Synthesis, Crystal Structures, High-Temperatures Phase Transition, Optic and Electric properties of Hybrid Halogenometallates: [(CH₃)₃N(CH₂)₂Br]₂[M^{II}Br₄] (M = Cu, Zn)

Karim Karoui ^{a*}, Fadhel Hajlaoui ^b, Nathalie Audebrand ^c, Thierry Roisnel ^c, Abdallah Ben Rhaïem ^a

^a Laboratoire des caractérisations spectroscopiques et optique des matériaux, Faculté des Sciences de Sfax, B.P. 1171, 3000 Sfax, Université de Sfax, Tunisia

^b Laboratoire Physico-chimie de l'Etat Solide, Département de Chimie, Faculté des Sciences de Sfax, B.P. 1171, 3000 Sfax, Université de Sfax, Tunisia

^c Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France

*Corresponding Authors' E-mail: karouikarim36@yahoo.com

Abstract

Two organic-inorganic hybrid compounds [(CH₃)₃N(CH₂)₂Br]₂[M^{II}Br₄] (M = Cu, Zn); ((2-bromoethyl)trimethylammonium cations [Br(CH₂)₂N(CH₃)₃]⁺) were successfully synthesized with slow evaporation conditions. The structures of the two compounds were determined using single-crystal X-ray diffraction. These materials crystallize in the monoclinic system, space group *P*2₁/*c*. In the molecular arrangement, the [M^{II}Br₄]²⁻ anions are linked to the organic cations through C-H...Br hydrogen bonds to form cation-anion-cation molecular units, giving a three-dimensional network. The phase transitions, electric and optical properties of [(CH₃)₃N(CH₂)₂Br]₂[CuBr₄] (**1**) and [(CH₃)₃N(CH₂)₂Br]₂[ZnBr₄] (**2**) were carefully characterized. Based on these results, both compounds underwent phase transitions at T₁=368 K and T₂=385K for (**1**) and at T₁=283K, T₂=330K, T₃=368K and T₄=402K for (**2**). The optical and electrical properties allow to determinate the gap energy and to characterize the phase transitions. These studies pave the pathway to explore new types of high-phase transition materials with targeted properties for electric and semiconductor applications.

Keywords: Hybrid materials, Crystal structure, Optic and Electric properties, Phase transitions.

1. Introduction

Solid-to-solid phase transition materials, with a significant number of promising applications such as switchable dielectric devices, shape memory, communication, signal processing, superelasticity and ferroelectric field-effect transistors have attracted special attention, owing to their excellent physical properties [1-8]. Although many researchers have been focused on the exploration of phase transition properties, it is still challenging to predict the formation of such materials combining excellent properties, such as the thermal capacity, photoelectric switches, magnetic, ferroelastic and nonlinear optical (NLO) properties [9-15]. Preparing new materials is crucial not only for the theoretical illustration of structure-property relationship but also for the exploration and exploitation of novel properties. One of the most viable approaches is to construct solid-to-solid phase transition materials induced by temperature, of which the structures change from the non-centrosymmetric to centrosymmetric phases. Fortunately, organic-inorganic hybrids have the advantage of adjustability to design and synthesize new phase transition materials with anticipated physical properties such as sensors and NLO responses [16-20]. Due to the advantages of convenient processing, light weight, diverse structures, discrete metal-halides anions and organic cations, the hybrid molecular systems are relatively more interesting [21-24]. The flexibility of organic structural moieties would enable remarkable structural changes, while inorganic frameworks account for superior electronic and optical properties.

Recently, many researchers have showed that the organic-inorganic hybrid halogenometallates have been proven to be excellent candidates to prepare phase transition materials [25]. Indeed, the motion and reorientation of the organic cations and deformation of the anionic framework were confirmed to easily induce the phase transitions. For instance, a series of hybrid molecular halogenometallates $(C_{10}H_{16}N)_2MnBr_4$ [26], $(C_6H_{13}NH)_2ZnBr_4$ [27], $[(C_6H_{14})NH_2]_2CuBr_4$ [28], $[BnNMe_2R]CdBr_4$ ($(BnNMe_2R)$: heteroleptic ammonium cation) ; (Bn = benzyl; R = Me or n-Pr) [29], have been successfully constructed and exhibited a series of distinct physical properties such as high Curie temperature, strong luminescence, switchable dielectric responses, electric and magnetic ordering properties, ferroelectric, strong piezoelectric coefficient and fast polarization switching behaviour.

Other hybrid halogenometallates compounds have also been prepared by the spherical components organic amine, which is considered to be structure-directing agent and easily induces the phase transition properties [30]. For example, $[(CH_3)_2NH_2]M^{II}(HCOO)_3$ (M = Mn, Fe, Co and Ni) [31], driven by order-disorder transformations of organic moieties, has been reported to exhibit structural phase transition in the range of 160-185 K. Among many types of the various hybrid halogenometallates, crystals with the formula A_2MX_4 (A = organic amines; M = bivalent metal; X = Cl, Br or I) often exhibit various successive structural phase transitions and lead to a

multifunctional material with excellent multiferroic properties. Especially, compound $[(\text{CH}_3)_4\text{N}]_2\text{ZnBr}_4$, which belongs to the A_2MX_4 family, with the structural phase transitions observed at 100K and 287 K related of the motion of the organic cations thus generating perfect ferroelastic properties [32]. However, the low temperature phase transitions have limited the applications that are more compatible with high temperature [33]. Therefore, the design and synthesis of molecular hybrid halogenometallates with high phase transition temperatures have become a new challenge [33]. Among them, the T_c of compounds $[(\text{CH}_3)_3\text{NCH}_2\text{Cl}]_2[\text{CoBr}_4]$ (1), and $[(\text{CH}_3)_3\text{NCH}_2\text{Br}]_2[\text{ZnBr}_4]$ (2) ($T_c \sim 387$ K), obviously shows that the values of T_c increase when different halogens are introduced with the cations [34-35]. It is expected that the long organic chains can help us to explore the individual function of organic cations and its influence on electrical conductivity [36]. In order to investigate this type of materials, we tried to build some new hybrid compounds with high-temperature phase transition. In this study, two molecular inorganic-organic halogenometallates compounds $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{M}^{\text{II}}\text{Br}_4]$ ($\text{M} = \text{Cu}, \text{Zn}$) were synthesized and characterized. Meanwhile, crystal structures of (1) and (2), phase transition temperatures, optic and electric properties have been reported.

2. Experimental section

2.1. Materials

Copper(II) bromide (CuBr_2), Zinc(II) bromide (ZnBr_2), hydrobromic acid HBr (48%), (2-bromoethyl)trimethylammonium bromide $[\text{Br}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3^+ \text{Br}^-]$ were purchased from Sigma-Aldrich and used without further purification.

2.2. Synthesis of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{CuBr}_4]$ (1) and $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (2)

CuBr_2 (1 mmol) and $[\text{Br}(\text{CH}_2)_2\text{N}(\text{CH}_3)_3^+ \text{Br}^-]$ (2 mmol) were mixed in hydrobromic acid aqueous solution (20 mL). After being stirred for 1 h at room temperature, the reaction solution was evaporated slowly at room temperature for several days. The block brown single crystals of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{CuBr}_4]$ (1) were collected, washed with a small amount of distilled water and dried in open air. Yield: 73.4% based on Cu.

The compound $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (2) was obtained in the same way except by using ZnBr_2 (1 mmol) instead of CuBr_2 . The colourless block crystals were collected washed with a small amount of distilled water and in open air. Yield: 81.5% based on Zn.

2.3. Single-crystal data collection and structure determination

The single-crystal X-ray diffraction data of compounds (1) and (2) were collected at 150 K on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, $\text{Mo-K}\alpha$ radiation, and processed with the APEX 3 program suite [37]. The used X-ray wavelength was the $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Frames integration and data reduction were carried out with the program SAINT [38]. The program SADABS [39] was employed for multiscan-type absorption

corrections. Structures were determined by dual space methods using the SHELXT program, [40] and refined with full-matrix least-square methods based on F^2 (SHELXL-2014) [41] through the WinGX program suite [42]. Non hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.98 Å. The graphics program Diamond [43] was used to draw the structures. Crystallographic data, details on data collections and refinement parameters of the crystal structures are listed in Table 1. The relevant selected bond lengths and angles are summarized Tables S2-S4.

2.4. Spectroscopies studies

2.4.1. Electrical measurements

Electrical measurements were performed on pellet disks of about 8 mm in diameter and 1 mm in thickness with SOLARTRON SI 1260 impedance equipment coupled to a dielectric interface in the 223–413 K and $1\text{--}10^6$ Hz temperature and frequency range.

2.4.2. Optical properties

The UV–vis diffuse reflectance spectrum was measured at room temperature using a Shimadzu-type 3101 PC UV spectrophotometer equipped with a double beam monochromator covering the spectrum range from 200 nm to 800 nm. This technique allows determining the absorbance (A) and reflectance (R) of material.

2.5. Thermal measurements

Differential scanning calorimetry (DSC) measurements were recorded on raw powders with NETZSCH DSC 200 F3 instrument (Pt crucibles, Al_2O_3 as a reference) under nitrogen atmosphere. The DSC measurements of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{M}^{\text{II}}\text{Br}_4]$ (M = Cu, Zn) were carried out in the temperature range from 200K to 433K with heating and cooling rate of $5\text{ K}\cdot\text{min}^{-1}$.

Thermogravimetric analysis (TGA) of the two compounds (1) and (2) were performed on raw powders with a TGA ‘SETSYS Evolution’ under air flow. The thermograms were collected on 10.3 mg sample in the RT–950K range (heating rate of $10\text{ K}\cdot\text{min}^{-1}$).

3. Results and discussion

3.1. Crystal structure

In order to understand the details of the structures of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{CuBr}_4]$ (1) and $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (2) compounds, single-crystal X-ray diffraction data were collected at 150 K. The analyses indicate that (1) and (2) crystallize in the monoclinic crystal system with the space group $P2_1/c$. The asymmetric unit of (1) consists of discrete $[\text{CuBr}_4]^{2-}$ anion and two symmetrically independent $[\text{Br}(\text{CH}_2)_2(\text{CH}_3)_3\text{N}]^+$ cations (Fig. 1(a)).

The $[\text{CuBr}_4]^{2-}$ complex anion adopts intermediate geometry between square-planar and regular tetrahedral coordination with Cu–Br bond distances ranging from 2.3684(4) Å to 2.4151(4) Å.

The Br-Cu-Br bond angles range between $96.797(14)^\circ$ and $136.897(16)^\circ$, which are seriously deviated from the ideal values of 109.5° (Table S1). The geometrical features of CuBr_4 entities agree well with those reported for other Cu(II) salts containing isolated tetrahedra [33-35]. In the case of the $[\text{Br}(\text{CH}_2)_2(\text{CH}_3)_3\text{N}]^+$ cation, the bond lengths of C-C and C-N are in the range from $1.495(3) \text{ \AA}$ to $1.520(3) \text{ \AA}$. The C-N-C and N-C-C angles are in the range of $107.35(2)^\circ$ to $114.31(2)^\circ$. All bond lengths and bond angles fall within the normal ranges [34-35].

The organic species interact with the inorganic entities via C-H $\cdots$ Br hydrogen bonds. Selected bond lengths and angles are given in Table S3. The crystal structure can be described as alternating of (2-bromoethyl)trimethylammonium cations and tetrabromocuprate(II) anions. The latter are alternated with organic parts forming infinite zigzag chains that run parallel to the *a*-axis (Figure 1(b)). The terminal Br atoms of the $[\text{Br}(\text{CH}_2)_2(\text{CH}_3)_3\text{N}]^+$ cations participate also in building intramolecular hydrogen bonds, in which the distances C3 $\cdots$ Br fall in the range of $3.640(3) - 3.831(3) \text{ \AA}$, and the C-H $\cdots$ Br bond angles range from 124° to 136° . Otherwise the four Br atoms of $[\text{CuBr}_4]^{2-}$ anions serve as acceptors and form C-H $\cdots$ Br hydrogen bonds with the organic cations. These weak interactions result in the formation of 3D supramolecular assembly architecture.

The asymmetric unit of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (**2**) is composed of four discrete $[\text{ZnBr}_4]^{2-}$ anions and eight $[\text{Br}(\text{CH}_2)_2(\text{CH}_3)_3\text{N}]^+$ cations (Figure 2(a)). The Zn^{II} ions adopt the distorted tetrahedral geometry with the Zn-Br bond lengths in the range of $2.3895(14) \text{ \AA}$ to $2.4298(15) \text{ \AA}$. The bond angles of Br-Zn-Br are in the range from $106.37(6)^\circ$ to $113.17(6)^\circ$. Moreover, the three-dimensional view of the crystal structure along the *b*-axis shows the inorganic anion organized as sheet of isolated tetrahedral ZnBr_4 moieties forming a zero dimensional network. Meanwhile, the interlayer spacing between these sheets is occupied by the organic chains $[\text{Br}(\text{CH}_2)_2(\text{CH}_3)_3\text{N}]$ as shown in Figure 2 (b).

Organic cations neutralize the negative charge of the anionic part. The C-C and N-C bond lengths vary from $1.457(13)$ to $1.530(11) \text{ \AA}$. The selected bond lengths and bond angles within the cationic part indicate that the N-C, C-C distances and the N-C-C, C-N-C, Br-C-C angles are comparable with those observed in other similar hybrid metal-halides with the same organic cation [34-35]. There are intra- and intermolecular hydrogen bonds in the crystal of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (**2**), with C-H $\cdots$ Br distances varying from $3.565(10)$ to $3.989(12) \text{ \AA}$. The C-H $\cdots$ Br bond angles are in the range of 111 to 175° . The hydrogen bonding data are summarized in Table S4. Finally, the organic and inorganic layers are connected by C-H $\cdots$ Br by hydrogen-bonding interactions to produce a 3D framework.

3.2. Thermal analysis

Figures 3 a and b show the DSC curves of samples (**1**) and (**2**) which depicts two endothermic peaks at $T_1=368 \text{ K}$ and $T_2=385\text{K}$ for (**1**) and four endothermic peaks at $T_1=283\text{K}$, $T_2=330\text{K}$, $T_3=368\text{K}$ and

$T_4=402\text{K}$ for (2). The two peaks for (1) are reversible at $T_1=313\text{K}$ and $T_2=320\text{K}$ with a thermal hysteresis of 55 K and 65K, respectively. For (2), the T_2 , T_3 and T_4 are reversible at 326K, 338K and 372K with a thermal hysteresis of 64 K, 42 K and 30K, respectively, respectively. The sharp peak-like anomalies and large thermal hysteresis are indicative of a first-order phase transition [44, 45].

The results of TG analyses (Figures 4 (a) and (b)) indicated that the $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{CuBr}_4]$ (1) and $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (2) are stable until 550K and 600K, respectively. The two compounds start losing weight at about 570 and 610K, respectively, above which a continuous decomposition of the samples take place. The thermogravimetric curve of compound (1) takes place in a single step. The transformation occurs in the temperature range 570–950 K. The weight loss is in agreement with the decomposition of the amine entity, the partial decomposition of the copper bromide and the formation of copper oxide CuO. For compound (2), the main weight loss can be attributed to the decomposition of the amine group together with the bromide is removed to support the charge neutrality (observed weight loss, 69.35%; calculated weight loss, 68.69%). The last transformation starts at about 700 K and corresponds to the formation of zinc oxide ZnO. The thermal stability analysis shows that (1) and (2) compounds are stable enough during the phase transition processes.

3.3. Optical properties

For new compounds, it is of fundamental importance to study the optical of (1) and (2) for potential application in the future. The measurements of UV/Vis diffuse reflectance and absorption spectra were carried out. The band gap type, direct band gap or indirect band gap, are highly related to the optical absorption characteristics. The absorption spectra for (1) and (2) (inset in figures 5 a and b) clearly display a sharp peak at (210 nm) of (2) and a most intense peak at (340 nm) of (1) in the ultraviolet spectral region, suggesting a direct band gap [46, 47]. According to Tauc equation [48], the corresponding optical band gap can be defined as 2.30 eV and 4.87 eV for (1) and (2), respectively (Figure 5) and indicates that (1) is a semiconductor and potential optoelectronic candidate [49]. The difference of gap energy between these compounds can be attributed to the change of metal where the semiconducting property is closely related with the structural assembly, that is the connectivity model of the inorganic framework, where the band gap shows the rules of “corner-sharing < edge-sharing < face-sharing” [50, 51].

3.4. Electrical properties

3.4.1. Impedance spectroscopy

Generally, materials with structural phase transitions display a variety of physical properties accompanied by anomalies as responses. The temperature-dependent electric properties can be characterized and confirmed the thermal anomalies. The two transition temperatures in the sample (1) are close and then it is difficult to take several electrical measurements in a weak temperature

range. In the following, we can assume that these two peaks correspond to a single transition. Figure 6 and 7 (a, b and c) show the Nyquist diagram of the samples (1) and (2) as a function of temperature. The radius of the semi-circles after 333K decreases with increasing temperature indicating that the conductivity is thermally activated. Below 333K, the conduction of the two compounds is not activated thermally (Fig. 6 (a) and 7 (a)) which proves the peak at 330K observed in the thermal properties of the compound (2). This result evidences the characteristic of a metallic conduction: when the temperature increases, the density of conduction electrons remains constant, but the thermal agitation increases the frequency of the collisions and thus decreases the conductivity [52]. The good conformity between the experimental and theoretical curves (figure 6 and 7) confirms the right choice of equivalent circuit based in the Z-View logical. This circuit is described by two cells in series, each one consisting of a resistance (R) parallel to a fractal capacity (CPE). These cells are attributed to the grain and grain boundaries effects.

The resistivity of the grain (R_g) is used to calculate the conductivity of the grain (σ_g) by the following relation:

$$\sigma_g = e/R_g * S$$

where (e/S (cm^{-1})) represents the sample geometrical ratio.

The temperature dependence of the conductivity $\ln(\sigma_g)$ (Figure 6 and 7 (d)) is described by the Arrhenius law and shows a change of the slope near T_1 for the compound (1) and near T_2 , T_3 and T_4 for the compound (2) which confirms the transitions temperatures observed in the thermal study. The calculated activation energies from linear fits to the data points are $E_{aII}=0.65\text{eV}$ and $E_{aI}=0.70\text{eV}$ for (1) and $E_{aIV}=0.92\text{eV}$, $E_{aIII}=0.70\text{eV}$ and $E_{aII}=0.52\text{eV}$ for the compound (2). The comparison between the conductivity σ_g of two compounds shows that the compound (1) is more conductive.

3.4.2. AC conductivity and conduction mechanism

AC conductivity at various temperatures and frequencies of the two synthesized compounds is shown in figures 8 and 9 (a, b). Weak temperature dependence and strong frequency dependence effects are observed in these spectra. The values of conductivities of the (1) vary in the range 10^{-5} - $10^{-4}\Omega^{-1}\text{cm}^{-1}$ which is higher than the observed conductivities of the sample (2) (10^{-8} - $10^{-7}\Omega^{-1}\text{cm}^{-1}$). This result confirms the value of gap energy of the sample (1) and shows their semiconducting character. The Ac conductivities curves show two dispersion domains attributed to the grain and grain boundary response at higher and lower frequencies, respectively. These curves are simulated with Jonscher's power law:

$$\sigma_{ac} = \sigma_{dc} + A\omega^s [53]$$

This simulation allows to determinate the exponent (S) which describes the degree of interaction of charge carriers with their environment, charges, and impurities [54]. Based in the Elliot Theory [55], the behavior of this exponent (Figure 8 and 9 (c)) as a function of the temperature was used to determine the origin of the conduction mechanism. For sample (1) (figure 8 (c)), the two phases are described by NSPT model where the exponent (S) increases with increasing temperature. For the sample (2) (figure 9 (c)), the exponent (S) increase with increasing temperature in the phase I and II which indicate that the NSPT model described well the conduction in these phase. The third and fourth phases are described by CBH model where the exponent decreases with increasing temperature.

Conclusion

In summary, we have prepared two new metal-halide hybrid perovskite materials $[(CH_3)_3N(CH_2)_2Br]_2[CuBr_4]$ (1) and $[(CH_3)_3N(CH_2)_2Br]_2[ZnBr_4]$ (2) which undergoes two phases transitions at $T_1=368$ K and $T_2=385$ K for (1) and four phases transitions at $T_1=283$ K, $T_2=330$ K, $T_3=368$ K and $T_4=402$ K for (2) confirmed by the DSC measurements together with electric anomalies. These compounds crystallize in the monoclinic system, space group $P2_1/c$. The cationic and anionic entities are linked with each other by C-H $\cdots$ Br hydrogen bonding to generate an interesting 3D supramolecular framework. The optical properties show that the sample (1) has a semiconducting character for which the gap energy is 2.30eV. For the sample (2) the gap energy is equal to 4.87eV. This result is confirmed by the values of conductivities which are higher for sample (1) comparing to sample (2). The conduction mechanisms of each phase in the two compounds are determined based on the Elliot theory.

4. REFERENCES

- [1] B. Champagne, A. Plaquet, J. L. Pozzo, V. Rodriguez and F. Castet, J. Am. Chem. Soc., 2012, **134**, 8101-8103.
- [2] M. E. Lines and A. M. Glass, Principles and applications of ferroelectric and related materials, Oxford University Press: New York, 2001.
- [3] A. Mardana, S. Ducharme and S. Adenwalla, Nano Lett., 2011, **11**, 3862-3867.
- [4] H. Wu, N. Reeves-McLaren, J. Pokorny, J. Yarwood and A. R. West, Cryst. Growth Des., 2010, **10**, 3141-3148.
- [5] D. A. Egger, A. M. Rappe and L. Kronik, Acc. Chem. Res., 2016, **49**, 573–581.
- [6] P. P. Shi, Y. Y. Tang, P. F. Li, W. Q. Liao, Z. X. Wang, Q. Ye and R. G. Xiong, Chem. Soc. Rev., 2016, **45**, 3811-3827.

- [7] F. Hao, C. C. Stoumpos, R. P. H. Chang and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2014, **136**, 8094–8099.
- [8] S. Burger, M. G. Ehrenreich and G. Kieslich, *J. Mater. Chem. A*, 2018, **6**, 21785–21793.
- [9] N. A. Spaldin, M. Fiebig, *Science*, 2005, **309**, 391–392.
- [10] W. Eerenstein, N. D. Mathur and J. F. Scott, *Nature*, 2006, **442**, 759–65.
- [11] E. K. H. Salje, *Annu. Rev. Mater. Res.*, 2012, **42**, 265–283.
- [12] W. Y. Zhang, Q. Ye, D. W. Fu and R. G. Xiong, *Adv. Funct. Mater.*, 2017, **27**, 1603945.
- [13] M. D. Hollingsworth, M. L. Peterson, J. R. Rush, M. E. Brown, M. J. Abel, A. A. Black, M. Dudley, B. Raghoeamachar, U. Werner-Zwanziger and E. J. Still, *Cryst. Growth Des.*, 2005, **5**, 2100–2116.
- [14] H. Yu, C.-C. Chung, N. Shewmon, S. Ho, J. H. Carpenter, R. Larrabee, T. Sun, J. L. Jones, H. Ade, B. T. O'Connor and F. So, *Adv. Funct. Mater.*, 2017, **27**, 1700461.
- [15] T. Khan, M. A. Asghar, Z. Sun, A. Zeb, C. Ji and J. Luo, *J. Mater. Chem. C*, 2017, **5**, 2865–2870.
- [16] K. Karoui, A. Ben Rhaïem and K. Guidara, *Ionics*, 2011, **17**, 517–525.
- [17] (a) Q. Gu, M. Yuan, S. Ma and G. Sun, *J. Lumin.*, 2017, **192**, 1211–1219 ; (b) W. Xu, C. He, C. Ji, S. Chen, R. Huang, R. Lin, W. Xue, J. Luo, W. Zhang and X. Chen, *Adv. Mater.*, 2016, **28**, 5886–5890.
- [18] (a) N. Mahfoudh, K. Karoui, M. Gargouri and A. Ben Rhaïem, *Appl. Organometal. Chem.*, 2020, **34**, 5404-5411; (b) F. Hajlaoui, I. Ben Hadj Sadok, H. Alamri Aeshah, N. Audebrand, T. Roisnel, N. Zouari, *J. Mol. Struct.*, 2019, **1182**, 47–53 ; (c) I. Ben Hadj Sadok, F. Hajlaoui, H. Ben Ayed, N. Ennaceur, M. Nasri, N. Audebrand, T. Bataille and N. Zouari, *J. Mol. Struct.*, 2018, **1167**, 316–326.
- [19] F. Hajlaoui, N. Audebrand, T. Roisnel, N. Zouari, *Appl. Organometal. Chem.*, 2019, **34** (2), 5293.
- [20] B. Saparov and D. B. Mitzi, *Chem. Rev.*, 2016, **116**, 4558-4596.
- [21] V. P. Ananikov, *Nanomaterials*, 2019, **9**, 1197-1202.
- [22] W. J. Peveler, J. C. Bear, P. Southern and I. P. Parkin, *Chem. Commun.*, 2014, **50**, 14418-14420.
- [23] (a) S. Pandey and S. B. Mishra, *J. Sol-Gel Sci. Techn.*, 2011, **59**, 73-94; (b) M. Faustini, L. Nicole, E. Ruiz, Hitzky and C. Sanchez, *Adv. Funct. Mater.*, 2018, **28**, 1704158.
- [24] (a) W. Sun, J. Shi, C. Chen and N. Li, *RSC Adv.*, 2018, **8**, 10040-10056 ; (b) C. Sanchez, B. Julián, P. Belleville and M. Popall, *J. Mater. Chem.*, 2005, **15**, 3559-3592
- [25] (a) L. Xu, J. X. Gao, X. G. Chen, X. N. Hua and W. Q. Liao, *Dalton Trans.*, 2018, **47**, 16995-17003 ; (b) C. Jiang, N. Zhong, C. Luo, H. Lin, Y. Zhang, H. Peng and C. G. Duan, *Chem.*

- Commun., 2017, **53**, 5954-5957 ; (c) Z. Wei, W. Q. Liao, Y. Y. Tang, P. F. Li, P. P. Shi, H. Cai and R. G. Xiong, J. Am. Chem. Soc., 2018, **140**, 8110-8113.
- [26] H. Fu, C. Jiang, J. Lao, C. Luo, H. Lin, H. Peng and C.-G. Duan, CrystEngComm., 2020, **22**, 1436-1441.
- [27] T. Khan, M. A. Asghar, Z. Sun, A. Zeb, L. Li, L. Sijie, S. Zhao, C. Ji and J. Luo, Chem. Asian J., 2016, **11**, 2876-2881.
- [28] M. A. Asghar, S. Zhang, T. Khan, Z. Sun, A. Zeb, C. Ji, L. Li, S. Zhao and J. Luo, J. Mater. Chem. C, 2016, **4**, 7537-7540.
- [29] S. Deswal, S. K. Singh, P. Rambabu, P. Kulkarni, G. Vaitheeswaran, B. Praveenkumar, S. Ogale and R. Boomishankar, Chem. Mater., 2019, **31**, 4545–4552.
- [30] (a) A. Zeb, Z. Sun, T. Khan, M. Adnan Asghar, Z. Wu, L. Li, C. Ji and J. Luo, Inorg. Chem. Front., 2017, **4**, 1485-1492; (b) M. Abdelkader and W. Gamal, Appl. Phys. A 2017, **13**, 123-153; (c) W.-Q. Liao, G.-Q. Mei, H.-Y. Ye, Y.-X. Mei and Y. Zhang, Inorg. Chem., 2014, **53**, 8913-8918 ; (d) I. Ben Hadj Sadok, F. Hajlaoui, H. Ben Ayed, N. Ennaceur, M. Nasri, N. Audebrand, T. Bataille and N. Zouari, J. Mol. Struct., 2018, **1167**, 316-326 ; (e) T. Zhang, C. Chen, W.-Y. Zhang and Q. Ye, J. Phys. Chem. C 2018, **122**, 20989-20995.
- [31] P. Jain, V. Ramachandran, R. J. Clark, H. D. Zhou, B. H. Toby, N. S. Dalal, H. W. Kroto and A. K. Cheetham, J. Am. Chem. Soc., 2009, **131**, 13625-13627.
- [32] T. Asahi, K. Hasebe, J. Phys. Soc. Jpn., 1994, **63**, 2827–2828.
- [33] (a) Y.-F. Gao, T. Zhang, W.-Y. Zhang, Q. Ye and D.-W. Fu, J. Mater. Chem. C, 2019, **7**, 9840-9849 ; (b) Y. Sui, D.-S. Liu, W.-T. Chen, L.-J. Wang, Y.-X. Ma, H.-Q. Lai, Y.-W. Zhou and H.-R. Wen, J. Chem. Asian, 2020, **15**, 1–7.
- [34] X.-N. Hua, C.-R. Huang, J.-X. Gao, Y. Lu, X.-G. Chen and W.-Q. Liao, Dalton Trans., 2018, **47**, 6218-6224.
- [35] J.-X. Gao, X.-N. Hua, P.-F. Li, X.-G. Chen, W.-Q. Liao, J. Phys. Chem. C 2018, **122**, 23111-23116.
- [36] C. Ortiz. Cervantes, P. I. Román Román, J. Vazquez; Chavez, M. Hernández; Rodríguez and D. Solis. Ibarra, Angew. Chem. Int. Ed., 2018, **57**, 13882-13886.
- [37] APEX3 program suite V2016.1–0, Bruker AXS Inc., Wisconsin, USA.
- [38] G. M. Sheldrick, SAINT Version 8.37A, Bruker AXS Inc., Wisconsin, USA 2013.
- [39] G. M. Sheldrick, SADABS version 2014/5, SADABS Bruker AXS Inc., Madison, Wisconsin, USA.
- [40] G. Sheldrick, Acta Crystallogr., A 2015, **71**, 3-8.
- [41] G. Sheldrick, Acta Crystallogr., C 2015, **71**, 3-8.
- [42] L. Farrugia, J. Appl. Crystallogr., 2012, **45**, 849-854.

- [43] W. T. Pennington, *J. Appl. Crystallogr.*, 1999, **32**, 1028–1029.
- [44] P. P. Shi, Q. Ye, Q. Li, H. T. Wang, D. W. Fu, Y. Zhang and R. G. Xiong, *Chem. Mater.*, 2014, **26**, 6042–6049.
- [45] W. Zhang, H. Y. Ye, H. L. Cai, J. Z. Ge, R. G. Xiong and S. D. Huang, *J. Am. Chem. Soc.*, 2010, **132**, 7300–7302.
- [46] E. R. Dohner, E. T. Hoke and H. I. Karunadasa, *J. Am. Chem. Soc.*, 2014, **136**, 1718–1721.
- [47] T. Hu, M. D. Smith, E. R. Dohner, M.-J. Sher, X. Wu, M. T. Trinh, A. Fisher, J. Corbett, X.-Y. Zhu, H. I. Karunadasa, A. M. Lindenberg, *J. Phys. Chem. Lett.*, 2016, **7**, 2258–2263.
- [48] J. Tauc, R. Grigorovici and A. Vancu, *Phys. Status. Solidi., B*, 1966, **15**, 627–637.
- [49] H.-J. Li, Y.-L. Liu, X.-G. Chen, J.-X. Gao, Z.-X. Wang and W.-Q. Liao, *Inorg. Chem.*, 2019, **58**, 10357–10363.
- [50] T. T. Palstra, *Inorg. Chem.*, 2017, **56**, 8408–8414.
- [51] L. Mao, C. C. Stoumpos and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2019, **141**, 1171–1190.
- [52] F. Akrouit, F. Hajlaoui, K. Karoui, N. Audebrand, T. Roisnel and N. Zouari. *J. Solid State Chem.*, 287 (2020) 121338.
- [53] A.K. Jonscher, *Nature*, 1977, **267**, 673–679.
- [54] M. Krimi, K. Karoui and A. Ben Rhaïem. *J. Alloys. Compd.*, 2017, 698, 510–517.
- [55] S.R. Elliott, *J. Adv. Phys.*, 1987, **36**, 135–217.

Conflicts of interest

There are no conflicts to declare.

Appendix

CCDC 1842843 and 1993753 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Acknowledgments

The authors thank the University of Sfax-Tunisia for financial support and CDIFX (UMR 6226, Univ. Rennes 1) for X-ray diffraction data collections.

Table 1. Crystal data for [Br-(CH₂)₂-N(CH₃)₃]₂CuBr₄ (**1**) and [Br-(CH₂)₂-N(CH₃)₃]₂ZnBr₄ (**2**)

Compound name	[Br-(CH ₂) ₂ -N(CH ₃) ₃] ₂ CuBr ₄	[Br-(CH ₂) ₂ -N(CH ₃) ₃] ₂ ZnBr ₄
Empirical formula	C ₁₀ H ₂₆ Br ₆ CuN ₂	C ₁₀ H ₂₆ Br ₆ ZnN ₂
Diffractometer	D8 VENTURE	D8 VENTURE
Color	brown	colourless
Formula weight (g.mol ⁻¹)	717.33	719.12
Temperature (K)	150	150
Crystal system	Monoclinic	Monoclinic
	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.9099 (11)	19.011 (2)
<i>b</i> (Å)	9.3350 (7)	18.982 (2)
<i>c</i> (Å)	18.8862 (18)	24.422 (2)
β (°)	90.479 (4)	94.184 (4)
<i>V</i> (Å ³)	2099.7 (3)	8790(2)
<i>Z</i>	4	16
<i>R</i> _{int}	0.065	0.134
ρ _{calc} , (g.cm ⁻³)	2.269	2.174
Absorption correction	Multi-scan	Multi-scan
Radiation (Å)	MoKα (0.71073)	MoKα (0.71073)

μ (mm ⁻¹)	12.45	12.02
Crystal shape	Block	Block
Crystal size (mm ³)	0.18*0.12*0.10	0.32*0.28*0.26
F (000)	1356	6596
θ range [°]	2.2 to 27.5°	2.5 to 27.6°
Collected reflections	4833	20231
No. parameters	179	6596
No. restraints	0	6
Unique reflections	4300	13279
R ₁ , wR ₂ [I > 2 σ (I)]	0.0258, 0.0500	0.1138, 0.1514
R ₁ , wR ₂ [all data]	0.0207, 0.0480	0.0656, 0.1353
Goodness-of-fit on F ²	1.007	1.054
Largest diff. peak/hole/e $\text{\AA}^3$	0.12/ -0.53	2.01/-2.26

Fig.1. (a)-The asymmetric unit of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{CuBr}_4]$ (**1**) ; (b)- View of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{CuBr}_4]$ (**1**) along the b -axis.

Fig.2. (a)-The asymmetric unit of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (**2**) ; (b)- View of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (**2**) along the *b*-axis.

Fig.3 : DSC curves of (a)- $[(CH_3)_3N(CH_2)_2Br]_2[CuBr_4]$ (1) and (b)- $[(CH_3)_3N(CH_2)_2Br]_2[ZnBr_4]$ (2) at $5 K.min^{-1}$.

Fig.4 : ATG curves (a)- $[(CH_3)_3N(CH_2)_2Br]_2[CuBr_4]$ (**1**) and (b)- $[(CH_3)_3N(CH_2)_2Br]_2[ZnBr_4]$ (**2**).

Fig. 5. Optical absorption spectra and determination of Gap energy of (a)- $[(CH_3)_3N(CH_2)_2Br]_2[CuBr_4]$ (1) and (b)- $[(CH_3)_3N(CH_2)_2Br]_2[ZnBr_4]$ (2).

Fig.6. (a, b and c): Theoretical and experimental Nyquist diagram and (d)-Variation of the $\ln(\sigma_g)$ versus $1000/T$ of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{CuBr}_4]$ (**1**).

Fig.7. (a, b and c): Theoretical and experimental Nyquist diagram and (d)-Variation of the $\ln(\sigma_g)$ versus $1000/T$ of $[(CH_3)_3N(CH_2)_2Br]_2[ZnBr_4]$ (2).

Fig.8. (a and b) Frequency dependence of the AC conductivity at various temperatures and (c)-Temperature dependence of the exponent S of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{CuBr}_4]$ (**1**).

Fig.9. (a and b) Frequency dependence of the AC conductivity at various temperatures and (c)- Temperature dependence of the exponent S of $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (**2**).

Highlights

- Two new compounds $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{CuBr}_4]$ (**1**) and $[(\text{CH}_3)_3\text{N}(\text{CH}_2)_2\text{Br}]_2[\text{ZnBr}_4]$ (**2**) are synthesized by slow evaporation conditions.
- The thermal analysis proves two transitions phase in the (1) sample and four transitions phase in the (2) sample.
- The optical and electrical show that the Cu-based compound is a semiconducting and can be used in the application of the photovoltaic cells.
- The all phase transitions are confirmed by the electrical properties.

Declaration of interest statement

The authors would like declare no competing interests.