
Composite materials in a binary CuBr – SbBr₃ system

Rustam K. Kamilov

Department of Materials Science,
Lomonosov Moscow State University,
Leninskie gory 1/3, 119991 Moscow, Russia
Email: rustamk-99@mail.ru

Nikolay I. Artemiev

Department of Chemistry,
Lomonosov Moscow State University,
Leninskie gory 1/3, 119991 Moscow, Russia
Email: artemievK707@gmail.com

Maqsudjon M. Ibrohimov

Department of Materials Science,
Lomonosov Moscow State University,
Leninskie gory 1/3, 119991 Moscow, Russia
Email: ibrohimov-00@bk.ru

Leonid S. Lepnev

Lebedev Physical Institute of the Russian Academy of Sciences,
Leninskiy prospect 53, 119333 Moscow, Russia
Email: llepn@mail.ru

Alexander V. Knotko

Department of Materials Science,
Lomonosov Moscow State University,
Leninskie gory 1/3, 119991 Moscow, Russia
Email: knotko@inorg.chem.msu.ru

Anastasia V. Grigorieva*

Department of Materials Science,
Lomonosov Moscow State University,
Leninskie gory 1/3, 119991 Moscow, Russia

and

Department of Chemistry,
Lomonosov Moscow State University,
Leninskie gory 1/3, 119991 Moscow, Russia
Email: anastasia@inorg.chem.msu.ru
*Corresponding author

Abstract: Simple bromides of copper and antimony are still in a focus of interest as compounds or products of decomposition of new complex halides for optoelectronics and photovoltaics. Here the interaction of copper(I) bromide and antimony(III) bromide are investigated on heating up to 650°C. No texturing effects are found for both simple bromides, the grains are shapeless and fused together. It has been demonstrated that SbBr₃ releases from the melt resulting in porous ceramic products with lack of antimony to copper. No new additional double bromides are observed in the binary system CuBr – SbBr₃.

Keywords: copper(I) bromide; indium(III) bromide; melt crystallisation; elemental composition; photoluminescence.

Reference to this paper should be made as follows: Kamilov, R.K., Artemiev, N.I., Ibrohimov, M.M., Lepnev, L.S., Knotko, A.V. and Grigorieva, A.V. (2024) ‘Composite materials in a binary CuBr – SbBr₃ system’, *Int. J. Nanotechnol.*, Vol. 21, Nos. 1/2, pp.88–98.

Biographical notes: Rustam K. Kamilov received his Master degree in Materials Chemistry, Physics and Mechanics from Lomonosov Moscow State University in 2017. He then became PhD student at Lomonosov Moscow State University under the supervision of Dr. Grigorieva A.V. He was successfully finished his postgraduate studies in solid state chemistry and is currently preparing to defend his dissertation. His current research is focused on complex bromides for photovoltaic applications.

Nikolay I. Artemiev is a student in the Department of Chemistry of the Lomonosov Moscow state University, Moscow Russia. He synthesised the samples and performed routine PL and UV-vis spectroscopy analysis of the samples discussed. His research interest is focused on synthesis of complex halides and analysis of its spectral characteristics.

Maqsudjon M. Ibrohimov is currently a Master’s student in the Department of Materials Science at Lomonosov Moscow State University, Moscow, Russia. In 2022, he successfully graduated from the Faculty of Natural Sciences of the Branch of Lomonosov Moscow State University in Dushanbe with a degree in “Chemistry, Physics and Mechanics of Materials”. His research interest is the optoelectronic application of lead-free double perovskites.

Leonid S. Lepnev is a Doctor of Physical and Mathematical Sciences (=dr.hab.) and a Leading researcher in P.N. Lebedev Physical Institute, Moscow, Russia. His research interest is focused on the studying of the optical properties of novel materials.

Alexander V. Knotko is a Professor of Faculty of Materials Sciences of Lomonosov Moscow State University (Moscow, Russia). In 2000, he received the PhD degree, and in 2011 – Doctor of Sciences degree in the Moscow

University. His main research interests are related to the chemistry of solids and solid-phase materials. Currently, his group is focused on the research of biomaterials based on calcium phosphates.

Anastasia V. Grigorieva is an Associate Professor in the Department of Materials Science of Lomonosov Moscow State University, Moscow, Russia, and a senior researcher in the Department of Chemistry. In 2004 and 2006 she graduated from the Department of Materials Science as a specialist in chemistry. In 2009, she received a PhD degree in Chemistry performing a thesis on nanotubular and nanocrystalline titania and vanadia. Nowadays, her research interests are focused on nanocomposite materials for optoelectronics, photovoltaics, optical sensors, photonics.

1 Introduction

A keen interest in systems containing copper(I) bromide or antimony tribromide existed due to the active search for new compounds with the highest possible ionic conductivity at room temperature [1]. Later, already in the 19th century, complex halides with perovskite structure reignited great interest as photovoltaic materials, demonstrating an energy conversion efficiency of 25.8% [2]. As part of light emitting diodes (LEDs), complex halides with perovskite-like structure showed external quantum efficiency (EQE) values of 32.8% in a short period of time [3]. Complex halide perovskites have become promising materials for optoelectronics due to their advantageous photovoltaic and tunable light properties, which are due to the wide variability of their compositions, as well as a successful combination of optical and electrical properties [4]. In addition to photoelectronics and photovoltaics, additional applications of such compounds are related to X-ray detection, photodetectors.

Most of the recent works focused on complex halides with perovskite or non-perovskite structure investigate new organic-inorganic compounds and composites. A wide range of new complex halides with a large inorganic cation B and a large organic cation A have been discussed recently in details [5,6].

Materials based on complex halides with low dimensionality (0D, 1D, 2D) of microstructure are of considerable interest. It has been observed that in several fully inorganic and hybrid organic-inorganic halide systems, such as 3D perovskite CsPbX_3 , changes in the anionic composition of the complex halide, crystallite size and particle dimensionality affect the emission colour and efficiency [7]. Moreover, the reduction of structural dimensionality from 3D to zero dimensionality (0D) leads to quantum confinement effects that yield exceptionally high coupled exciton energies [8].

In addition to the search for new compositions with double perovskite structure, there are the study of phase equilibria in halide systems [9] and the search for new composite materials based on complex halides [10], promising as fragments of photovoltaic or other types of devices. The issues of studying the mechanisms of degradation of complex halides as a result of temperature, radiation, oxidants, traces of moisture remain relevant.

Copper(I) bromide is itself an isoelectronic analogue of a typical semiconductor, similar to germanium [11]. Creation of substituted compositions, as well as the study of new composite compositions based on copper(I) bromide is currently an urgent task. In the framework of this work we studied the compositions formed in the system of simple

bromides CuBr – InBr₃, phase equilibria for which are described in the literature very shallowly.

The phase diagram of the RbBr–CuBr system is described in the literature [12]. In the binary RbBr – CuBr system two intermediate compounds are formed. The phase RbCu₂Br₃ melts congruently at 537 K, and the phase Rb₃CuBr₄ melts congruently at 544 K. The coordinates of two eutectic points are 501 K, 54 mol% CuBr and 522 K, 74 mol% CuBr. The phase diagram of the CsBr–CuBr system is investigated by the same authors [1]. In this diagram two compounds have been found, namely, Cs₂CuBr₃, CsCu₂Br₃ and CsCu₁₉Br₂₀ and seven invariances: two eutectics, two peritectics, two polymorphic transitions and one eutectoid have been found in the system.

Recently, the phase equilibria in the ternary system of CsBr – CuBr – InBr₃ has been investigated to find a route for synthesis of the double perovskite phase Cs₂CuInBr₆ which was predicted in literature [13]. Authors have shown no traces the binary perovskite phase in the samples. The section CsCu₂Br₃ – Cs₃In₂Br₉ is quasi-binary. The solid-state interaction of CuBr and Cs₃In₂Br₉ has been observed, the products are crystalline CsCu₂Br₃ and InBr₃. This ternary system is similar to the reported here double system of CuBr and SbBr₃ because the compounds (CuBr and InBr₃) have very different melting and condensing temperatures.

A new solid electrolyte Rb₄Cu₁₆I₇Cl₁₃ with high copper ion conductivity was found in the ternary system CuCl – CuI – RbCl. This complex halide compound has a copper ion conductivity of $0.34 (\Omega\text{-cm})^{-1}$ at 25°C and a conductivity activation energy of 7.0 kJ/mol at 130°C to 25°C and 19 kJ/mol at –25°C and –140°C, respectively. Powder X-ray diffraction analysis shows that the crystal structure of this compound is simple cubic with parameter $a = 10.02 \text{ \AA}$ [14]. Solid electrolytes with high copper ionic conductivity and low electron hole conductivity of RbCl – CuCl were found in the RbCl – CuCl system. The highest conductivity of RbCu₃Cl₄ was $2.25 \cdot 10^{-3} (\Omega\text{-cm})^{-1}$ at 25°C [15].

A composite-based photovoltaic devices with the TiO₂/CH₃NH₃PbI_xSb_xI_{3-2x}Br_{3-x} composite compound were fabricated using antimony tribromide and the effect of the addition of SbBr₃ on the photovoltaic properties of the device compared with the CH₃NH₃PbI₃ phase was investigated. The short-circuit current density and photoconversion efficiency were improved by adding a small amount of SbBr₃ to the perovskite phase, which may be due to the doping effect of Sb or Br atoms at the Pb or I position [16].

In another work, the optoelectronic properties of CsPbBr₃ quantum dots were improved by subsequent treatment with antimony tribromide. The photoluminescence quantum yield (PLQY) was increased from 72 to 89% after doping compared to quantum dots. High-resolution transmission electron microscopy (HR-TEM) analysis shows the formation of uniformly sized CsPbBr₃ particles ($9.4 \pm 1.3 \text{ nm}$) after SbBr₃ treatment. Temperature-dependent photoluminescence and X-ray photoelectron spectroscopy (XPS) confirm the effective passivation of defects upon subsequent SbBr₃ treatment. The lifetime of nonequilibrium charge carriers for CsPbBr₃ quantum dots increased from 24.80 ± 0.10 to $37.71 \pm 0.09 \text{ ns}$ after SbBr₃ post-treatment. The CT-based self-powered photodetector device showed a high sensitivity of $48.1 \mu\text{A/W}$ after postprocessing compared to the sensitivity of the CT-based device after synthesis of $10.2 \mu\text{A/W}$ [17].

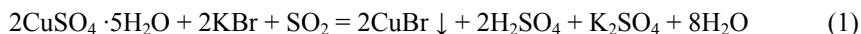
CuBr has unique optical properties. Copper bromide vapour laser (CuBr-laser) has a number of attractive features in comparison with conventional copper vapour laser – the possibility to significantly reduce the temperature of the laser tube wall, longer generation pulse duration and the possibility of obtaining high pulse repetition rates of

radiation [18]. In addition, the CuBr-laser active medium requires much lower operating temperatures than the traditional Cu-laser, and it was possible to obtain stable generation with a 3-5 times decrease in the specific electrical input into the discharge compared to the energy input of a simple copper vapour laser of the same volume in a wide range of repetition frequencies of pump pulses [19].

2 Experimental

Solid-phase and heterophase ampoule synthesis was used as the main approach to synthesise compositions of double perovskites, binary bromides, and to investigate different binary sites within these ternary systems [20].

Copper(I) bromide was synthesised by the solution method according to equation (1). A strong stream of pure sulphur disulphide SO_2 was passed into a solution filtered through a filter of appropriate amounts of pure copper(II) sulphate pentahydrate ("Sigma Tech", pure) and potassium bromide ("Ruschim", pure) in distilled water at moderate temperature heating ($T = 60^\circ\text{C}$) for 2 h. A light precipitate CuBr precipitates as thin yellowish-white crystals. Carefully protecting the precipitate from daylight, it was filtered off, kept in boiled water enriched with SO_2 for 5–7 s and filtered again. The precipitate was then washed with 96% alcohol. The salt was dried over H_2SO_4 and KOH for three days under hydrogen atmosphere and then in vacuo. In general, the synthesis can be described by equation (1):



Antimony tribromide was prepared by bromination of metallic antimony ("RedkyMetall.RF", 99.9%) in carbon tetrachloride (Component Reactant, 99.93%) [13,21]:



20 g Sb and a solution of 39.4 g bromine (~13 mL) in 420 g (~264 mL) CCl_4 were placed in a 500 mL round bottom flask connected by a slit to a reflux condenser. The mixture was heated (in a draught) to a low boiling point and boiled for 0.5–1 h until almost complete discolouration of the solution. Then the refrigerator was switched off and the liquid from the antimony residue was quickly poured into a dry beaker. On cooling, thin needle-shaped bromine crystals, sometimes pale yellow with traces of bromine, are released. The crystals were washed on a filter and dried in a vacuum-exicator over P_2O_5 . The yield was 49 g of SbBr_3 as snow-white crystals.

Sample preparation of samples for studying the phase composition of composite materials was the preparation of reagent suspensions taken in the required ratio of SbBr_3 and CuBr in unsoldered ampoules. The total mass of the mixture in each ampoule was 0.5 g. The reagents were weighed using AND GR-300 analytical scales with an accuracy of 10^{-4} g.

The calculated and rounded quantities and masses of antimony tribromide and copper(I) bromide for nine samples are presented below (Table 1). The samples were heat treated at 650°C for 12 h, after which the ampoules were cooled to room temperature by reaction furnace cooling.

Table 1 The weighted weights of SbBr₃ and CuBr for a synthesis of (1) – (9) sample by an ampoule method

Sample	Calculated quantity SbBr ₃ , mmol	Weight of SbBr ₃ , mg	Mole fraction of SbBr ₃ :CuBr	Calculated quantity CuBr, mmol	Weight of CuBr, mg
1	0.3026	109.4	0.1:0.9	2.7231	390.6
2	0.5346	193.2	0.2:0.8	2.1384	306.8
3	0.7182	259.6	0.3:0.7	1.6758	240.4
4	0.8672	313.5	0.4:0.6	1.3000	186.5
5	0.9903	358.0	0.5:0.5	0.9903	142.0
6	1.0938	395.4	0.6:0.4	0.7292	104.6
7	1.1822	427.3	0.7:0.3	0.5067	72.7
8	1.2584	454.9	0.8:0.2	0.3146	45.1
9	1.3249	478.9	0.9:0.1	0.1472	21.1

X-ray diffraction data were obtained using a diffractometer Rigaku 2500 D-max (Rigaku, Tokyo, Japan) with a rotating copper anode ($\lambda = 1.5418 \text{ \AA}$). Diffractograms were registered in the 2θ range of $10\text{--}80^\circ$, and a step was 0.02° . The XRD data were processed using software Jana2006 (ECA-SIG#3/Institute of Physics, Prague, Czech Republic) software.

The sample morphologies of the samples have been examined with a Leo Supra 50 VP scanning electron microscope (SEM) equipped with an EDX Oxford Instruments X-MAX attachments for the local chemical analysis.

The absorption spectra of the materials were recorded on a Lambda950 spectrophotometer (PerkinElmer, USA) in the diffuse reflection mode in the wavelength range from 200 to 2000 nm with a step of 1 nm with preliminary subtraction of the baseline. A Labsphere WS-1-SL sample with known diffuse scattering characteristics was used as a calibration standard for the instrument.

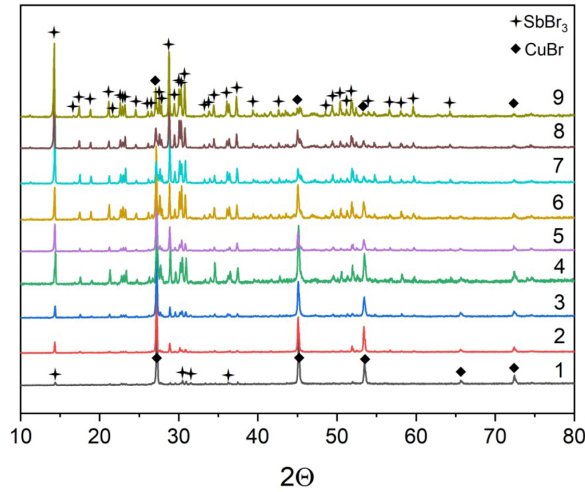
Photoemission spectra are collected with a multichannel spectrometer S2000 (Ocean Optics) with a nitrogen LGI-21 ($\lambda_{\text{exc}} = 337 \text{ nm}$) as an excitation source at 77 K. All spectra were corrected for the wavelength response of the system.

3 Results and discussion

The results of XRD of the samples are presented in Figure 1. It is shown that all the reflections of the obtained samples belong only to CuBr (PDF2 (6-292)) and SbBr₃ (PDF2 (30-77)) phases. The reflections of both phases are narrow, indicating a high degree of crystallinity of both simple bromides. No new reflections relating to hypothetically possible compositions of binary bromides were found.

For the CuBr phase, the maximum intensity of the reflexes (111), (220) and (311), which is also characteristic of well ground powdered samples of this phase. Thus, no effects of anisomerism of copper bromide crystals in the obtained samples are observed as observed in other systems with copper(I) bromide [9].

Figure 1 XRD data for the samples (1)–(9) in the binary system CuBr-SbBr₃. The scanning step 0.05° (see online version for colours)



To determine the uniformity of element distribution in the synthesis products the EDX analysis was performed at the top and bottom points of the formed ceramic samples. The signal was collected in different parts of probes including parts where there were differences in the microstructure of the crystals. The EDX data are summarised in Table 2. From the EDX data it follows that the content of SbBr₃ in the obtained samples is less than that given during synthesis which may be due to the fact that SbBr₃ is volatile. As a result, the obtained samples differ in composition from the theoretically specified ones.

Table 2 EDX data and Sb:Cu ratios for CuBr-SbBr₃ composite materials

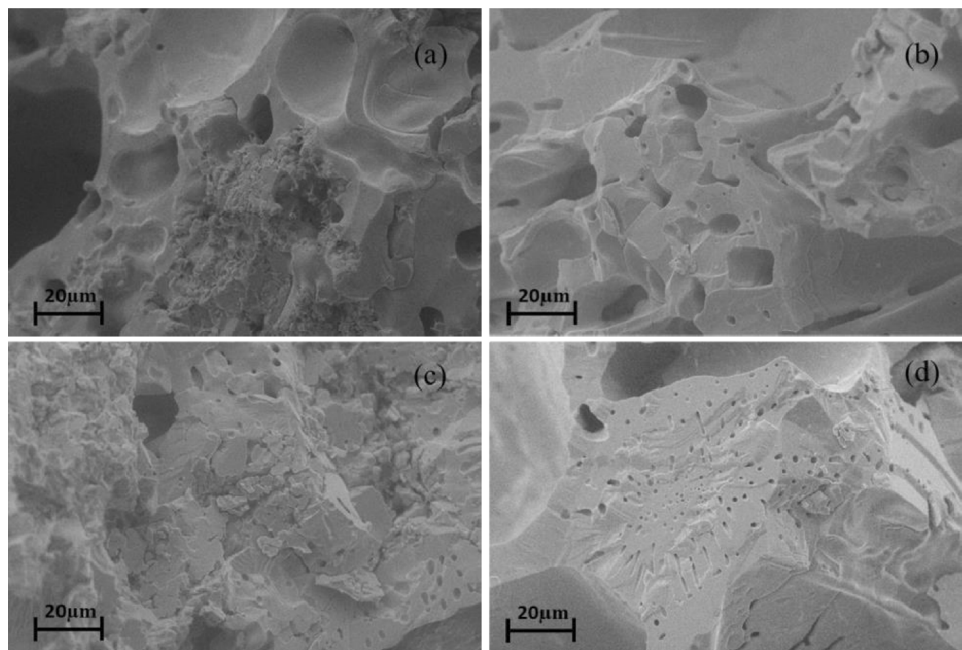
Sample	<i>Sb : Cu</i>	<i>Cu</i>	<i>Sb</i>	<i>Br</i>	<i>Sb:Cu</i>	<i>Cu</i>	<i>Sb</i>	<i>Br</i>	<i>Sb:Cu</i>
	<i>Total ratio</i>	<i>Bottom probe</i>			<i>Top probe</i>				
1	0.11	47	1.0	52	0.02	49	0	51	0
2	0.25	49	51	60	1.04				
3	0.43	44	2.0	54	0.05				
4	0.67	2.0	22	76	11	49	0	51	0
5	1	47	1.0	52	0.02	48	1.0	51	0.02
6	1.5	7.0	18	75	2.57				
7	2.33	2.0	24	74	12	1.0	15	84	15
8	4	0.5	82	17.5	164	1.0	22	77	22
9	9	12	13	75	1.08				

In addition to the heterogeneity of element distribution in the upper and lower parts of the ampoule, the results allow us to correlate the obtained XRD data with the experimentally confirmed elemental composition of the samples. Thus, samples (1), (2), (4), (9) showed maximum compliance with the theoretical composition. It should be noted that the deviations of cationic stoichiometry, expressed through the Sb/Cu ratio, in different

regions of the ampoule differ from sample to sample less than from sample to sample. This means that the EDX results are significantly influenced by the microstructure and distribution of elements in the most analysed region of the sample. It is evident also that samples are non-uniform and even grounded samples are different from point to point. This effect is characteristic both for top and bottom parts of the samples (see Table 2). Most probably, the mean grain size in the samples is large and is bigger than the analysing area by EDX spectroscopy. To get more information about microstructure of the samples SEM analysis was performed.

SEM results for samples (1)–(4) are presented in Figure 2. The samples represent a homogeneous alloy, not demonstrating the presence of faceted crystallites of one of the phases. The samples differ in porosity. The alloy photographs show imprints of crystallites from which particle size can be determined. Presumably, CuBr grains have a spherical smooth shape, their size reaches $50\text{ }\mu\text{m}$.

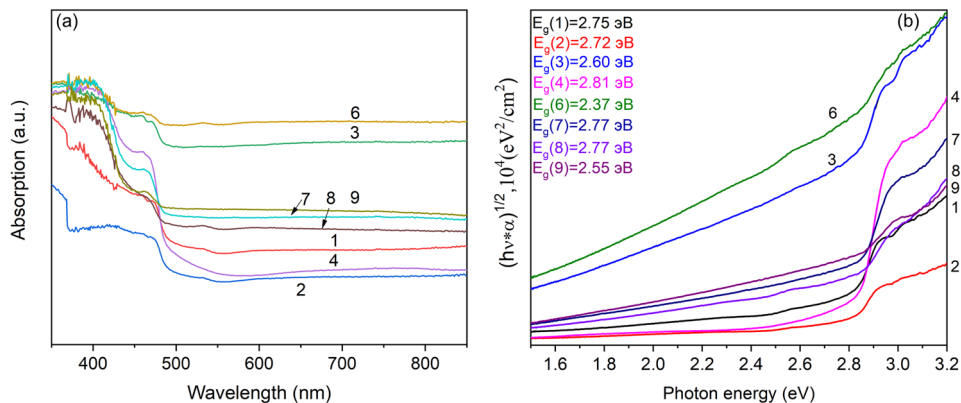
Figure 2 SEM images for the (1)–(4) samples obtained by a melt crystallisation in closed vials via a reaction cooling from 650°C to room temperature: (a–d) SEM images for the (1)–(4) samples respectively, obtained by a melt crystallisation in closed vials via a reaction cooling from 650°C to room temperature



The samples are characterised by the presence of macropores with a relatively narrow size distribution of $1\text{--}2\text{ }\mu\text{m}$. The number of pores in the samples increases with growing up antimony percentage in the sample. This assumption is confirmed also in the case if we consider only samples with minimal error of EDX data – (1) and (4). Probably, the appearance of pores in the alloyed samples can be explained by the release of one of the components from the volume of the solidifying mass of the alloy at the eutectic temperature. This may be the release of gaseous SbBr_3 as a result of the gas-peritectic transition.

Figures 3 and 4 demonstrate optical characteristics and photoluminescence spectra for the samples (1)–(9), respectively. Figure 3 shows optical spectra of the samples and a Tauc plot to reveal an optical bandgap for one or more phases. It is demonstrated that most of the samples shows an adsorption edge at 480 nm (stronger) and that corresponds to 2.6 eV and 2.9 eV, respectively. Very likely, the edge of 2.9 eV is related to the bandgap of copper(I) bromide.

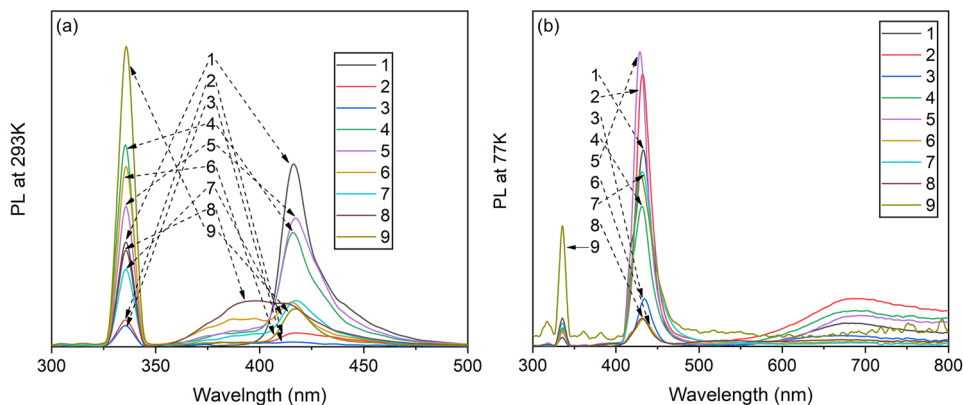
Figure 3 Characteristic UV-vis spectra for (1)–(9) samples in the binary system CuBrSbBr₃. (a) Diffuse reflectance (absorption) spectra. (b) Tauc plot for a direct-bandgap semiconductor (see online version for colours)



The photoluminescence spectroscopy data well confirm biphasic nature of the obtained samples. The maximum of photoluminescence for CuBr phase at $440 \pm 10 \text{ nm}$ and also at $680 \pm 30 \text{ nm}$ at 77 K. The intensity of the photoluminescence peaks correlates well with the theoretical content of these phases in the samples.

The SbBr₃ phase is characterised by a broad maximum at $390 \pm 20 \text{ nm}$. It is clearly visible at 293 K, but disappears at 77 K.

Figure 4 Photoluminescence spectra for the samples (1)–(9) in the binary system CuBr-SbBr₃. The scanning step 0.05°, collected (a) at 293 K, and (b) at 77 K, respectively. The excitation of 337 nm (see online version for colours)



4 Conclusions

Phase analysis of samples showed that all samples are two-phase. No other phases, such as binary bromides or impurities, were observed. Optical and photoluminescent properties of samples correspond well to the mixture of simple bromides.

Microstructure analysis of the samples indicates crystallisation of phases from the melt. The microstructure is homogeneous, does not contain faceted crystallites of one of the phases, but is characterised by a uniform distribution of narrow pores 1–2 microns in size, which may be associated with a gas-peritectic transition. Melt crystallisation is an easy methods which could be especially beneficial in the development of new porous materials based on copper bromide or other copper halides for porous bulk of film composite materials.

Acknowledgements

Authors are grateful to colleagues from Lomonosov Moscow State University for their assistance in experiments and fruitful discussion of experiments, namely, Dr. Tatyana V. Filippova, Mr. Shodruz T. Umedov.

The project is performed using the equipment and setups of the collective resource center of Moscow State University “Technologies for synthesis of new nanostructured materials and their complex characterization”. The project is supported by the Russian Science Foundation (grant 22-23-00585).

References

- 1 Wojakowska, A., Krzyżak, E. and Wojakowski, A. (2000) ‘Phase diagram for the CuBr–CsBr system’, *Thermochim. Acta*, Vol. 344, Nos. 1–2, pp.55–59, [https://doi.org/10.1016/S0040-6031\(99\)00326-3](https://doi.org/10.1016/S0040-6031(99)00326-3)
- 2 Ghosh, S., Shankar, H. and Kar, P. (2022) ‘Recent developments of lead-free halide double perovskites: a new superstar in the optoelectronic field’, *Mater. Adv.*, Vol. 3, No. 9, 742–3765, <https://doi.org/10.1039/D2MA00071G>
- 3 He, Y., Yan, J., Xu, L., Zhang, B., Cheng, Q., Cao, Y., Zhang, J., Tao, C., Wei, Y., Wen, K., Kuang, Z., Chow, G.M., Shen, Z., Peng, Q., Huang, W. and Wang, J. (2021) ‘Perovskite light-emitting diodes with near unit internal quantum efficiency at low temperatures’, *Adv. Mater.*, Vol. 33, No. 14, p.2006302, <https://doi.org/10.1002/adma.202006302>
- 4 Xiang, W., Wang, Z., Kubicki, D.J., Tress, W., Luo, J., Prochowicz, D., Akin, S., Emsley, L., Zhou, J., Dietler, G., Grätzel, M. and Hagfeldt, A. (2019) ‘Europium-doped CsPbI₂Br for stable and highly efficient inorganic perovskite solar cells’, *Joule*, Vol. 3, No. 1, pp.205–214, <https://doi.org/10.1016/j.joule.2018.10.008>
- 5 Shestimerova, T.A., Bykov, M.A., Grigorieva, A.V., Wei, Z., Dikarev, E.V. and Shevelkov, A.V. (2022). Synthesis and characterization of amantadinium iodoacetatobismuthate, a hybrid compound with mixed iodide–carboxylate anions’, *Mendeleev Commun.*, Vol. 32, No. 2, pp.194–197, <https://doi.org/10.1016/j.mencom.2022.03.014>
- 6 Bykov, A.V., Shestimerova, T.A., Bykov, M.A., Lyssenko, K.A., Korshunov, V.M., Metlin, M.T., Taydakov, I.V. and Shevelkov, A.V. (2022). Molecular and supramolecular structure of a new luminescent hybrid compound: (C₃N₂H₁₄)₂[BiBr₆]br·H₂O’, *Inorganics*, Vol. 10, No. 11, p.181, <https://doi.org/10.3390/inorganics10110181>

- 7 Son, A.G., Krivogina, E.V., Romanov, N.V., Presnyakov, M. Yu., Shapovalov, S.S. and Kozyukhin, S.A. (2019) 'CsPbI₃ perovskite nanoparticles: Room-temperature synthesis and optical study', *Russ. J. Inorg. Chem.*, Vol. 64, No. 12, pp.1587–1591, <https://doi.org/10.1134/S0036023619120180>
- 8 Liu, X., Gao, X., Xiong, L., Li, S., Zhang, Y., Li, Q., Jiang, H. and Xu, D. (2023) 'A□site coordinating cation engineering in zero□dimensional antimony halide perovskites for strong self□trapped exciton emission', *SmartMat*, p.e1224, <https://doi.org/10.1002/smm2.1224>
- 9 Kamilov, R.K., Yuldoshev, J.Z., Knotko, A.V. and Grigorieva, A.V. (2023) 'Phase equilibria in ternary system CsBr-AgBr-InBr₃', *Materials*, Vol. 16, No. 2, p.559, <https://doi.org/10.3390/ma16020559>
- 10 Umedov, S.T., Grigorieva, A.V., Sobolev, A.V., Knotko, A.V., Lepnev, L.S., Kolesnikov, E.A., Charkin, D.O. and Shevelkov, A.V. (2023) 'Controlled reduction of Sn⁴⁺ in the complex iodide Cs₂SnI₆ with metallic gallium', *Nanomaterials*, Vol. 13, No. 3, p.427, <https://doi.org/10.3390/nano13030427>
- 11 Roccanova, R., Yangui, A., Seo, G., Creason, T.D., Wu, Y., Kim, D.Y., Du, M.-H. and Saparov, B. (2019) 'Bright Luminescence from Nontoxic CsCu₂X₃ (X = Cl, Br, I)', *ACS Mater. Lett.*, Vol. 1, No. 4, pp.459–465, <https://doi.org/10.1021/acsmaterialslett.9b00274>
- 12 Wojakowska, A., Krzyzak, E. and Wojakowski, A. (2001) 'Phase diagram for the RbBr–CuBr system', *J. Therm. Anal. Calorim.*, Vol. 65, No. 2, pp.491–495, <https://doi.org/10.1023/A:1012481105117>
- 13 Kamilov, R.K., Yuldoshev, J.Z., Knotko, A.V. and Grigorieva, A.V. (2023) 'In search of a double perovskite in the phase triangle of bromides CsBr-CuBr-InBr₃', *Materials*, Vol. 16, No. 10, p.3744, <https://doi.org/10.3390/ma16103744>
- 14 Takahashi, T., Yamamoto, O., Yamada, S. and Hayashi, S. (1979) 'Solid□state ionics: high copper ion conductivity of the system CuCl–CuI–RbCl', *J. Electrochem. Soc.*, pp.0013–4651; *The Electrochemical Society*, Vol. 126, No. 10, pp.1654–1658, <https://cir.nii.ac.jp/crid/1361137044099848704>
- 15 Yamamoto, O. (2017) 'Solid state ionics: a Japan perspective', *Sci. Technol. Adv. Mater.*, Vol. 18, No. 1, pp.504–527, <https://doi.org/10.1080/14686996.2017.1328955>
- 16 Oku, T., Ohishi, Y. and Suzuki, A. (2017) *Effects of SbBr₃ Addition to CH₃NH₃PbI₃ Solar Cells*, p.020007, <https://doi.org/10.1063/1.4974789>
- 17 Subramaniam, M.R., Pramod, A.K., Hevia, S.A. and Batabyal, S.K. (2022) 'Enhanced photoluminescence quantum yield, lifetime, and photodetector responsivity of CsPbBr₃ quantum dots via antimony tribromide posttreatment', *J. Phys. Chem. C*, Vol. 126, No. 3, pp.1462–1470, <https://doi.org/10.1021/acs.jpcc.1c07493>
- 18 Gubarev, F.A., Fedorov, V.F., Evtushenko, G.S. and Sukhanov, V.B. (2009) 'Energy characteristics of a capacitively pumped kubra laser in the assembly of circuits based on lamp formation', *Bulletin of the Tomsk Polytechnic University*, Vol. 314, No. 4, 106 pp.
- 19 Evtushenko, G.S., Petrash, G.G., Sukhanov, V.B. and Fedorov, V.F. (1999) 'CuBr laser with a pulse repetition rate up to 300 kHz', *Quantum Electron.*, Vol. 29, No. 9, pp.775–777, <https://doi.org/10.1070/QE1999v029n09ABEH001570>
- 20 Umedov, S.T., Grigorieva, A.V., Lepnev, L.S., Knotko, A.V., Nakabayashi, K., Ohkoshi, S. and Shevelkov, A.V. (2020) 'Indium doping of lead-free perovskite Cs₂SnI₆', *Frontiers in Chemistry*, Vol. 8, p.564, <https://doi.org/10.3389/fchem.2020.00564>
- 21 Revzin, G.E. and Arkhipov, S.M. (1967) *The USSR Reagent Industry Bulletin*, IREA Publishing, Moscow, Vol. 10, p.27.