Coordinating Compounds

Synthesis and Crystal Structure of Cs₃ZnBr₅


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Abstract—The compound Cs₂ZnBr₅ was synthesized from cesium and zinc bromides. The single crystals were grown by the Bridgman method. The structure of Cs₂ZnBr₅ was studied. The compound crystallizes in the tetragonal system with the unit cell parameters: \(a = b = 9.635(2) \text{ Å}, c = 15.141(5) \text{ Å}, V = 1404.8(6) \text{ Å}^3\). The compound Cs₂ZnBr₅ was not hygroscopic and congruently melts at 530°C; it is transparent at 2.5 to 25 μm. The refractive indices are \(N_p = 1.682\), \(N_g = 1.686\). The microhardness is 560 MPa.

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The first mention of compound Cs₂ZnBr₅ dates back to 1893 [1] when it was obtained by crystallization from aqueous solutions of the appropriate amounts of cesium and zinc bromides. The obtained crystals were not analyzed. Later [2], Cs₂ZnBr₅ was prepared by fusion stoichiometric amounts of CsBr and ZnBr₂ in an evacuated quartz tube. The single crystals were grown by the Bridgman–Stockbarger technique in a conical quartz tube, which was slowly cast in a two-zone furnace (700 and 400°C). The unit cell parameters were determined: \(a = b = 9.653 \pm 0.005 \text{ Å}, c = 15.149 \pm 0.007 \text{ Å}\). The attempts to prepare Cs₃ZnBr₅ from saturated solutions of CsBr and ZnBr₂ were unsuccessful and resulted in isolation of Cs₃ZnBr₅ [3]. Asker et al. [4] reported the synthesis of Cs₃ZnBr₅ by fusing together CsBr and Cs₂ZnBr₅ obtained by crystallization from an aqueous solution [3]. In the study cited [4], Cs₂ZnBr₅ was assigned to the tetragonal system of the Cs₂CoCl₄ structural type, space group \(I4/mcm\). The unit cell parameters of Cs₂ZnBr₅ were determined: \(a = b = 9.639 \pm 0.002 \text{ Å}, c = 15.128 \pm 0.003 \text{ Å}\) [4]. It was assumed [4–6] that some of the compounds \(M_3MBr_4\) (\(M = Rb, Cs, NH₄\); \(X = Cl, Br, I\)) crystallize in the tetragonal system of the Cs₂CoCl₄ structural type, space group \(I4/mcm\). These compounds include Rb₂ZnCl₄, Cs₂ZnCl₄, and Cs₂ZnBr₅. Other compounds, Rb₂ZnBr₅, (NH₄)₂ZnBr₅, and Cs₂ZnI₅, crystallize in the orthorhombic system, (NH₄)₂ZnCl₅ structural type, space group \(Pnma\). The compound Cs₂ZnI₅ was first assigned to the tetragonal system, space group \(I4/mcm\). However, later, in view of single crystal X-ray diffraction data, this compound was assigned to the orthorhombic system, space group \(Pnma\). Rb₂ZnBr₅ structural type, because the measured reflections were at variance with the extinction conditions for space group \(I4/mcm\) [4].

The purpose of this study was to determine the structural type of Cs₂ZnBr₅ and to study some physical, optical, and other properties of this compound. No data on this compound are present in the ASTM card-file.

EXPERIMENTAL

The compound Cs₂ZnBr₅ was studied by differential thermal analysis (DTA), X-ray diffraction analysis, and IR spectroscopy; the refractive indices, microhardness, and density of the compound were determined. DTA was carried out on an HTP-64 pyrometer with a Pt–Pt/Rh thermocouples using calcined alumina as the reference. The heating rate was 8–10 K/min, the temperature effects were determined to an accuracy of ±5 K. The X-ray diffraction study of Cs₂ZnBr₅ was carried out on a Bruker Smart Apex II automated diffractometer (MoKα-radiation, \(\lambda = 0.71073 \text{ Å}\), graphite monochromator, \(\omega\) scan mode, room temperature). The absorption corrections were applied with a set of equivalent reflections (SADABS program [7]). IR spectra were measured on a Specord M80 spectrophotometer for the powdered product as a mineral oil mull. The refractive indices were determined by immersion method on a MIN-4 microscope. The microhardness was measured on a PMT-3 microhardness meter with a 30 g load; the density was determined by hydrostatic weighing of samples in air and in toluene with an error of ±0.001 g/cm³.

The compound Cs₂ZnBr₅ was prepared from purified CsBr and ZnBr₂ taken in a stoichiometric ratio. The method of preparing ZnBr₂ and the methods for purification of zinc and cesium bromides were...
Fig. 1. (a) General view of the structure of $\text{Cs}_3\text{ZnBr}_5$ with layers of two sorts parallel to the (001) plane; (b) three-dimensional view of the structure of $\text{Cs}_3\text{ZnBr}_5$ with designations of all atoms.