Synthesis, crystal structure, thermal analysis and dielectric properties of two mixed trichlorocadmiates (II)

ABDESSATTAR BEN CHRIFA*, ABDELHAMID BEN SALAH and **MOHAMED LOUKIL**

Laboratoire des Sciences des Matériaux et d'Environnement, Faculté des Sciences de Sfax, Université de Sfax, BP 1171, Route de Soukra, 3018 Sfax, Tunisia

Abstract. $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$ are orthorhombic, space group *Pnma*, Z = 4, with a = 8.8760(4) Å, b = 3.9941(2) Å, c = 14.7004(7) Å, and Z = 4, a = 8.9567(9) Å, b = 3.9957(4) Å, c = 14.855 (2) Å, respectively. Final R values are 0.01 and 0.02 for 608 and 834 reflections, respectively. In both the materials, the crystal structure has been determined by X-ray single crystal analysis at room temperature (293 K). The compound structures consist of K^+ (or NH_4^+) cations and double chains of $CdCl_6$ octahedra sharing one edge extending along b-axis. The mixture of K^+/NH_4^+ cations are located between the double chains ensuring the stability of the structure by ionic and hydrogen bonding contacts N/K–H…Cl. Spectroscopic, dielectric and differential scanning calorimetry (DSC) measurements were performed to discuss the mechanism of the phase transition. These studies show that these materials, $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$, undergo a phase transition at 438 and 454 K, respectively.

Keywords. X-ray diffraction; dielectric study; phase transition; DSC; IR absorption; Raman scattering.

1. Introduction

The compounds of general formula ABX_3 (A being alkali, B, Hg or Cd and X, a halide ion), undergo structural phase transitions and interesting physical properties such as ferro-electricity [1–4]. Their structures are slightly distorted from ideal perovskite-type structures [5,6]. Its phase transitions have been intensively studied using Landau theory and lattice dynamics analysis. These systems include the well-defined and extensive class of hexagonal magnetic ABX_3 compounds in which A and B are cations and X is a halogen ion [7–9]. In fact, most ABX_3 compounds are quasi-one-dimensional magnets [10].

Crystalline $KCdCl_3$ consists of double chains of regular octahedra $CdCl_6$ sharing edges [11], with two short Cd–Cl bond lengths and always close to the sum of the covalent radii, the additional four Cl atoms are significantly further away, but at a distance which is less than the sum of the Vander Waals radii. To examine the effect and the influence of cationic substitution over symmetry and physical properties, we have extended these investigations to $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$.

In the present study, we report and discuss the results of a structural investigation, concerning new solid solutions: $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$. We have performed preliminary X-ray diffraction (XRD) measurements providing information about the complete crystal structure at room temperature of the new compounds. These materials were examined by electrical properties, infrared (IR) and

Raman vibrational spectroscopies and differential scanning calorimetry (DSC) thermal technique. The aim of the present work is to determine the title compounds' phase transitions.

2. Experimental

2.1 *Synthesis*

The crystals of $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$ were synthesized dissolving a mixture of KCl, NH_4Cl and $CdCl_2 \cdot H_2O$ in aqueous solution:

$$x\,KCl + (1-x)\,NH_4Cl + CdCl_2 \cdot H_2O \xrightarrow{\;H_2O\;} K_x(NH_4)_{(1-x)}CdCl_3.$$
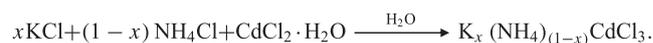
Colourless single crystals were obtained by cooling the mixture for 15 days. The composition of the compound was determined by chemical analysis and density measurements.

2.2 *X-ray structure determination*

Two transparent parallelepipedic crystals with dimensions, $0.20 \times 0.12 \times 0.04$ and $0.26 \times 0.14 \times 0.12$, were chosen from the preparation. The intensity data were collected on An APEX II diffractometer with graphite–crystal monochromated MoKα radiation (0.71073 Å). Lorentz and polarizing effect corrections were carried out before the refinement. Data collection procedure and structure refinement at room temperature are given in table 1.

The cadmium positions were determined using a three-dimensional Patterson synthesis. Chlorine, nitrogen and potassium atoms were located by three-dimensional Fourier

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*Author for correspondence (abdessattarbenchrifa@yahoo.fr)

Table 1. Crystal structure data and experimental conditions of the structure determination of $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$.

Summary of crystallographic data	$T = 293(2)$ K	$T = 293(2)$ K
Formula	$K_{0.57}(NH_4)_{0.43}CdCl_3$	$K_{0.25}(NH_4)_{0.75}CdCl_3$
Formula weight	217.97	118.71
Space group	*Pnma*	*Pnma*
a (Å)	8.876(4)	8.9567(9)
b (Å)	3.9941(2)	3.9957(4)
c (Å)	14.7004(7)	14.855(2)
V (Å^3)	521.15(4)	531.64(9)
Z	4	4
ρ_{calc} (g cm^{-3})	2.778	2.966
μ (mm^{-1})	5.343	5.723
Crystal size (mm^3)	$0.22 \times 0.14 \times 0.06$	$0.28 \times 0.16 \times 0.10$
Crystal shape	Parallelepipedic	Parallelepipedic
$F(000)$	400	436
Data collection instrument	Kappa-APEX II	Kappa-APEX II
Radiation, graphite monochromator	$\lambda_{K\alpha Mo}$ (0.71073 Å)	$\lambda_{K\alpha Mo}$ (0.71073 Å)
θ range for data collection (°)	3.60–26.40	2.66–30.03
Index ranges	$-11 \leq h \leq 10$	$-12 \leq h \leq 12$
	$-4 \leq k \leq 4$	$-4 \leq k \leq 2$
	$-17 \leq l \leq 18$	$-10 \leq l \leq 20$
Total reflections	608	834
Reflection with $(F > 4\sigma(F))$	580	760
$R(F)^a$ (%)	0.01	0.02
WR_2^b (%)	0.04	0.07
$R_{int} - R_\sigma$	0.01–0.02	0.03–0.02
CCDC diposit number*	1050833	1050820

*For more details: http://www.ccdc.cam.ac.uk/conts/retrieving.html or e-mail: deposit@ccdc.cam.ac.uk.

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

Table 2. Fractional atomic and equivalent thermal parameters.

Atoms	x	y	z	U_{eq}	Occupation	Sites
$K_{0.57}(NH_4)_{0.43}CdCl_3$						
Cd	0.16919(3)	1/4	0.056108(2)	0.02099(1)	1	2d
K	0.57125(1)	−1/4	0.17631(8)	0.0274(5)	0.568(6)	2d
N	0.57125(1)	−1/4	0.17631(8)	0.0274(5)	0.432(7)	2d
H1	0.6166(7)	−0.0534(7)	0.1884(8)	0.033	1	1d
H2	0.549(3)	−1/4	0.1166(4)	0.033	1	2d
H3	0.4831(1)	−1/4	0.2067(2)	0.033	1	2d
Cl1	0.28833(1)	1/4	0.21039(6)	0.0256(2)	1	2d
Cl2	0.02344(9)	1/4	−0.10149(5)	0.02005(2)	1	2d
Cl3	0.33271(9)	−1/4	−0.00735(6)	0.0226(2)	1	2d
$K_{0.25}(NH_4)_{0.75}CdCl_3$						
Cd	0.16702(3)	3/4	0.943568(2)	0.02007(2)	1	2d
Cl1	0.33101(9)	1/4	1.00534(6)	0.0209(2)	1	2d
Cl2	0.02455(1)	3/4	1.10065(5)	0.0192(2)	1	2d
Cl3	0.28492(1)	3/4	0.79011(6)	0.0246(2)	1	2d
K	0.0689(2)	1/4	0.67525(1)	0.0285(7)	0.253(7)	2d
N	0.0689(2)	1/4	0.67525(1)	0.0285(7)	0.747(7)	2d
H1	−0.0213(1)	1/4	0.702(2)	0.034	1	2d
H2	0.138(2)	1/4	0.7195(1)	0.034	1	2d
H3	0.0778(1)	0.0535(7)	0.6461(3)	0.034	1	1d

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a *_i a *_j a_i a_j$.

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

Atoms	U11	U22	U33	U23	U13	U12
$K_{0.57}(NH_4)_{0.43}CdCl_3$						
Cd	0.02351(2)	0.01688(2)	0.02261(2)	0	−0.00411(9)	0
K	0.0321(7)	0.0212(7)	0.0287(7)	0	−0.0013(5)	0
N	0.0321(7)	0.0212(7)	0.0287(7)	0	−0.0013(5)	0
Cl1	0.0290(5)	0.0239(5)	0.0238(4)	0	−0.0054(3)	0
Cl2	0.0209(4)	0.0199(4)	0.0193(4)	0	−0.0009(3)	0
Cl3	0.0207(4)	0.0174(4)	0.0295(4)	0	0.0032(3)	0
$K_{0.25}(NH_4)_{0.75}CdCl_3$						
Cd	0.0241(2)	0.0152(3)	0.0209(2)	0	0.00373(8)	0
Cl1	0.0213(4)	0.0155(5)	0.0261(4)	0	−0.0031(8)	0
Cl2	0.0220(4)	0.0186(5)	0.0171(4)	0	0.0009(3)	0
Cl3	0.0296(5)	0.0226(5)	0.0217(4)	0	0.0043(3)	0
K	0.035(1)	0.0200(1)	0.0305(1)	0	−0.0027(8)	0
N	0.035(1)	0.02(1)	0.0305(1)	0	−0.0027(8)	0

Table 4. Principal interatomic distances (Å) and bond angles (°) in CdCl$_6$ octahedra.

$K_{0.57}(NH_4)_{0.43}CdCl_3$		$K_{0.25}(NH_4)_{0.75}CdCl_3$	
Cd–Cl1	2.5025(9)	Cd–Cl3	2.5123(9)
Cd^i–Cl3^i	2.6391(6)	Cd–Cl1^i	2.6440(6)
Cd–Cl2	2.6534(8)	Cd–Cl2	2.6597(9)
Cd–Cl2^{ii}	2.7123(6)	Cd–Cl2^x	2.7142(6)
Cd–K^{iii}	4.1208(1)	Cd–K^{xi}	4.176(2)
K–Cl1^{iv}	3.2365(1)	K–Cl3^v	3.2628(2)
K–Cl1^v	3.2474(1)	K–Cl3^{xii}	3.2754(2)
K–Cl3^{iii}	3.2991(1)	K–Cl1^{xiii}	3.3415(2)
K–Cl2^{vi}	3.3728(1)	K–Cl1^{xiv}	3.3415(2)
K–Cl3	3.4310(1)	K–Cl1^{xii}	3. 426(2)
K–Cl2^{iii}	3.7619(1)	K–Cl2^{xv}	3. 433(2)
K–K^{vii}	3.9941(2)	K–K^{vii}	3.9957(4)
K–Cd^{iii}	4.1208(1)	K–Cd^{iii}	4.176(2)
K–H1	0.8999(1)	K–H1	0.9(1)
K–H2	0.9(1)	K–H2	0. 8999(1)
K–H3	0.9(1)	K–H3	0. 8999(1)
Cl1–K^{viii}	3.2365(1)	Cl2–K^{xv}	3.433(2)
Cl2–K^{ix}	3.2991(1)		

$K_{0.57}(NH_4)_{0.43}CdCl_3$				$K_{0.25}(NH_4)_{0.75}CdCl_3$			
Cl1	Cd1	Cl3^i	95.04(2)	Cl3	Cd1	Cl1^i	94.67(3)
Cl3^i	Cd1	Cl3	98.35(3)	Cl1^i	Cd1	Cl1	98.16(3)
Cl1	Cd1	Cl2	175.82(3)	Cl3	Cd1	Cl2	176.18(3)
Cl3^i	Cd1	Cl2	87.68(2)	Cl1^i	Cd1	Cl2	87.82(2)
Cl1	Cd1	Cl2^{ii}	92.49(2)	Cl3	Cd1	Cl2^{ii}	92.64(3)
Cl3^i	Cd1	Cl2^{ii}	172.22(3)	Cl1^i	Cd1	Cl2^{ii}	172.46(3)
Cl3	Cd1	Cl2^{ii}	82.904(2)	Cl1	Cd1	Cl2^{ii}	83.05(2)
Cl2	Cd1	Cl2^{ii}	84.69(2)	Cl2	Cd1	Cl2^{ii}	84.78(2)
Cl1	Cd1	Cl2^{iii}	92.49(2)	Cl3	Cd1	Cl2^{vi}	92.64(3)
Cl2^{ii}	Cd1	Cl2^{iii}	94.83(3)	Cl2^i	Cd1	Cl2^{vi}	94.79(3)

Symmetry codes: (i) $x. y + 1.z$; (ii) $-x. -y. -z$; (iii) $-x + 1. -y. -z$; (iv) $x + 1/2.y - 1. -z + 1/2$; (v) $x.y - 1. z$; (vi) $-x + 1/2.-y. z + 1/2$; (vii) $-x. -y + 1. -z$; (viii) $x - 1/2. y. -z - 1/2$; (ix)$-x + 1. -y - 1. -z$; (x) $-x.-y + 1. -z + 2$; (xi) $-x + 1/2.y + 1/2.-z + 1/2$; (xii) $x - 1/2. y + 1/2. -z + 1/2$; (xiii) $-x + 1/2.y - 1/2.z - 1/2$; (xiv) $-x + 1/2. y - 1/2. z - 1/2$; (xv) $-x + 1. -y + 1. -z + 2$.
Symmetry codes: (i) $x. y + 1.z$; (ii) $-x. -y. -z$; (iii) $-x. -y + 1. -z$; (iv) $-x. -y + 2. -z + 2$.

function. The H atoms were located geometrically, and attributed isotropic thermal factors equal to those of the atoms on which they are linked. Structure solution and refinement were carried out using SHELXS and SHELXL programmes [12,13]. The nonhydrogen atoms were refined anisotropically. The final atomic coordinates are given in table 2. Main geometrical features, bond distances and angles are reported in tables 3 and 4.

Interatomic distances, bond angles and details of the hydrogen bonding scheme are given in table 5.

2.3 *DSC*

DSC measurements were carried out using a DSC 822P METTLER TOLEDO calorimeter. DSC was recorded in 340–460 K regions at a heating rate of 5 K min^{-1} using a polycrystalline sample in a flowing nitrogen atmosphere.

2.4 *IR spectrum*

For the IR measurement, a small quantity of the powder was used. The IR spectrum was recorded at room temperature in 400–4000 cm^{-1} region using a KBr pellet on Perkin Elmer spectrometer. The spectral resolution was 1 cm^{-1}.

2.5 *Raman spectra*

Raman spectra were measured with a LABRAMHR 800 triple monochromator. Raman spectra were recorded in 50–3500 cm^{-1} region.

2.6 *Dielectric studies*

Polycrystalline pellets, 12 mm in diameter and 1 mm in thickness, were obtained at room temperature by pressing under 200 MPa. In the electrical measurement, the sample was pasted with Ag on the two sample faces, as the electrodes with Ni paste or sputtered Au make amalgams with cadmium compounds.

3. Results and discussion

3.1 *Structure of $K_x(NH_4)_{(1-x)}CdCl_3$ description*

The crystal structure of $K_{0.57}(NH_4)_{0.43}CdCl_3$ is depicted in figure 1.

At room temperature, $K_{0.57}(NH_4)_{0.43}CdCl_3$ is orthorhombic. The space group is *Pnma*, the unit cell dimensions are $a = 8.8760(4)$ Å, $b = 3.9941(2)$ Å, $c = 14.7004(7)$ Å and $Z = 4$. It consists of double chain of $CdCl_6$ octahedra running along the *b*-axis (figure 2). Each Cd–Cl bond ranges from 2.5025(9) to 2.7123(6) Å (figure 4b). The Cl–Cd–Cl angles extend from 82.903(19) to 175.82(3)° (table 4).

The K^+ or NH_4^+ tetrahedra reside in the 2(d) site of the orthorhombic cell. The presence of NH_4^+ cations induces the
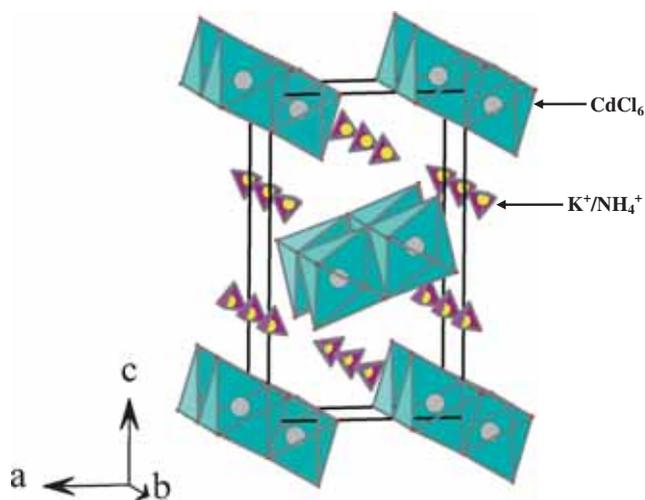

Figure 1. Perspective view of the structure of $K_{0.57}(NH_4)_{0.43}CdCl_3$.
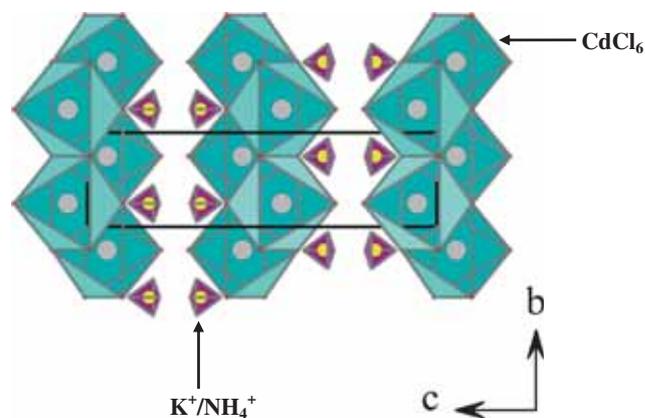
Table 5. Principal interatomic distances (Å) and bond angles (°) involved in the hydrogen bonds.

	N–H	H...Cl	N/K...H...Cl	N/K...Cl
$K_{0.25}(NH_4)_{0.75}CdCl_3$				
N–H1...Cl1^i	0.9	2.451	146.03	3.236
N–H2...Cl3	0.9	2.646	146.24	3.431
N–H2...Cl3^{ii}	0.9	2.77	118.82	3.299
N–H3...Cl1^{iii}	0.9	2.642	125.4	3.247
N–H3...Cl2^{iv}	0.9	2.822	120.83	3.373
$K_{0.57}(NH_4)_{0.43}CdCl_3$				
N–H1...Cl3^v	0.9	2.649	127.44	3.275
N–H1...Cl2^{vi}	0.9	2.933	116.70	3.433
N–H2...Cl3^{iii}	0.9	2.614	129.63	3.263
N–H3...Cl1^{vii}	0.9	2.552	146.79	3.341

Symmetry codes: (i) $x+1/2, y, -z+1/2$; (ii) $-x+1, -y-1, -z$; (iii) $x, y-1, z$; (iv) $-x+1/2, -y, z+1/2$; (v) $x-1/2, -y+1/2, -z+3/2$; (vi) $-x, -y+1, -z+2$; (vii) $-x+1/2, y-1/2, z-1/2$.

Figure 2. Projection of the *a*-axis of the atomic arrangement of $K_{0.57}(NH_4)_{0.43}CdCl_3$ structure.

coexistence of H bonding contacts N–H...Cl, which provide a linkage between cationic entities NH_4^+ and $[CdCl_6]^{4-}$ anionic complexes.

Nitrogen or potassium atoms are coordinated nine fold by Cl atom neighbours. The K/N–H...Cl distances range from 3.236 to 3.431 Å (table 4).

For the second substituted compound of $K_{0.25}(NH_4)_{0.75}CdCl_3$, it has the same structure, so it may be described as consisting of double rutile-like columns of $CdCl_6$ octahedra running along the *b*-axis (figure 3). The cell parameters are $a = 8.9567(9)$ Å, $b = 3.9957(4)$ Å, $c = 14.8552(2)$ and $Z = 4$. Each Cd atom is surrounded by six chlorine atoms in the form of a compressed ideal octahedron with distance between 2.5123(9) and 2.7142(6) Å (figure 4a). The Cl–Cd–Cl angles extend from 83.05(2) to 176.18(3)° (table 4).

The ammonium groups are located between the chains ensuring the stability of the structure by hydrogen bonding
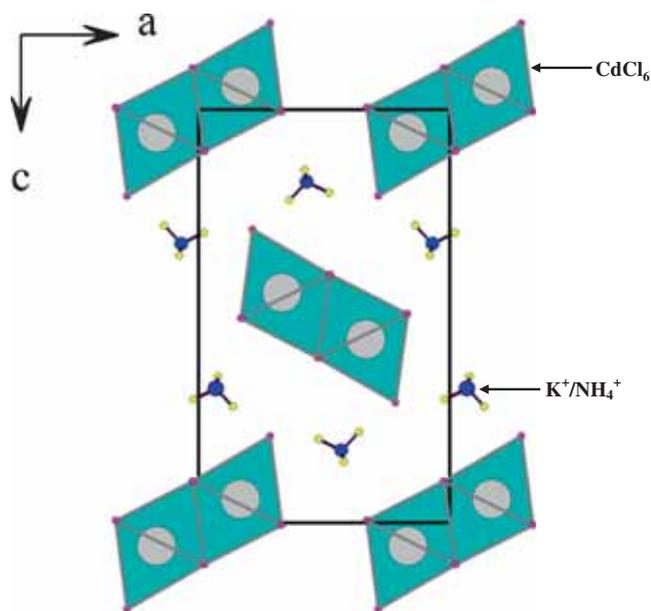
Figure 3. Projection of the $K_{0.25}(NH_4)_{0.75}CdCl_3$ structure along the *b*-axis.
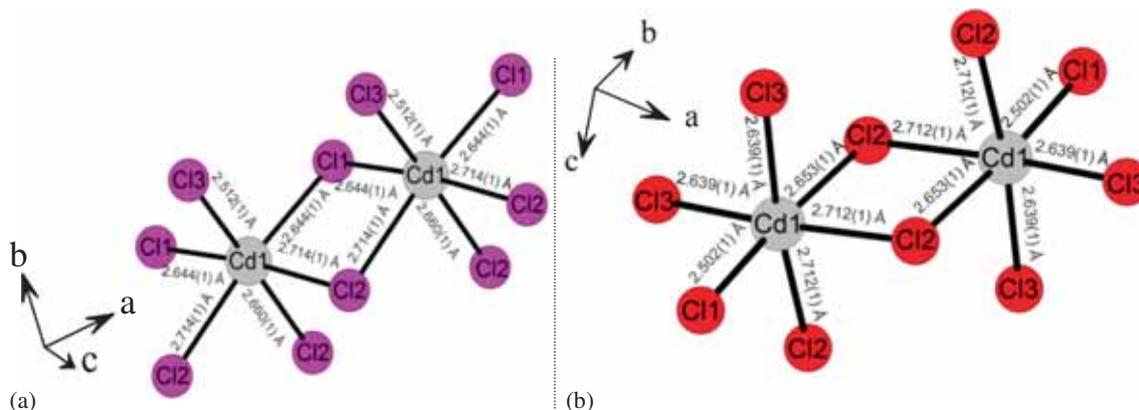
contacts (N–H . . . Cl) (figure 5). The K/N–H. . .Cl distances range from 3.263 to 3.433 Å (table 5).

At room temperatures, the ammonium coordination polyhedra remains essentially unchanged. The groups are coordinated by nine chlorine atoms (four Cl(1), two Cl(2) and three Cl(3)) (figure 6), belonging to the $CdCl_6$ octahedral at distance between 3.2365(1) and 3.7619(1) Å (table 4).

In conclusion, at room temperature, the ammonium group (NH_4^+) exhibits a dynamic orientational disorder, which might be similar to that observed in NH_4Cl [14]. However, this ammonium disorder at room temperature influences the distortion of the octahedral $[CdCl_6]^{4-}$.

3.2 *Ammonium rate effect on the structure*

3.2a *The effect on the parameters and cell volume*: With reference to the earlier studies of $ACdCl_3$ compounds, we note that the size of the monovalent cation A^+ significantly affects the lattice parameters of the crystal. For this, we led to study the behaviour of these parameters with ammonium introducing into the $KCdCl_3$ system.

This study confirms the hypothesis already established, in fact, the ammonium dependence of *a*, *c* lattice parameters and the cell volume show an increasing behaviour, which indicates that the size of the NH_4^+ cation added to the network causes the cell expansion (figures 7 and 8).

From $K_{0.57}(NH_4)_{0.43}CdCl_3$ to $K_{0.25}(NH_4)_{0.75}CdCl_3$ compounds, we note that the hydrogen bonding N–H...Cl along the *a* and *c* axes becomes higher than the others (from 3.236 to 3.275 Å and from 3.247 to 3.263 Å, respectively), so, the chlorine atoms become more and more directed to NH_4^+ groups, which causes this behaviour after the increase of the *a* and *c* parameters (table 5).

The net behaviour is an increase of the unit cell volume *V* (figure 9) as well as the *a* and *c* parameters with increase in the rate of ammonium in the system. This corresponds to the increases of Cd–Cl distances, directed parallel to the *a* and *c* axes (table 4).

In spite of these parameters expansion, it appears that an abnormal decrease of the *b* parameter with increase in ammonium rate. This corresponds to the decrease in Cd–Cl
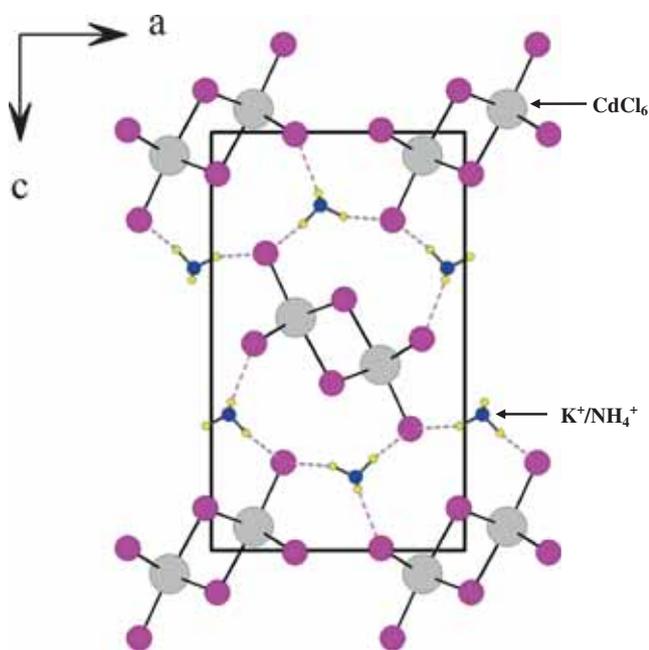

Figure 4. Environment of cadmium in (**a**) $K_{0.25}(NH_4)_{0.75}CdCl_3$ and (**b**) $K_{0.57}(NH_4)_{0.43}CdCl_3$.

Figure 5. The structure of $K_{0.25}(NH_4)_{0.75}CdCl_3$ projected according to the *b*-axis and including the hydrogen bonding.
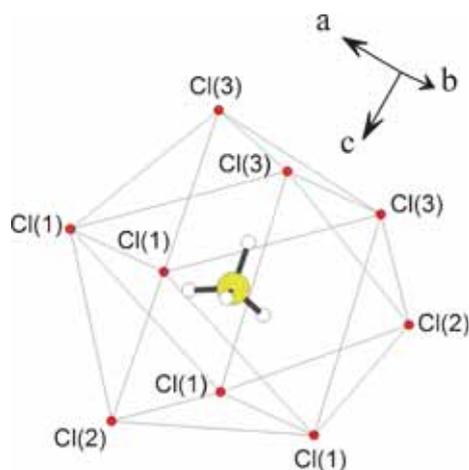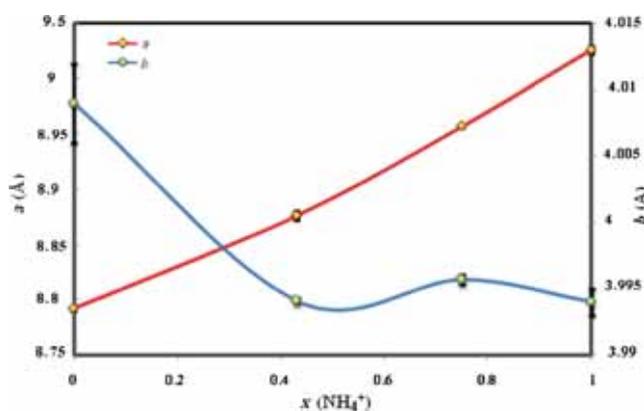

Figure 6. K^+/NH_4^+ environment.

Figure 7. Percentage of ammonium dependence of the lattice parameters *a* and *b* for $K_x(NH_4)_{(1-x)}CdCl_3$.
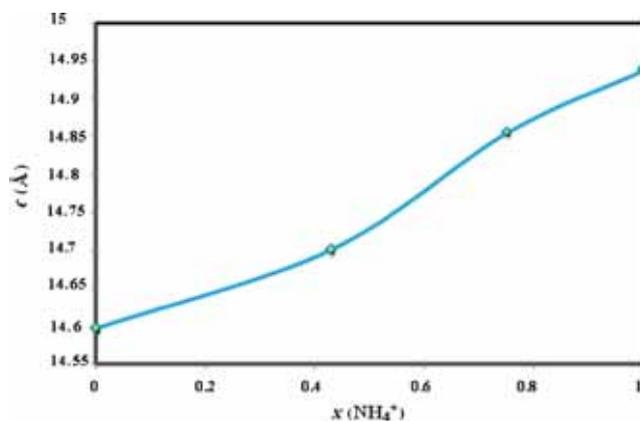

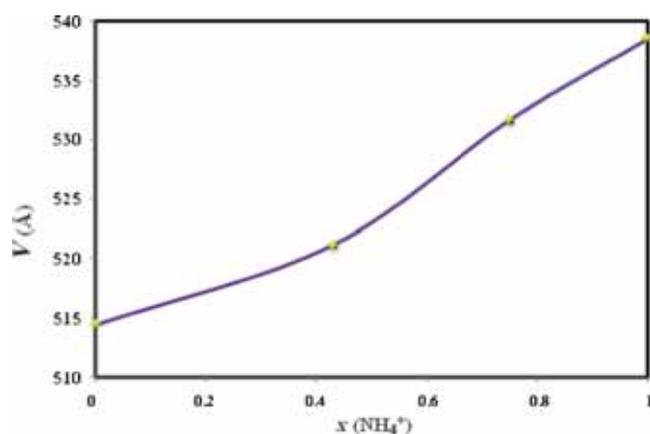**Figure 8.** Percentage of ammonium dependence of the lattice parameters *c* for $K_x(NH_4)_{(1-x)}CdCl_3$.

Figure 9. Percentage of ammonium dependence of the lattice volume *V* $K_x(NH_4)_{(1-x)}CdCl_3$.

equatorial bond distances, directed parallel to the *a*-axis (chains direction). The observed behaviour is clearly confirmed while referring to the data of table 6.

3.2b *The effect on the cation environment*: Increasing rate of ammonium from $K_{0.57}(NH_4)_{0.43}CdCl_3$ to $K_{0.25}(NH_4)_{0.75}CdCl_3$ materials leads to a displacement of the nitrogen/potassium atoms (0.57125(1), −0.25, 0.17631(8) to 0.0689(2), 0.25, 0.67525(1), respectively) accompanied by a relative increase in the thermal motion of NH_4^+/K^+ groups from 0.0274(5) to 0.0285(7). This increase exhibits more dynamic orientational disorder of ammonium groups in the $K_{0.25}(NH_4)_{0.75}CdCl_3$ compound.

3.3 *Transition characterization*

3.3a *DSC measurements*: In figure 10, typical DSC traces in 420–500 K temperature range for $K_{0.25}(NH_4)_{0.75}CdCl_3$ and $K_{0.57}(NH_4)_{0.43}CdCl_3$ material are shown. Two endothermic peaks at $T_1 = 454$ K and $T_2 = 438$ K have been observed on heating. The corresponding enthalpy changes are $\Delta H_1 = 21.25$ J g^{-1} and $\Delta H_2 = 20.70$ J g^{-1}, respectively.

Table 6. Comparison of Cd–Cl bond distances.

	$KCdCl_3$	$K_{0.57}(NH_4)_{0.43}CdCl_3$	$K_{0.25}(NH_4)_{0.75}CdCl_3$	NH_4CdCl_3[11]
Cd–Cl (Å)	–	2.502(1)–2.712(1)	2.512(1)–2.714(1)	2.513(2)–2.72(2)
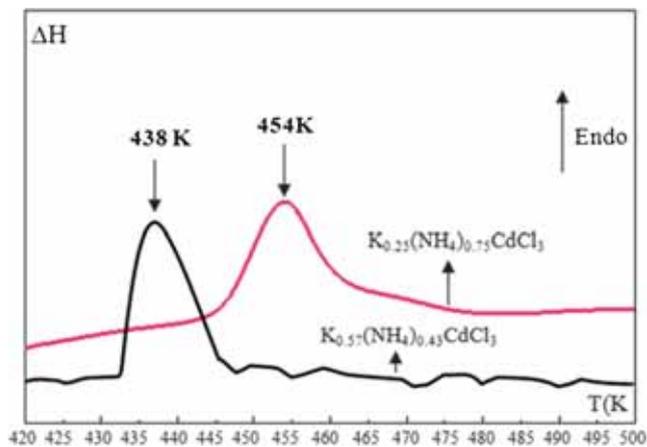
Figure 10. DSC thermogram of $K_{0.25}(NH_4)_{0.75}CdCl_3$ in the temperature range of 420–500 K.
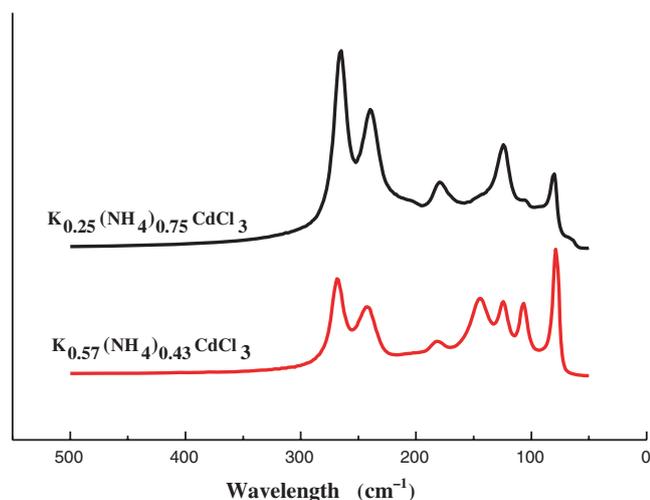
Figure 11. Raman spectra of $K_x(NH_4)_{(1-x)}CdCl_3$ between 50 and 500 cm^{-1}.

3.3b *Raman spectroscopic study*: Raman spectroscopic studies are realized to confirm results of the radiocrystallographic method of the mixed compounds $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$. This study is restricted to the low frequency range (50–500 cm^{-1}) (figure 11 and table 7). The Raman bands associated with K$^+$ and NH$_4^+$ cations were assigned by comparison with other compounds based on cadmium [15]. The two spectra of $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$ are similar.

The Raman bands observed at 80 and 105.5 cm^{-1} are associated with K$^+$ and Cl$^-$ translations, respectively. The band at 124.2 cm^{-1} corresponds to the CdCl$_2$ libration. The

Table 7. Raman spectra of $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}$ CdCl$_3$ at room temperature (v: stretching).

$K_{0.57}(NH_4)_{0.43}CdCl_3$	$K_{0.25}(NH_4)_{0.75}CdCl_3$	Attribution
78.9	80	K$^+$ translation
106.5	105.5	Translation Cl$^-$
124	124.2	CdCl$_2$ libration
144.5	145	NH$_4^+$ translation
181.4	179.6	NH$_4^+$ libration
242.5	240.5	v(CdCl) covalent
268.8	264.9	v(CdCl) coordination

Table 8. IR spectra at room temperature of $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$ (δ: deformation).

$K_{0.57}(NH_4)_{0.43}CdCl_3$	$K_{0.25}(NH_4)_{0.75}CdCl_3$	Assignment
558	558	H$_2$O libration in KBr
1395	1395	δ_{as} (NH$_4^+$)
1625	1625	δ_s (NH$_4^+$)
3156	3153	δ_s (NH$_4^+$)
3556	3497	H$_2$O libration in KBr

libration mode of NH$_4^+$ appears at 145 cm^{-1}, where the translational mode appears at 179.6 cm^{-1}. The relatively most intense band at 282 cm^{-1} and the shoulder at 247 cm^{-1} correspond to vCdCl stretching. The presence of two modes of Cd–Cl vibrations which differs in magnitude and frequency, supports the radiocrystallographic results concerning the octahedral coordination of the cadmium and the coexistence of two types of Cd–Cl bondings: strong covalent bonds and coordination bonds.

3.3c *IR spectroscopy investigation*: At room temperature, the frequencies of the observed two phases are listed in table 8. The IR bands associated with the NH$_4^+$ group were assigned by comparison with the spectra of NH$_4$CdCl$_3$ [16]. The bands observed at 3497 and 558 cm^{-1} are characteristic of water molecules from KBr. The band observed at 3153 cm^{-1} is due to v(NH$_4^+$) stretching modes. The symmetric and asymmetric bending vibrations of NH$_4^+$ appear in two bands at 1625 and 1395 cm^{-1}.

The spectral evolution with increasing temperature is shown in figures 12 and 13. The transitions are clearly characterized. To gain more information on the crystal dynamics and to determine the nature of the high temperature phase
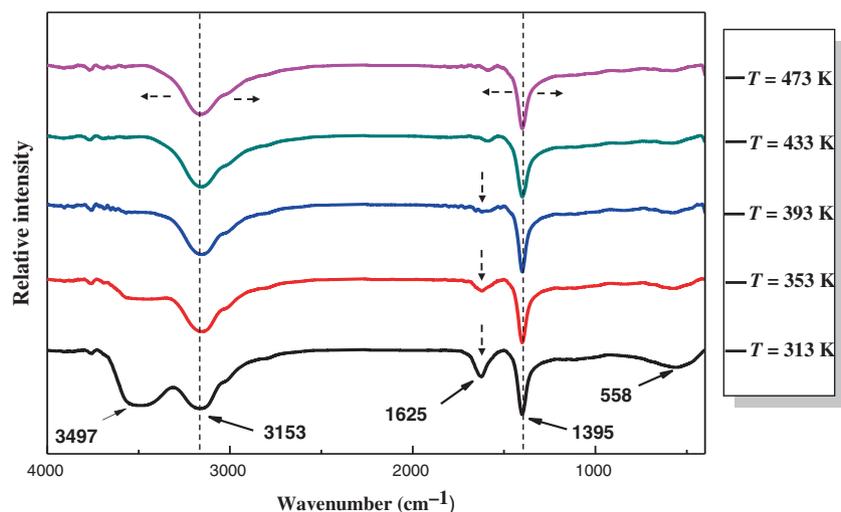
Figure 12. IR spectra at different temperatures of $K_{0.57}(NH_4)_{0.43}CdCl_3$.
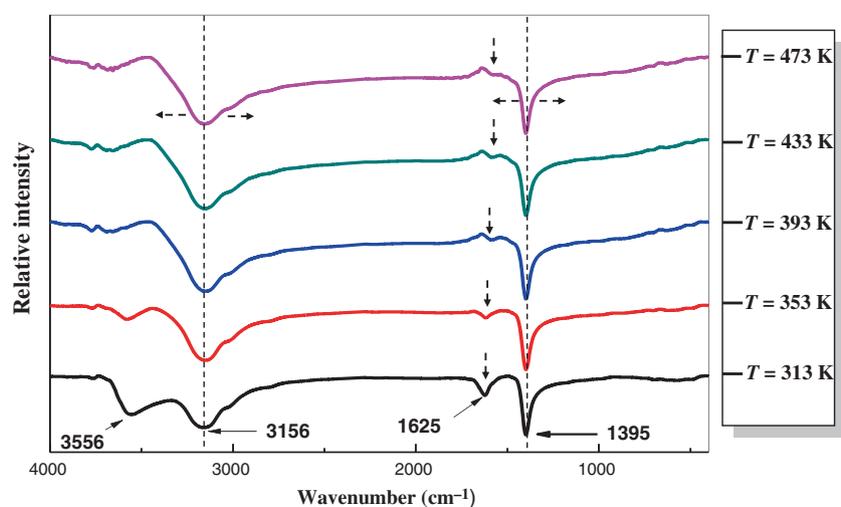

Figure 13. IR spectra at different temperatures of $K_{0.25}(NH_4)_{0.75}CdCl_3$.

transitions, we have undertaken an IR study between 303 and 463 K.

From these curves, it could be seen that at about 400 K, changes in the IR band are the characteristics of the ammonium groups. The spectral changes concern the internal vibrations of NH_4^+ tetrahedra. This transition is defined by the following changes:

(1) The band at 3153 cm^{-1} increases in intensity and increases in halfwidth.
(2) Disappearance of the librational modes of NH_4^+ cations at 1625 cm^{-1} indicate the large dynamic motion of NH_4^+ at high temperature.
(3) The halfwidth of the band at 1395 cm^{-1} increases.

DSC measurements, infrared and raman spectra show that the title compounds probably undergo an orientational 'order–disorder' phase transition of NH_4^+ tetrahedra at 454 K for $K_{0.25}(NH_4)_{0.75}CdCl_3$ and at 438 K for $K_{0.57}(NH_4)_{0.43}CdCl_3$.

It follows that the increase in temperature probably does not affect the structural arrangement, but it leads to an 'order–disorder' phase transition.

3.3d *Dielectric study*: The dielectric study is an important source of valuable information about conduction processes. To obtain more information on the crystal dynamics, we have undertaken a dielectric study between 300 and 550 K in the frequency range of 100 Hz–5 MHz for $K_{0.25}(NH_4)_{0.75}CdCl_3$.

Figures 14 and 15 illustrate respectively, the temperature dependence of the real ε'_r part of the complex electric and dielectric losses tan δ. From these curves, we can observe an anomaly at about 454 K. This transition can be attributed to the 'order–disorder' phase transition, which probably characterizes the motion of a rapid NH_4^+ reorientation and H^+ diffusion. However, if the temperature is raised, the reorientation of NH_4^+ ions becomes more excited and the protons jump over the potential barrier [17].
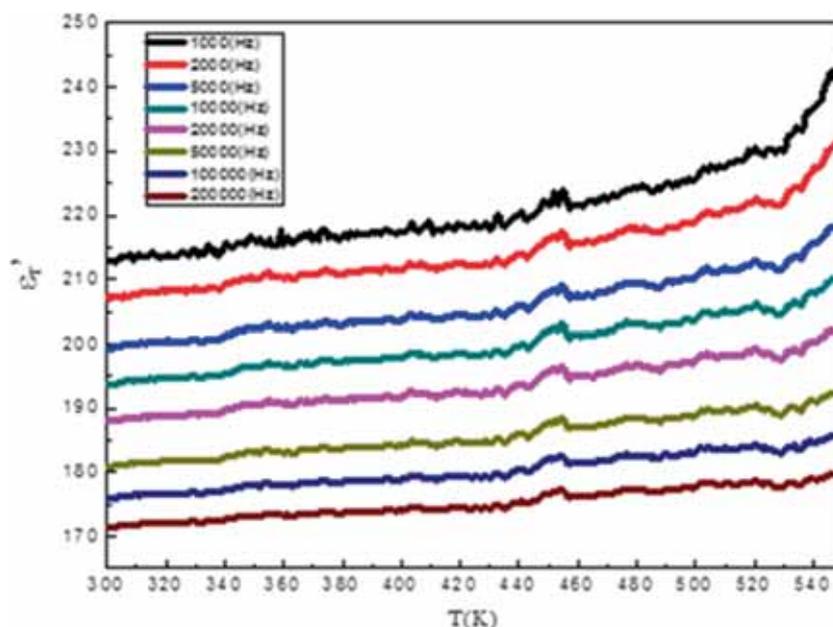
Figure 14. Temperature dependence of ε'_r at different frequencies for $K_{0.25}(NH_4)_{0.75}CdCl_3$.
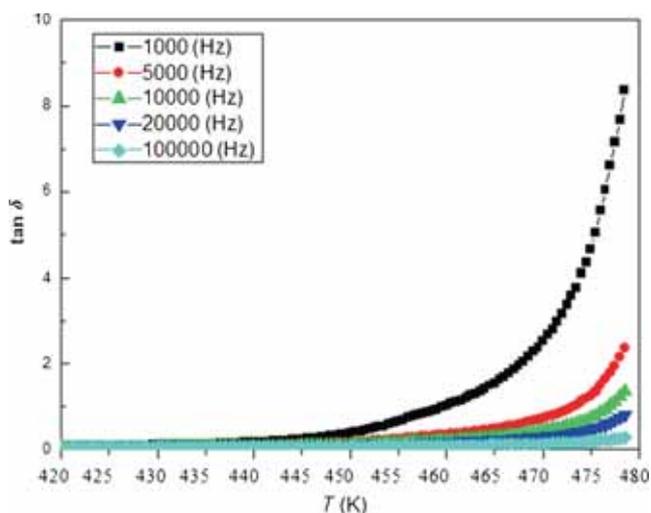

Figure 15. Variation of the dielectric loss factor (tan δ) as a function of temperature at various frequencies for $K_{0.25}(NH_4)_{0.75}CdCl_3$.

Dielectric studies confirm the presence of the same anomaly that has been observed by thermal analysis using the DSC measurements. We can conclude that the phase transition is probably governed by an order–disorder mechanism.

4. Conclusions

The two new mixed compounds, $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$, were crystallized in the orthorhombic system with the space group *Pnma* at room temperature 293 K. The crystal structure of the title compound is characterized by $CdCl_6$ octahedra linked in endless chains running along the *b*-axis. The potassium or ammonium cations are inserted between these chains ensuring the stability of the structure by ionic and hydrogen bonding contacts N–H...Cl.

From the study of the influence of substitution, we concluded that the ammonium introduction into the network of $KCdCl_3$ does not affect structural arrangement, but it leads to an increase of the *a*, *c* parameters and *V* cell volume. However, we observe a decrease of the parameter *b*.

This study shows that the title compounds, $K_{0.57}(NH_4)_{0.43}CdCl_3$ and $K_{0.25}(NH_4)_{0.75}CdCl_3$, undergoes an orientational 'order–disorder' phase transition of NH_4^+ tetrahedra at about 454 and 438 K as determined by electrical properties, DSC and IR *vs.* temperature. This can be explained by a disordering of the NH_4^+ groups and a distortion of the $CdCl_6$ octahedra in the high temperature phases.

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