Letter

Structure and thermal behaviour of Sr-doped $(NH_4)_2TeBr_6$ material

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A R T I C L E   I N F O

A B S T R A C T

The crystal structure of the new Sr-doped material $Sr_{0.02}(NH_4)_{1.98}TeBr_6$, has been investigated using X-ray single crystal analysis at room temperature. The space group is $Fm\bar{3}m$ with lattice parameter $a = 10.7136(2)$ Å and $Z = 4$. The refinement converged to $R_{(F)} = 0.017$ and $W_{R2} = 0.036$. This compound belongs to antifluorite $K_2[PtCl_6]$ family. The main structure of this material is based on $TeBr_6{}^{2-}$ regular octahedron. Sr^{2+} ions replace at random and in the same site the $NH_4{}^+$ ions within the structure of the undoped compound, $(NH_4)_2TeBr_6$. The mixture of $Sr^{2+}/NH_4{}^+$ cations are located between the $TeBr_6{}^{2-}$ octahedral ensuring the stability of the structure by ionic and hydrogen bonding contacts N–H...Br. By comparison with $(NH_4)_2TeBr_6$ the Sr-doping does not affect the structural arrangement, but it leads to decrease the cubic lattice cell dimensions and the Te–Br distances and gives more disorder of $NH_4{}^+$ groups. The presence of the ammonium groups was confirmed using the infrared spectroscopy.

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1. Introduction

Materials based on tellurium are attractive from both fundamental and engineering applications points of view. This is partly due to the lone pairs of tellurium atoms which are generally stereochemically active and which confer good non-linear optical properties on the materials. Tellurium A_2TeX_6 salts (A being an alkali metal and X an halogen) and tellurium dopped compounds are promising for glass and rubber applications since they exhibit interesting physical and magnetic properties like luminescence, piezoelectric and ferroelectric [1–6]. Most compounds in this family crystallize at room temperature in the cubic antifluorite K_2PtCl_6 structure with $Fm\bar{3}m$ (O_h^5) space group. The K_2TeCl_6 compound [1] is the only exception. It has the same structure but at higher temperature, because of the small size of K^+ cations.

The room temperature structure of $(NH_4)_2TeBr_6$ has been determined in 1964 by Das et al. [7]. At low temperature, this material undergoes a phase transition from cubic $Fm\bar{3}m$ to tetragonal $P4/mnc$ (D_{4h}^6) space group. However, spectroscopic and calorimetric methods have never been undertaken on this material to determine their phase transformations at high temperatures.

In order to examine the effect and the influence of the cationic substitution on symmetry and physical properties related to the ammonium dynamics, we have investigated the structure of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ material.

This work is devoted to DSC, IR vibrational analysis and crystal structure investigation of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ at room temperature. In particular, the effect of Sr-doping on the structure and thermal behavior in the corresponding materials based on tellurium.

2. Experimental

2.1. Synthesis

As in the majority of A_2TeX_6 compounds (where X is a halogen) we have used the same preparation method [7,12]. In fact, tellurium dioxide (TeO_2) was dissolved in the minimum amount of concentrated boric acid by heating. Two solutions of ammonium bromide and strontium bromide were prepared in boric acid. The hot solutions were slowly added to the hot tellurium containing solution. A few drops of concentrated hydro-bromidic acid were added to the hot solution until there was a permanent precipitate.

Slow cooling gave bright transparent orange octahedral single crystals of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$. As the crystals of the hexabromotellurate are very sensitive to moisture, they were filtered and stored for several days in a desiccators containing a small beaker of potassium hydroxide pellets in addition to silica gel.

2.2. Characterization

The $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ formula was determined by refinement of the crystal structure at room temperature then the purity was identified by standard tests: Tellurium is determined gravimetrically by reduction of (SO_2) to the element (9); using a Kjeldahl 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; bromine is determined after hydrolysis by titration with silver nitrate using a potentiometric method. The presence of strontium was confirmed by energy dispersive X-ray (EDX) analysis which is a valuable tool for qualitative element analysis. This method allows a fast and non-destructive chemical analysis with a spatial resolution in the micrometer regime. It is based on the spectral analysis of the characteristic X-ray radiation emitted from the sample atoms upon irradiation by the focussed electron beam of a SEM.

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Table 1
Crystallographic data for $Sr_{0.02}(NH_4)_{1.98}TeBr_6$.

Summary of crystallographic data	$T = 299(2)$ K
Formula	$Sr_{0.02}(NH_4)_{1.98}TeBr_6$
Formula weight	709.19
Space group	$Fm\bar{3}m$
a (Å)	10.7136(2)
V (Å^3)	1229.72(4)
Z	4
ρ_{calc} (g/cm^3)	3.831
μ (mm^{-1})	26.146
Crystal size (mm^3)	$0.17 \times 0.22 \times 0.46$
Crystal shape	Octahedral
$F(0\,0\,0)$	1230
Data collection instrument	Kappa-APEX II
Radiation, graphite monochromator	$\lambda_{Mo\,K\alpha}$ (0.71073 Å)
θ range for data collection (°)	5.38 to 35.60
Total reflections	3256
Reflection with ($F > 4\sigma_{(F)}$)	184
$R_{(F)}$[a] (%)	1.74
WR_2[b] (%)	3.64

[a] $R = \dfrac{\sum ||F_O| - |F_C||}{\sum |F_O|}$.

[b] $WR_2 = \left[\dfrac{\Sigma[w(|F_O|^2 - |F_C|^2)]^2}{\Sigma[w(|F_O|^2)]^2} \right]^{1/2}$.

The differential scanning calorimetry measurement was performed using a Setaram DSC121 calorimeter. The DSC curve was recorded between 300 and 600 K at a heating rate of 5 K min^{-1} using a polycrystalline sample in flowing of nitrogen atmosphere.

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

2.3. Crystal data determination of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$

Crystal data collection procedure and structure refinement at room temperature, are given in Table 1. Total reflections were collected with APEX II diffractometer, correction were made for Lorentz-Polarisation and absorption effects.

The positions of the tellurium atoms were determined using a three dimensional Patterson synthesis. Bromine, nitrogen, strontium and hydrogen atoms were located by three-dimensional Fourier function. Structure solution and refinement were carried out using SHELX programs [8,9]. The non-hydrogen atoms were refined anisotropically. The atomic coordinates at room temperature are given in Table 2, the bond lengths and angles in Table 3.

3. Results and discussion

3.1. Structure determination

Te atoms are located in the 4(a) sites of the 8 $Fm\bar{3}m$ (O_h^5) space group, surrounded by an octahedron bromine atoms in the 24(e) positions with coordinates (0, x, 0.5) and $x \simeq 0.25$. The Sr or N atoms occupy the 8(c) (1/4, 1/4, 1/4) sites, as shown in Fig. 1, the anisotropic displacement parameters in Table 4, and the H atoms (by implication) the 32(f) (x, x, $-x$) sites. Schlemper and all (1966) [10] have provided information about the orientation and the thermal motion of the ammonium group in the isomorphous $(NH_4)_2SiF_6$. We have used similar models of ordering in this structural refinement of the title compound.

Table 3
Selected bond lengths (Å) and angles (°).

Bond lengths	
Te–Br	2.6805(5)
Sr/N–H . . . Br	3.7878(3)
Angles	
Br–Te–Br	90°
Br–Te–Br	180°
Te–Br–Sr	89.968(7)°

Table 4
Anisotropic displacement parameters (in 10^{-3} Å^2).

	U11	U22	U33	U23	U13	U12
Te	0.0231(2)	0.0231(2)	0.0231(2)	0	0	0
N/Sr	0.057(3)	0.057(3)	0.057(3)	0	0	0
Br	0.0816(3)	0.0219(2)	0.0816(3)	0	0	0
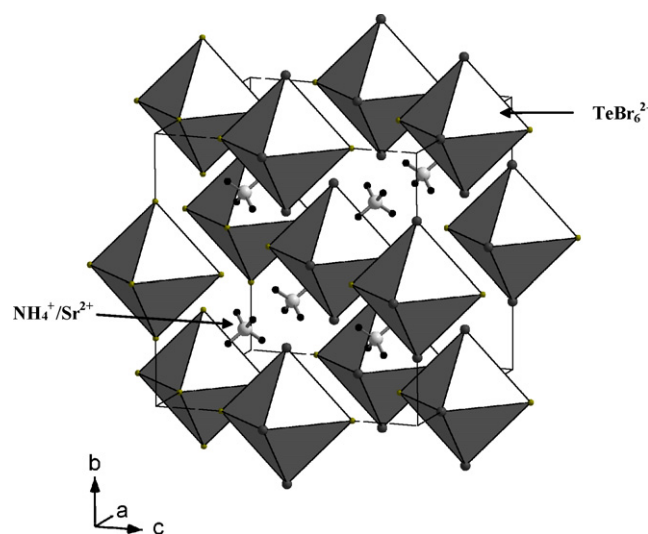
Fig. 1. Room temperature cubic unit cell of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$.

In these models the ammonium tetrahedron may be placed in two similar positions with its axis along [1 1 1] direction, but with either the base or the apex towards the origin. H atoms occupy the 32(f) positions with $x \simeq 0.19$ and $x \simeq 0.31$, respectively.

3.2. Structure of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ description

As shown in Fig. 1, the studied compound crystallizes in the known antifluorite $K_2[PtCl_6]$ cubic face-centered lattice with the $Fm\bar{3}m$ space group. The isolated $TeBr_6$ octahedra are found to be regular despite the coexistence of two different types of bromine bounding, with x_{Br} value: 0.25036(8).

The Sr^{2+} or NH_4^+ tetrahedra, reside in the tetrahedral site of the f.c.c. cell. The presence of NH_4^+ cations induces the coexistence of

Table 2
Fractional atomic and equivalent thermal parameters.

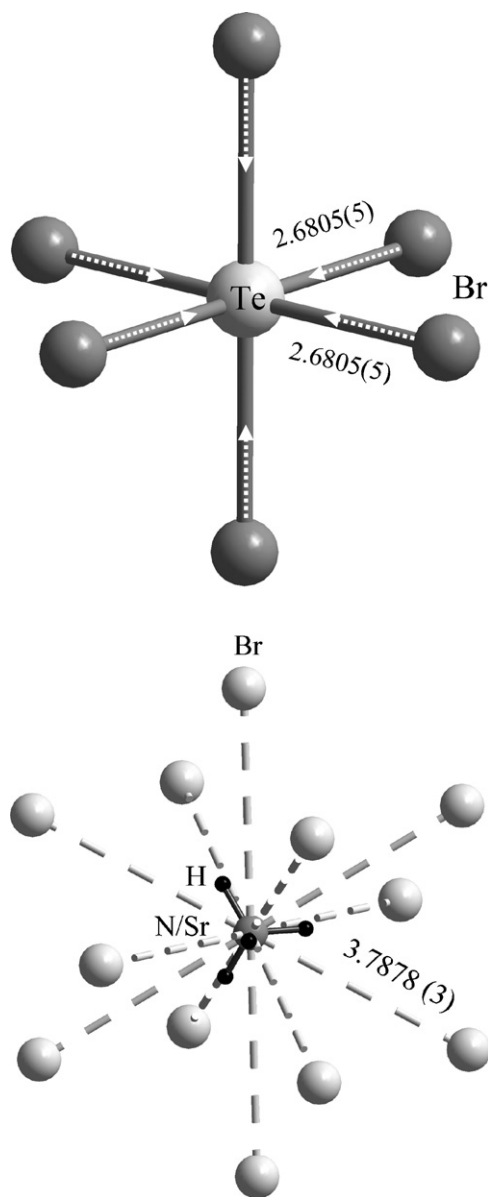|		x	y	z	Occupation	Ueq
$T = 299(2)$	Te	0	0	1/2	0.2083	0.0231(2)
K	N	1/4	1/4	1/4	0.0412(3)	0.057(3)
	Sr	1/4	1/4	1/4	0.0004(1)	0.057(3)
	Br	0	0.25020(5)	1/2	0.1250	0.0617(2)
	H	0.29742(6)	0.29742(6)	0.20258(6)	0.1651	0.069(2)

Ueq = $\frac{1}{3}\sum_i \sum_j Uija_i^* a_i^* a_i a_j$.

Fig. 2. Te and Sr/N environments in $Sr_{0.02}(NH_4)_{1.98}TeBr_6$.

H bonding contacts N–H...Br which providing a linkage between cationic entities NH_4^+ and $[TeBr_6]^{2-}$ anionic complexes.

Nitrogen or Strontium atoms are twelve fold coordinated by Br atom neighbors (Fig. 2). The average distance Sr/N–H...Br is = 3.7878 Å.

3.3. Influence of Sr-doping on the structure of $(NH_4)_2TeBr_6$

Comparison with $(NH_4)_2TeBr_6$ compound we can deduce that the title compound crystallizes in the same structure but with more contraction in the cavity around Sr/N atoms. This decrease is accompanied by a relative contraction of Te–Br bonds. The values of Te–Br distances in $(NH_4)_2TeBr_6$ (2.681(2)Å) [7] are relatively higher than those in $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ (2.6805(5)Å).

Hence, the most significant effect of the partial substitution of NH_4^+ by Sr^{2+} is a decrease of the unit cell parameter "a" as well as the Cation–Bromine distances (3.793(1)Å) in $(NH_4)_2TeBr_6$ and 3.7878(3)Å in $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ especially with partial substitution of the ammonium cations by strontium cations.
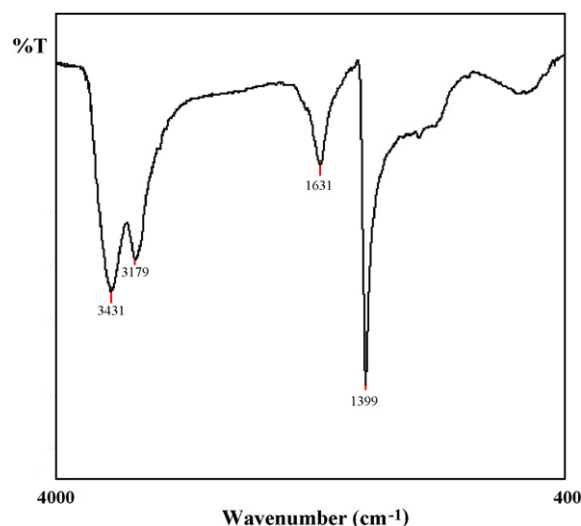

Fig. 3. IR spectrum of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ at room temperature.

This behaviour is clearly due to the relative difference between the ammonium and strontium sizes. The ionic radius of Sr^{2+} is substantially 10% smaller than that of NH_4^+ cation.

By comparison between the undoped and the Sr-doped compound we can compare also the equivalent thermal parameters of the nitrogen atoms. We noted a relative increase of those values from 0.048 to 0.057 Å^2 with substituting ammonium by strontium cations. This increase indicates that the NH_4^+ groups have a slightly more dynamic motion in $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ than in $(NH_4)_2TeBr_6$.

So we deduce that the Sr-doping in these type of compouds gives more disorder of the ammonium groups in the structure.

3.4. Infrared spectroscopic study

IR spectroscopy at room temperature was used to confirm the crystallographic results of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ compound. To assign the IR peaks to vibrational modes, we examined the modes and frequencies observed in $(NH_4)_2TeCl_6$ [11] and $[Rb_{0.8}(NH_4)_{0.2}]_2TeCl_6$ [12].

In the IR spectrum (Fig. 3) the presence of NH_4^+ group can be confirmed by a large absorption centered at 3434 cm^{-1} and another band at 3179 cm^{-1} resulting from NH_4^+ antisymmetric stretching vibration, and two other absorption bands at 1631 and 1399 cm^{-1} resulting from NH_4^+ bending vibration.
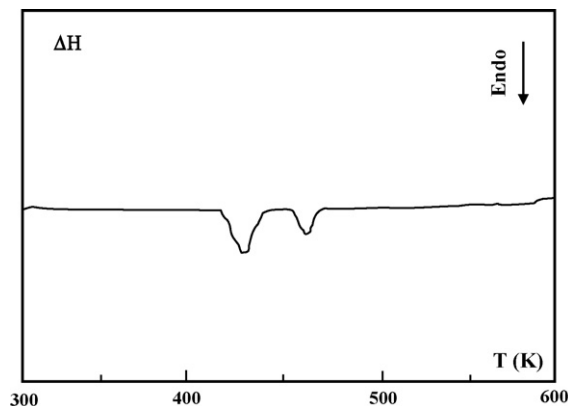

Fig. 4. DSC curve of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$.

3.5. DSC measurements

The DSC (differential scanning calorimetry) measurements were used to identify the phase transformation in the synthesized compound.

From the DSC curve of $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ crystals for the heating run shown in Fig. 4 in the studied temperature range [300–600] K, we observe two endothermic anomalies, at $T_1 = 429$ K and at $T_2 = 459$ K. The corresponding enthalpy changes are $\Delta H_1 = 23.32$ J/g and $\Delta H_2 = 6.71$ J/g, respectively.

These transformations can be attributed to the orientation and the thermal motion of the ammonium groups as already shown in $[Rb_{0.8}(NH_4)_{0.2}]_2TeCl_6$ [12].

4. Conclusions

The new $Sr_{0.02}(NH_4)_{1.98}TeBr_6$ compound crystallizes in the cubic $Fm\bar{3}m$ space group at room temperature. The main feature of this compound structure is the existence of an antifluorite-type arrangement of Sr^{2+}/NH_4^+ and octahedral $TeBr_6^{2-}$ anions. The Sr-doping in $(NH_4)_2TeBr_6$ compoud gives more disorder of the ammonium groups in the structure and leads to a decrease of the volume and the cubic lattice parameter.

DSC measurements probably show two phase transitions for the title compound at $T_1 = 429$ K and at $T_2 = 459$ K in the temperature range [300–600] K.

Additional studies on the nature of the phase transitions (dielectric measurements, Raman scattering, high-temperature structures investigations) are under way and shall give more insight into the nature of the structural phase transitions.

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