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Letter

The effect of the combined substitution of NH_4^+ and Cl^- on the structure of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ powder

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ABSTRACT

The structure of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ has been determined from conventional X-ray powder diffraction data, by Rietveld method, in *Fm*−3*m* cubic space group [$a = 10.6798(6)$ Å, $Z = 4$] and was further investigated by IR spectroscopy. The refinement of the structure led to final factor $\chi^2 = 0.068$. The studied $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ compound has an antifluorite-type arrangement. The tellurium atoms are surrounded by a disordered of chlorine or bromine atoms octahedron. The Cs or N atoms are located between the octahedral ensuring the stability of the structure by ionic and hydrogen bonding. Two endothermic peaks in thermal behaviour were detected for this compound at 328 K and 461 K, by DSC experiment. An IR spectroscopic study is employed as a means to obtain preliminary structural information and shows the presence of the NH_4^+ groups.

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1. Introduction

The structure of tellurium materials has been extremely popular these last years due to the peculiar electronic configurations of tellurium IV, whose electron lone pair induces several coordinations and unusual structures [1–3]. Tellurium and its alloys are promising for thermoelectric generators and coolers applications because of their high thermopower such as for tellurium nanotubes which are considered as important semiconductor materials [4] and also for tellurium glasses applications since they present good non-linear optical properties [5–8].

The A_2TeX_6 family (A being alkali metal and X a halogen) represents also a vast class of semiconductors. They have been attracting considerable attention because of their potential applications in optical modulation and scanning devices [9].

In view of this, there has been considerable interest to examine the influence of both cation and anion substitutions on the structure and especially on the bonding within the TeX_6^{2-} anions. Several investigations on this direction resulted in the discovery of a new substituted tellurium $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ powder. In this paper, the vibrational behaviour of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ powder is studied using IR spectroscopy.

In addition we report the preparation of the title compound and its Rietveld structure analysis obtained from the powder diffraction data.

2. Experimental

Tellurium dioxide (TeO_2) was dissolved in the minimum amount of concentrated hydrochloric acid by heating. A mixture of ammonium bromide and cesium bromide with the molar ratio of 8:2 was prepared in hydrochloric acid. The hot solutions were slowly and simultaneously added to the hot tellurium containing solution. A few drops of concentrated hydrochloric acid were added to the hot solution until there was a permanent precipitate. All starting components were of a 99.99 wt.% purity.

Slow cooling from 370 K to 299 K gave orange powder of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ which was filtered and stored for several days in a desiccators containing a small beaker of potassium hydroxide pellets in addition to silica gel.

The sample was mounted in the top-loaded sample holder and investigated by X-ray powder diffraction (XRPD). Powder X-ray data were collected at room temperature using a transmission geometry (STOE) diffractometer equipped with Ni-filtered Cu-L2,3 X-rays were employed ($\lambda 1 = 1.5405$ Å and $\lambda 2 = 1.5443$ Å) at 40 kV/40 mA generator power. In order to limit the axial divergence, 0.02 rad primary and secondary soller slits were inserted. The X-ray powder diffraction data were refined by the Rietveld method [10] using the Fullprof program [11].

The Rietveld refinement was carried out with the pseudo-Voigt function [12] used for the simulation of the peak shapes. In a first step, a Le Bail profile refinement was used to find the profile and instrumental parameters such as the zero error and asymmetry effects. The background was fitted with a linear interpolation between the 26 given points [13]. The refinement with the halfwidth parameters U, V, W, unit cell parameters mixing coefficient η and the symmetry parameters converged to $\chi^2 = 6.89\%$. Then the assumed structure was refined while fixing the profile and instrumental parameters. A final refinement taking into account the overall isotropic displacement factor (Bov) converged to $R_P = 12.2\%$, $R_{wp} = 16.6\%$ and $R_{exp} = 6.29\%$ and conventional Rietveld agreement factors, i.e. excluding background, but with true $\sigma(I)$, $R_P = 18.3\%$, $R_{wp} = 21.8\%$ and $R_{exp} = 8.29\%$.

The occupancy probability of the Cl and Br atoms was refined in such a way that the 24(e) site was totally occupied. However, the occupancy probability of the Cs and N atoms was refined using a totally occupied 8(c) site.

The compound formula was confirmed by standard tests: tellurium is determined gravimetrically by reduction to (SO_2) to the element (9); using a Kjeldahl

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Table 1
Crystal structure data and experimental conditions of structure determination of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$.

Crystallographic data and refinement summary	
Formula	$[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$
Temperature (K)	293
Space group	$Fm\bar{3}m$
a (Å)	10.6801(3)
V (Å^3)	1218.2(2)
Z	4
Radiation (Å)	Cu $K_{\alpha 1}$ 1.5405, Cu $K_{\alpha 2}$ 1.5443
Diffractometer	Transmission geometry (STOE)
2θ range of refinement (°)	8.12–120
No. of structural variables[a]	6
No. of profile parameters[b]	34
R_P (%)	12.2
R_{wp} (%)	16.6
χ^2 (%)	6.89
R_{bragg} (%)	7.99
R_{exp} (%)	6.29
R_f (%)	5.84

[a] Including the scale factor.
[b] Including background coefficients, cell parameters, pseudo-Voigt function parameters, and asymmetry parameters.

Table 2
Positional and isotropic for the structure of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$.

Atoms	Site	x	y	z	B_{iso} (Å^2)	Occ. factor
Te	4a	0	0	0	0.97(2)	1
Br	24e	0.24149(2)	0	0	1.14(1)	0.9304(3)
Cl	24e	0.24149(2)	0	0	1.14(1)	0.0688(3)
Cs	8c	1/4	1/4	1/4	2.413(2)	0.816(1)
N	8c	1/4	1/4	1/4	0.413(1)	0.182(1)
H	32f	0.29742	0.29742	0.20258	0.413(1)	0.0455

apparatus, ammonia is determined by boiling out after the addition of NaOH, collecting the vapor in an aqueous boric acid solution and titrating against standard acid; cesium is determined using a flame photometer.

Crystal structure data and experimental conditions are collected in Table 1. Positional and isotropic thermal parameters are summarized in Table 2. Fig. 1 illustrates the final Rietveld plot for $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$.

Thermal techniques were employed to characterize phase transitions of the title compound. Differential scanning calorimetry (DSC) measurements were carried out using a Setaram DSC121 calorimeter in the temperature range from 300 K to 500 K at a heating rate of 5 K min^{-1} using a polycrystalline sample in a flowing nitrogen atmosphere.

The infrared absorption spectrum was carried out on a Perkin-Elmer 1750 spectrophotometer in the 4000–400 cm^{-1} range on a pressed pellet of powdered sample dispersed in KBr.

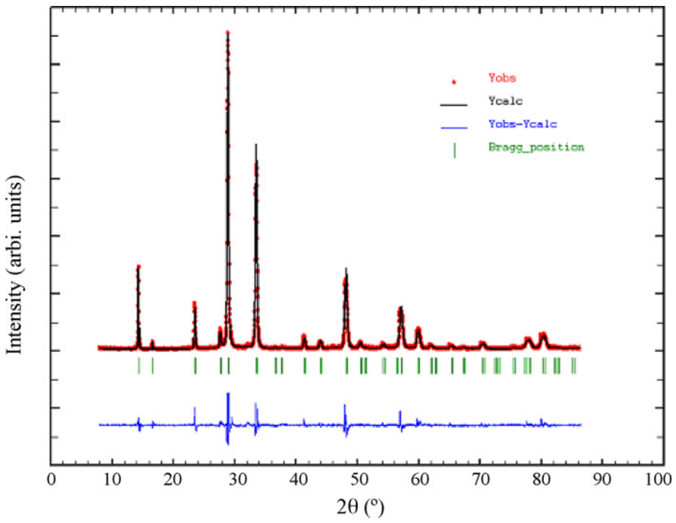

Fig. 1. Powder X-ray diffraction pattern and refinement of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$.

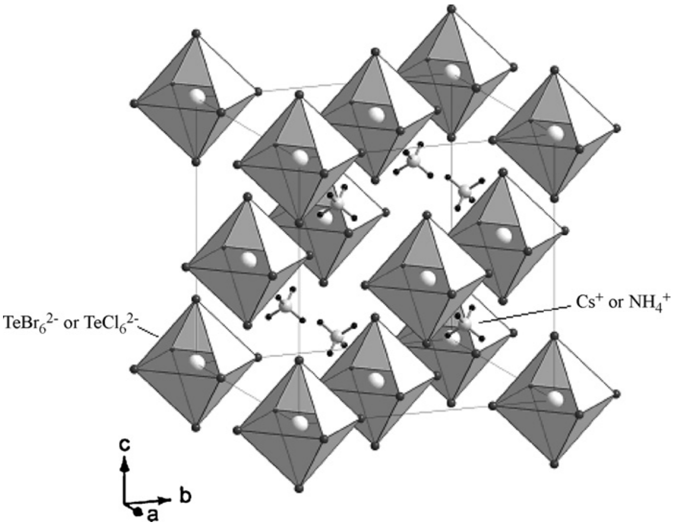

Fig. 2. The structure of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$.

3. Results and discussion

3.1. Structure description

The Cs_2TeBr_6, Cs_2TeCl_6, $(NH_4)_2TeBr_6$ and $(NH_4)_2TeCl_6$ materials are isostructural, they possess the K_2PtCl_6 structure which is based on a face-centered cubic array of the octahedral TeX_6^{2-} ions (where X is a halogen) oriented with the Te–X bonds along the principal cubic axis. In this respect, the title compound is not exceptional: the Te atoms occupy the 4(a) (0,0,0) sites of the $Fm-3m$ space group, surrounded by Br/Cl atoms lying in the 24(e) positions. The Cs or N atoms occupy the 8(c) (1/4,1/4,1/4) sites.

Perspective of the unit-cell content is shown in Fig. 2. The coordination polyhedron of Cs/N cations is represented in Fig. 3.

The Cs/N atoms are 12-fold coordinated with Br/Cl atoms with Cs/N–Br/Cl distances about 3.777(1) Å and X–Cs/N–X angles varying from 62.25° to 119.98° then to 177.24°. On the other hand, the Te atoms are sixfold coordinated with halogen Br/Cl atoms at the corners of a regular octahedron with Te–Br/Cl distances of about 2.579(1) Å and Br/Cl–Te–Br/Cl angles equal to 90.00(1)° or 180.00(1)°.

The Cs^+/NH_4^+ groups are located between the TeX_6 (X = Br or Cl) octahedra ensuring the stability of the structure by ionic and hydrogen bonding contacts.

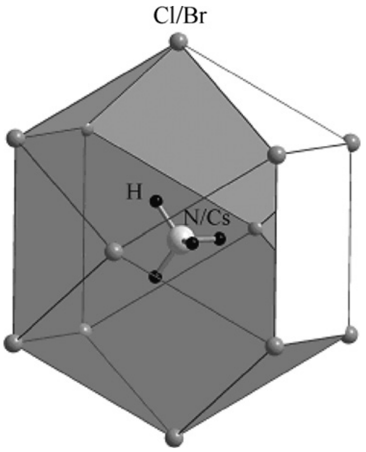

Fig. 3. Cs^+/NH_4^+ environment.

Table 3
Lattice parameters and interatomic distances for Cs_2TeBr_6, Cs_2TeCl_6, $(NH_4)_2TeBr_6$, $(NH_4)_2TeCl_6$ and $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ samples.

Compounds	a (Å)	Te–X (Å)	M–X (Å)
Cs_2TeBr_6	10.918(2)	2.695(4)	3.860(1)
Cs_2TeCl_6	10.449(5)	2.508	3.696
$(NH_4)_2TeBr_6$	10.728(3)	2.681(2)	3.793(1)
$(NH_4)_2TeCl_6$	10.2	2.578	3.606
$[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$	10.6801(3)	2.579(1)	3.777(1)

X = Br or Cl; M = Cs or N.

The lattice parameters and the interatomic distances for Cs_2TeBr_6 [14], Cs_2TeCl_6 [15], $(NH_4)_2TeBr_6$ [14], $(NH_4)_2TeCl_6$ [16], and $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ samples are compared in Table 3.

In comparing the structural data of the five phases, we note that the Te–X distance values of the substituted material are very close to those observed in $(NH_4)_2TeCl_6$. However, the lattice parameter "*a*" of the studied material is close to that observed in $(NH_4)_2TeBr_6$. This appears to be related to the similarity of M–X distances in $(NH_4)_2TeBr_6$ and $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ samples (see Table 3). It is observed that the lattice parameter "*a*" of the five samples progressively decreases with substituting bromine by chlorine and also cesium by ammonium and this is due to the strong difference between Br^- and Cl^- sizes and between Cs^+ and NH_4^+ sizes. So this partial combined substitution may lead to an intermediate solid solution $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ having interesting physical properties.

From Table 3 we note also that the Te–X distances vary, at most 0.187 Å from Cs_2TeBr_6 structure to Cs_2TeCl_6 structure. On the other hand, the M–X distances vary at most 0.254 Å from Cs_2TeBr_6 structure to $(NH_4)_2TeCl_6$ structure. So, the substitutions of Cs^+ by NH_4^+ and Br^- by Cl^- lead especially to an important increase of the cation cavities. This phenomenon is clearly attributed to the increase of the anionic and the cationic sizes.

3.2. Infrared spectroscopic study

IR spectroscopy at room temperature was used to confirm the presence of ammonium groups in $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ compound. The major observed bands associated with NH_4^+ were assigned by comparison with the spectrum of $[Rb_{0.8}(NH_4)_{0.2}]_2TeCl_6$ [17].

The IR spectrum (Fig. 5) is restricted to the frequency range from 400 cm^{-1} to 4000 cm^{-1}. The presence of NH_4^+ group can be confirmed by a large absorption centered at 3122 cm^{-1} and a band at 3002 cm^{-1} resulting from NH_4^+ antisymmetric stretching vibration, and two other absorption bands at 1665 cm^{-1} and 1372 cm^{-1} relative to NH_4^+ bending vibration.

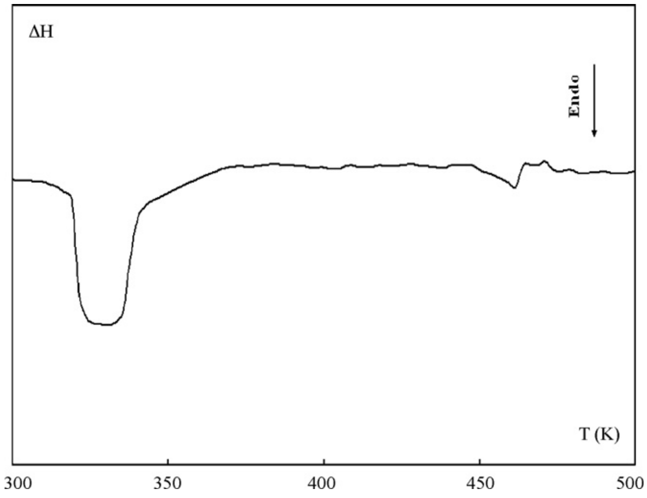

Fig. 4. The DSC curve of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ at room temperature.

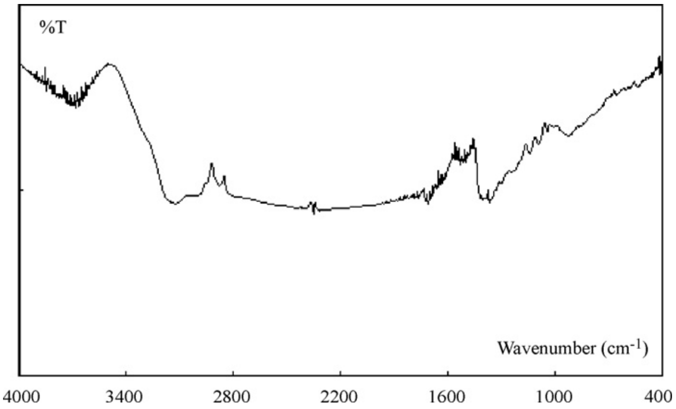

Fig. 5. The Infared spectrum of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$.

3.3. Thermal analysis

The DSC curve of the $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ powder material for heating-up run is shown in Fig. 4. We observe two endothermic anomalies, at 328 K and 461 K with corresponding enthalpies changes $\Delta H_1 = 27.21\ J\ mol^{-1}$ and $\Delta H_2 = 3.07\ J\ mol^{-1}$. As we do not observe any weight loss during the measurement, we cannot attribute any decomposition phenomenon to these anomalies.

By comparison with the pure compounds, only the title compound is analyzed at high temperatures by DSC technique. However in the M_2TeX_6 family we note also a thermal high temperature study of the K_2TeBr_6 material [18] which presents a phase transition sequence from monoclinic through a tetragonal to cubic room temperature structure. These phase transformations was explained by anti-ferro rotations of $TeBr_6$ octahedra around the *c*-axis and *b*-axis. Such work suggests that the title compound probably undergoes a rotational phase transitions of the TeX_6 octahedra. In order to clarify the nature of these transformations it is necessary to make high-temperature structure investigations of the title compound.

4. Conclusions

A combined substituted compound $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ has been synthetised. The structure was refined using Rietveld analyses of powder X-ray diffraction. The title compound crystallises in $Fm-3m$ cubic space group. The main feature of the structure of this material is based on isolated TeX_6 (X = Cl or Br) octahedra connected by ionic and hydrogen bonding through the Cs or N atoms which are located between the octahedral ensuring the stability of the structure. The interesting peculiarity of $[Cs_{0.8}(NH_4)_{0.2}]_2TeBr_{5.6}Cl_{0.4}$ comparing with pure materials that it undergoes two phase transitions on heating at 328 K and 461 K. High-temperature structure and luminescence measurements investigations of the title compound is in our future plans in order to confirm these transformations natures and study the influence of distortion of the Te(IV) coordination octahedron on its luminescence.

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