3	47	3.2160	0.05737	0.05743	–0.00006	–102
4	100	3.0890	0.06219	0.06191	0.00028	002
5	28	2.9690	0.06731	0.06732	–0.00001	012
6	61	2.8290	0.07414	0.07424	–0.00010	–221
7	47	2.0250	0.14470	0.14470	0.00000	013
8	47	1.9180	0.16130	0.16136	–0.00006	–223
9	24	1.8450	0.17431	0.17435	–0.00004	–133
10	28	1.8080	0.18152	0.18152	0.00000	–303
11	25	1.7770	0.18791	0.18791	0.00000	–251
12	22	1.7130	0.20221	0.20233	–0.00012	123
13	28	1.6860	0.20874	0.20872	0.00002	160
14	14	1.5425	0.24938	0.24935	0.00003	–431
15	13	1.5310	0.25314	0.25304	0.00010	014

Reflection positions, their intensities, and interplanar distances d (Å) were found from the X-ray powder diffraction patterns of $CsZn_2Br_5$. The unit cell parameters were calculated using the strongest 15 reflections with the TREOR program. The structure of $CsZn_2Br_5$ was indexed as monoclinic. The space group was chosen from systematic extinctions. Systematic extinctions make the following space groups possible: $C_{2h}^1 = P2/m$, $C_2^1 = P2$, and $C_s^1 = Pm$ [4]. The unit cell parameters are $a = 6.8880 \pm 0.0012$, $b = 10.4703 \pm 0.0019$, $c = 6.5197 \pm 0.0009$ Å; $\beta = 108.25°$, and $V = 446.55$ Å^3. The factors $M = 15$ and $F = 9$ are indicative of a high reliability of the results. The X-ray powder diffraction data found experimentally and calculated for $CsZn_2Br_5$ are compiled in the table.

The X-ray density of $CsZn_2Br_5$ ρ_{calcd} (g/cm^3) was calculated as

$$\rho_{calcd} = ZFWg/V,$$

where Z is the number of formula units per unit cell (two), FW stands for the formula weight of $CsZn_2Br_5$ (663.1854), g is the hydrogen atom weight (1.67×10^{-24} g), and V is the unit cell volume (446.55×10^{-24} cm^3).

The flotation density of $CsZn_2Br_5$ was higher than the density of methylene iodide CH_2I_2 (3.3254 g/cm^3), which suggests that the number of formula units is two. Consequently, the X-ray density of $CsZn_2Br_5$ is 4.960 g/cm^3. The refractive indices of $CsZn_2Br_5$ crystals are $n_p = 1.640$ and $n_g = 1.754$.

To summarize, the conditions for the preparation and single crystal growth of $CsZn_2Br_5$ have been found, an X-ray diffraction study of this compound performed for the first time. The X-ray density of $CsZn_2Br_5$ has been calculated, and the refractive indices determined.

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