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Influence of the growth method upon the phase transition of $RbCdCl_3$

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Abstract. Structural properties of two $RbCdCl_3$ samples grown either from the melt or from aqueous solution are studied via X-ray diffraction over a closed temperature cycle between 20 °C and 300 °C. During cooling step (300 °C → 20 °C), the crystal grown from the melt undergoes a phase transition at 110 °C that drives it from the cubic structure into a tetragonal structure that still persists at 20 °C. It undergoes exactly the reverse phase transition at the same temperature during the heating (20 °C → 300 °C) step that immediately follows. The other crystal grows from aqueous solution at 20 °C in an orthorhombic structure (i.e. not tetragonal as that of the crystal grown from the melt and cooled down to this temperature). During the heating (20 °C → 300 °C) step, it undergoes a direct orthorhombic-cubic phase transition at 240 °C (without passing through the tetragonal phase) whereas, during subsequent cooling (300 °C → 20 °C), it does not exhibit the corresponding reverse phase transition but rather exhibits exactly the same cubic-tetragonal phase transition at 110 °C as the crystal grown from the melt. However, for both crystals, this tetragonal phase observed at room temperature is unstable and slowly converts into an orthorhombic phase over the course of time. Complementary Differential Scanning Calorimetry (D.S.C.) and Thermo Gravimetric Analysis (T.G.A.) measurements have been carried out over the range (20 → 300) °C in order to interpret diffraction experiments.

PACS. 61.10.Nz X-ray diffraction – 64.70.Kb Solid-solid transitions – 65.40.Ba Heat capacity

1 Introduction

The ABX_3 perovskites (A and B are cations and X an anion) are inorganic crystals, the physical properties of which are used extensively in a number of technological applications. Among these materials, special attention has been paid to the $ABCl_3$-type crystals in which A is an alkali metal and B is a divalent one. These crystals are acousto-optic materials [1]. They are also models for the study of phase transitions. These compounds belong to the perovskite-like structure, slightly distorted by cation displacements or by tilts of BCl_6-octahedra as compared with the ideal cubic structure [2]. Many studies have been undertaken on one of the crystals belonging to this family, namely $RbCdCl_3$, and several contradictory observations have been reported. Bohac et al. [3] suggested that the presence of water could influence the structure of the compound and hence its phase transition sequence. Experiments performed on $RbCdCl_3$ crystals assumed a priori to contain water were carried out from room temperature up to about 250 °C by Natarajan and Secco [4]. According to them, the compound follows a cubic-tetragonal-orthorhombic phase transition sequence. Kind and Roos [5] confirmed the occurrence of the cubic-tetragonal phase transition but they found two other phase transitions they were unable to assign.

In the first part of this paper, two samples of $RbCdCl_3$ crystals grown via different methods are studied using X-ray diffraction. The first sample was grown in situ by fusing RbCl with $CdCl_2$ at 505 °C. The second sample was crystallized from aqueous solution so that the presence of water in it cannot be a priori discarded. For reasons to be given later, experiments relating to this second sample were performed on the powder obtained from it.

For both samples a systematic recording of reflections (leading to the determination of unit cell parameters and structure) was performed every 10 °C in order to detect the phase transitions and, from this, to provide better insight into the behaviour of BCl_6-octahedra in the sequence of phase transitions.

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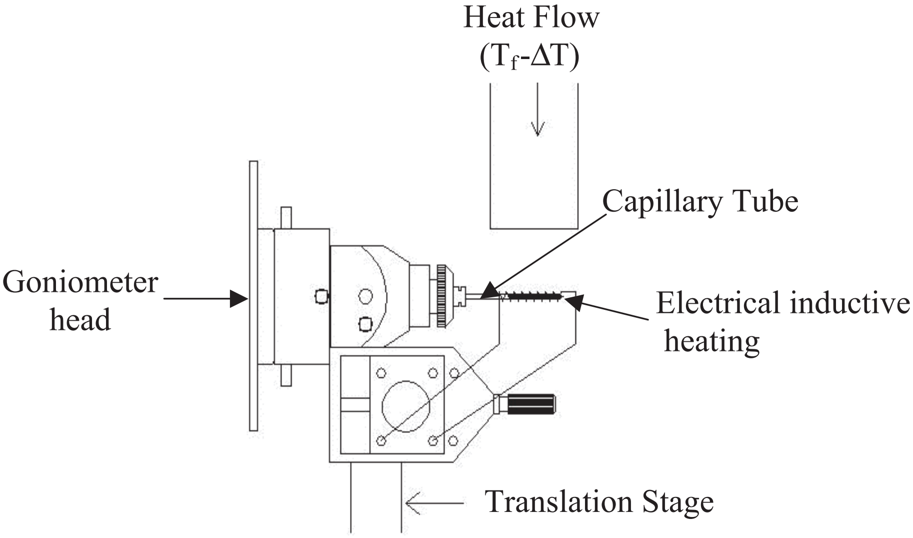


Fig. 1. Method of crystallization of $RbCdCl_3$ M-crystal grown from the melt. RbCl-$CdCl_2$ compounds were inserted in the capillary and melt at $T_f = 505$ °C (fusion temperature). The heat flow was regulated at $T_f - \Delta T$, with the missing ΔT generated by the electrical inductive heating. A single crystal grew when the temperature was very slowly decreased by translation of the electrical inductive heating.

In the second part of this paper, the results of T.G.A. measurements that aimed at determining the presence (or absence) of water are reported. This study is completed by D.S.C. experiments in order to characterize the phase transformations observed via X-ray diffraction.

2 Experimental procedure

2.1 Sample preparation

2.1.1 Single crystal grown from the melt (M-sample)

The first sample of $RbCdCl_3$ (hereafter referred to as M-sample; M for melt) was prepared in situ in a quartz capillary by fusing RbCl with anhydrous $CdCl_2$ at 505 °C. The heat flow was at $T_f - \Delta T$ temperature where T_f is the fusion temperature (505 °C) and ΔT is a difference of temperature (50 °C). The missing ΔT needed to melt the sample was provided via an electrical inductive heating (see Fig. 1). A single crystal could be grown by slowly moving the electrical inductive heating away, thus decreasing the crystal temperature down to 455 °C ($T_f - \Delta T$). Then the temperature was further decreased slowly down to 300 °C using a compressed hot air stream system. This provided a single crystal that could be studied at various temperatures via classical X-ray diffraction, decreasing the temperature stepwise from 300 °C to room temperature.

2.1.2 Powder grown by aqueous solution (A-sample)

The second sample (hereafter referred to as A-sample; A for Aqueous) was grown by slow evaporation of an aqueous solution of RbCl and $CdCl_2$ in stoechiometric proportions at room temperature. The resulting single crystal was more fragile then the first one: when the temperature was raised above about 220 °C the crystal showed severe twinning or even broke. Since it had to be studied by X-ray diffraction at high temperature, it was decided to grind it into fine powder on which all experiments were carried out from 20 °C to 300 °C. For clarification, only the results obtained on powder will be presented in the following section (at temperatures below 220 °C, i.e. in the range over which single crystals are stable, single crystal and powder experiments gave identical results).

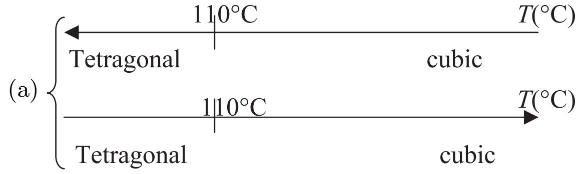
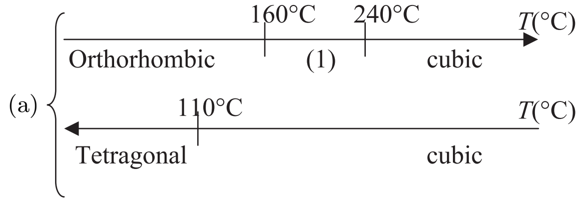
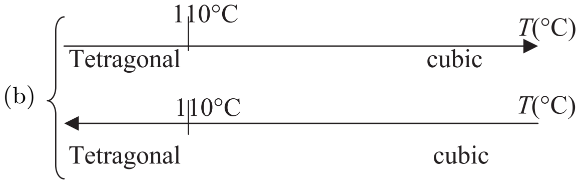
2.2 Experimental methods

2.2.1 X-ray diffraction

The structure of the M-sample at different temperatures was studied with the help of an Enraf-Nonius CAD-4 diffractometer with graphite-crystal monochromated MoK_α radiation ($\lambda = 0.71069$ Å) using an ω-2θ scan in the range $2.5° < \theta < 45°$. Reflections for which $I > 2\sigma(I)$ were used to determine and refine the structure. No significant intensity variations were noticed throughout the measurements. Some reference reflections were recorded in order to control the stability of the incident beam. Accurate lattice parameters were obtained from a least-squares fit to the angular settings of 25 selective reflections. The structure was solved using direct methods with the SHELXS86 program [6]. The refinement was carried out using the SHELXL93 program [7]. The lattice parameters and structure were recorded at different temperatures in steps of 10 °C from 300 °C down to 20 °C, then from 20 °C up to 300 °C. High temperatures were reached directly heating the compound using a compressed hot air stream system.

The A-sample was inserted into a 0.4 mm diameter Lindemann glass capillary that continuously rotated

Table 1. Phase transitions observed: (a) In the first (20 °C–300 °C) closed thermal cycle for the two samples of $RbCdCl_3$ (cooling-heating cycle for the sample grown from the melt; heating-cooling cycle for the sample grown from aqueous solution). (1) Intermediate structural domain before the formation of the cubic phase. (b) After the first cycle, all subsequent cycles become identical for both samples with a tetragonal-cubic phase transition at about 110 °C on heating as on cooling.

Samples	Phase transition sequence
M-sample (grown from the melt)	
A-sample (grown from aqueous solution)	
After the first thermal cycle, for both samples	

around the vertical axis of a goniometer. The X-ray diffraction intensities ($\lambda_{\mathrm{CuK}_\alpha 1} = 1.5406$ Å) were collected in the horizontal plane of the diffractometer by a curved multidetector (INEL, CPS 120). This powder was studied, firstly by heating it from room temperature up to 300 °C, and then by cooling it back to room temperature. Line shapes were refined using pseudo-Voigt functions. The cell parameter and the space group were determined with the help of the Louër dichotomy method (DICVOL) [8]. The structure was solved using direct methods with the EXPO software [9] and then refined using the Rietveld program called Fullprof. The X-ray powder diffraction pattern was also recorded at different temperatures in steps of 10 °C from 20 °C up to 300 °C, then from 300 °C down to 20 °C. For high temperatures the experimental setup was the same as that previously described for the M-sample.

2.2.2 Thermodynamic measurements

The D.S.C. experiments were performed with a D.S.C.7 of Perkin-Elmer. During all the measurements, the calorimeter head was flushed with highly pure nitrogen gas. Temperature was calibrated using pure indium and pure zinc at the same scanning rates used in the experiments. Powder was encapsulated in a metallic cell containing 15 mg. The calorimeter operated between 20 °C and 300 °C. For each scanning rate, both heating and cooling runs were performed.

The T.G.A. experiments were carried out with the T.G.A. 7 of Perkin-Elmer. During all the measurements the sample was placed in an open platinium sample pan and flushed with a highly pure nitrogen gas. The temperature reading was calibrated using the Curie points of alumel and nickel, while the mass reading was calibrated using balance tare weights provided by Perkin-Elmer.

3 Results and discussion

3.1 X-ray diffraction

The X-ray diffraction results presented below are displayed schematically in Table 1. This table aims to act as a guide for the reader.

3.1.1 Single crystal grown from the melt (M-crystal)

The single crystal grows at high temperature (300 °C) in the cubic phase with one formula unit per unit cell. The space group is $Pm\overline{3}m$ from the systematic extinctions of the reflections (the reliability factor $\Re$ is equal to 2.24). The cubic lattice parameter is: $a = 5.217$ Å. As expected for the perovskite structures, each cadmium atom is bounded to six chlorine neighbours at the vertices of a regular octahedron with Cd-Cl = 2.609 Å. The octahedra are linked in endless chains. Twelve chlorines surround each of the rubidium ions that are localized at the vertices of the cell. This agrees with the results of Kind and Roos [5] but contradicts both those of Natarajan and Prakash [10] and those of Sadanandam et al. [11] who claimed the structure was analogous to that of a cubic perovskite but with a doubling of parameters.

On decreasing temperature, the lattice parameter variations versus temperature exhibit a phase transition around 110 °C (Fig. 2). The structure of the M-crystal becomes tetragonal (P4/mmm; $\Re = 3.31$). The a and

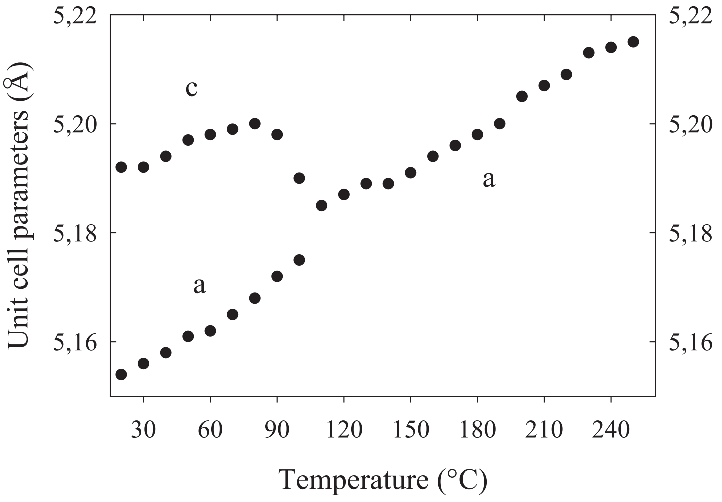


Fig. 2. Temperature dependence of the unit cell parameters of the $RbCdCl_3$ M-crystal.

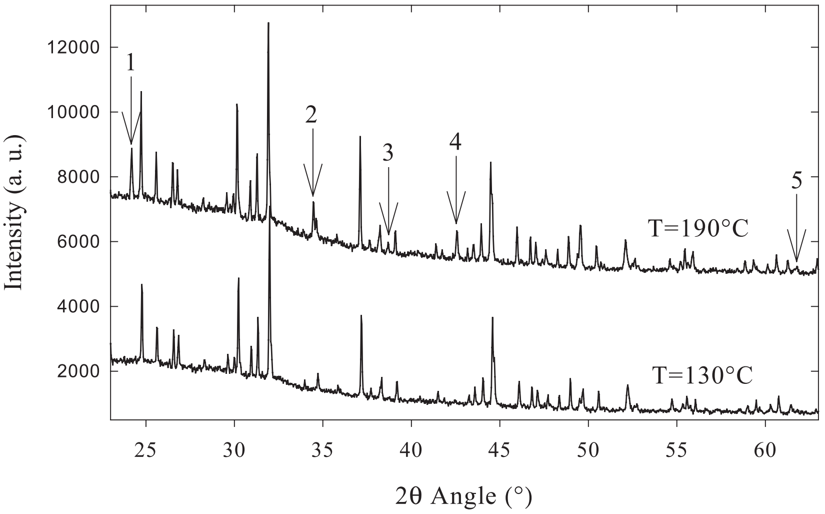


Fig. 3. Superposition of the powder diffraction patterns observed in the orthorhombic phase at 130 °C and at 190 °C of the $RbCdCl_3$ A-crystal. The peaks indicated by numbers appear above 160 °C and are characteristic of the cubic phase.

c lattice parameters are quite close: $a = 5.155$ Å and $c = 5.192$ Å at room temperature. They are very similar to the cell parameter of the cubic phase and accordingly there is also one formula unit per unit cell. Our results thus go against different previous experimental studies [5,12,13] that suggested a superstructure ($Z = 2$ or $Z = 4$) with a P4/mbm space group. The chlorine ions have two different coordinations as noticed previously from ^{87}Rb nuclear magnetic resonance experiments that clearly show two chemically inequivalent Cl sites and one Rb site [12]. Each octahedron has an equatorial plane formed by four Cl atoms (Cd-Cl = 2.585 Å) and two Cl atoms on each side of this base (Cd-Cl = 2.600 Å). As in the cubic phase, the octahedra are linked in endless chains running along the three axes with six corners shared by six adjacent octahedra. On increasing temperature, one observes the same phase transition sequence as on cooling. The tetragonal phase becomes a cubic phase at about 110 °C.

3.1.2 Powder of $RbCdCl_3$ from aqueous solution (A-crystal)

As mentioned in the previous section, it was impossible to keep the single crystal grown from aqueous solution stable at temperatures above 200 °C. Therefore X-ray diffraction experiments have been carried out on powder. The experimental measurements had to be performed in two steps. In the first step (heating) the temperature was raised from room temperature to 300 °C and in the second step (cooling) it was decreased back from 300 °C to room temperature. At room temperature, our experiments on the powder give exactly the same results as those previously obtained by Hamzaoui et al. [14] on the single crystal (that is stable at this temperature): the sample grown from aqueous solution crystallizes in an orthorhombic phase with four formula units per unit cell. The space group is Pnma and the lattice parameters are: $a = 8.99$ Å, $b = 4.05$ Å and $c = 15.04$ Å. This structure is also characterized by the presence of octahedra. These are linked in endless chains running along the b axis, with two edges shared by two adjacent octahedra.

From room temperature to 240 °C, all the X-ray powder diffraction patterns have been fitted assuming an orthorhombic structure. However, it should be noted that above 160 °C, five new diffraction peaks clearly appear (Fig. 3). These five peaks, indicated in Figure 3, could be

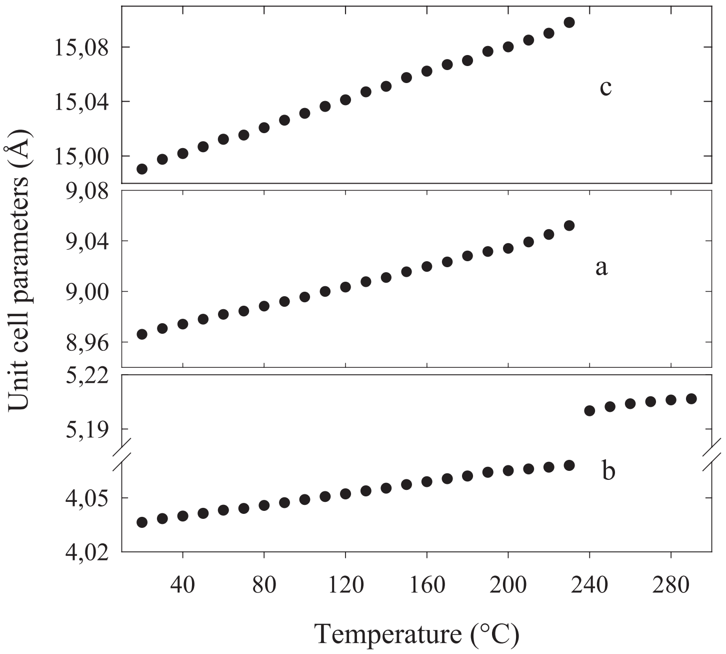


Fig. 4. Temperature dependence of the a, b, c unit cell parameters of the orthorhombic phase of the $RbCdCl_3$ A-crystal as appearing during heating.

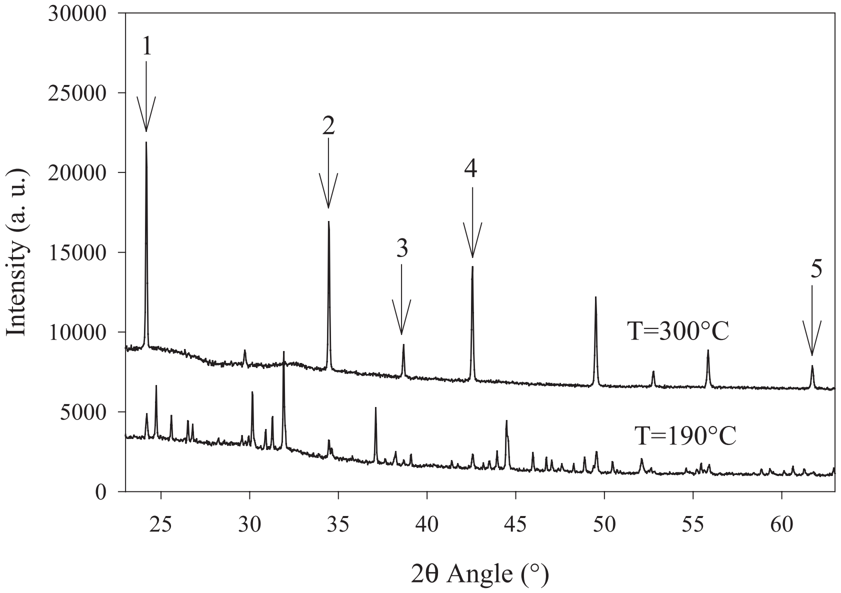


Fig. 5. Superposition of the powder diffraction patterns observed in the orthorhombic phase at 190 °C and in the cubic phase at 300 °C during heating of the $RbCdCl_3$ A-crystal.

considered as revealing of an underlying phase or an intermediate state towards a new phase as discussed below.

On increasing temperature, the phenomenon at 110 °C reported for the M-sample is not observed. For the A-sample, a phase transition clearly appears around 240 °C. The lattice parameter changes versus temperature are given in Figure 4. Above 240 °C the structure becomes that of a perovskite ($Pm\overline{3}m$, $Z = 1$, $a = 5.21$ Å), i.e. exactly the same as that observed at high temperature for the M-sample. This indicates that the (cubic) phase that appeared above 110 °C in the single M-crystal appears only above 240 °C in the powder obtained from the A-crystal. The variation of volume of a cell containing 4 formula units (i.e. one orthorhombic unit cell or four cubic unit cells) versus temperature exhibits a marked discontinuity at 240 °C characteristic of a first order transition.

The five additional peaks that were observed between 160 °C and 240 °C may suggest a possible underlying phase preceding the formation of the cubic phase. Figure 5 shows a superposition of the powder diffraction patterns observed in the orthorhombic phase at 190 °C and in the cubic phase at 300 °C. From this figure all the lines of the powder diffraction pattern of the cubic phase are seen to be present in the powder diffraction pattern of the orthorhombic phase recorded above 160 °C, i.e. above the temperature around which five additional diffraction peaks are observed. As the orthorhombic space group (Pnma) is not a sub-group of the cubic space group ($Pm\overline{3}m$), it is obvious that the indexing of the diffraction peaks is not the same, so that a quantitative interpretation cannot be made definitely. However, this observation suggests that a biphase zone exists between 160 °C and 240 °C in which both the orthorhombic and cubic structures co-exist. Then, above 240 °C, the transformation to the cubic structure occurs. The energy required to produce this transition is expected to be fairly large since, as said above, the Pnma space group is not a sub-group of $Pm\overline{3}m$. This is probably connected with the breaking of the single crystal in this temperature range.

After the heating step, powder X-ray diffraction patterns were recorded from 300 °C down to room temperature. In this cooling step the transition observed at 240 °C during the heating step does not appear. The first transition, revealed by a splitting of the lattice parameter variation, occurs at 110 °C i.e. just as in the sample grown from the melt (previous section). Below 110 °C, the X-ray powder patterns were indexed as corresponding to a tetragonal distorted perovskite (P4/mmm, a = 5.154 Å and c = 5.201 Å). Again, the structure of the A-sample is similar to that obtained at room temperature for the single M-crystal. The number of formula units per unit cell is still equal to one, contrary to an earlier claim that the cell parameter is doubled in the tetragonal phase [12].

3.2 Thermodynamic measurements

The first heating run (Fig. 6) recorded using D.S.C. reveals a spread phenomenon that covers the 160 °C–245 °C temperature range. It can be separated into two parts: the first between 160 and 220 °C shows a significant variation of the baseline; the second, between 220 °C and 245 °C, exhibits a broad peak. The total differential enthalpy is significant: ΔH = 19.94(1) J/g. Note that the temperature at which this peak appears (220 °C) corresponds to the temperature at which the crystal breaks. During the cooling run (Fig. 6) this broad phenomenon is not apparent. However an endothermic peak appears at 110.7(1) °C with a differential enthalpy equal to −0.46(1) J/g. This peak seems to be characteristic of a first-order transition. Thus, whatever the scanning rate (cooling and heating runs performed without delay time) it always appears. During the heating runs (second and further ones) the transition peak appears at 114.2(1) °C with ΔH = 0.56(1) J/g. During the cooling runs (first and next) it appears at 110.7(1) °C with ΔH = −0.46(1) J/g. This temperature shift between cooling and heating run experiments can be interpreted as a thermal hysteresis of this transition.

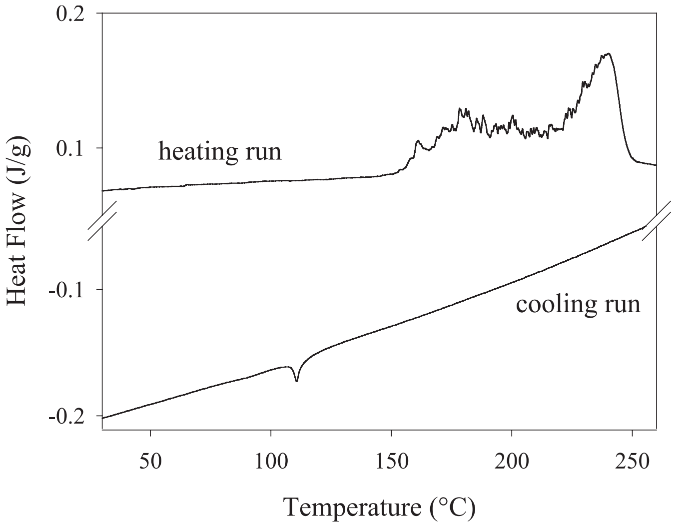


Fig. 6. Evolution of heating and cooling runs of the differential energy of the RbCdCl$_3$ A-crystal.

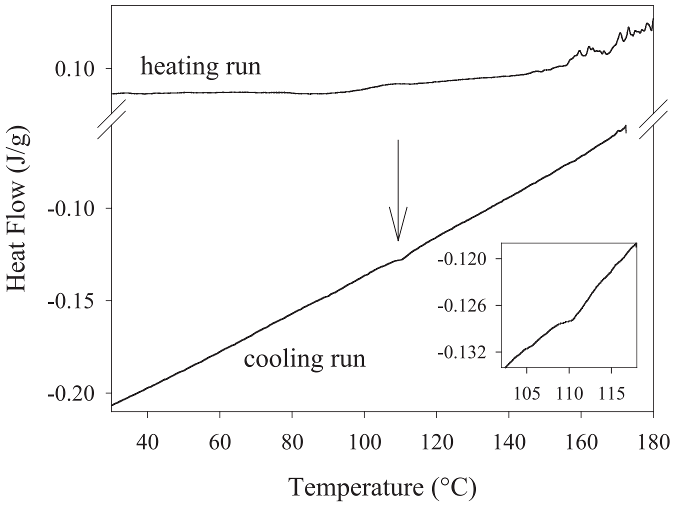


Fig. 7. Evolution of heating and cooling runs of the differential energy for the first thermal cycle (20–180) °C of the RbCdCl$_3$ A-crystal.

In order to know whether the cubic phase appears at 160 °C (when the five new peaks are present in X-ray diffraction) and to study its thermodynamic aspects, a very strict succession of thermal cycles has been carried out. In each cycle, temperature was increased from room temperature up to a reference temperature $T_{\max}^{(1)}$ ($T_{\max}^{(1)}$ = 180 °C in this first cycle). At this $T_{\max}$ temperature, an isotherm was maintained for 12 hours in order to stabilize the system. After this delay, temperature was decreased back to room temperature (Fig. 7) to complete the cycle. Then, immediately, a similar second cycle (temperature increase up to $T_{\max}^{(2)}$ – 12 hours isotherm – temperature decrease) was performed, but up to a $T_{\max}^{(2)}$ temperature 10 °C higher than in the previous cycle (i.e. $T_{\max}^{(2)} = T_{\max}^{(1)} + 10$ °C = 190 °C). This process was repeated a number of times, increasing $T_{\max}$ by 10 °C at each cycle, until a final cycle in which $T_{\max}^{(13)}$ = 300 °C. At each cycle, the amount of product converted was determined by Differential Scanning Calorimetry. For the first thermal cycle the scanning rate points out a very weak

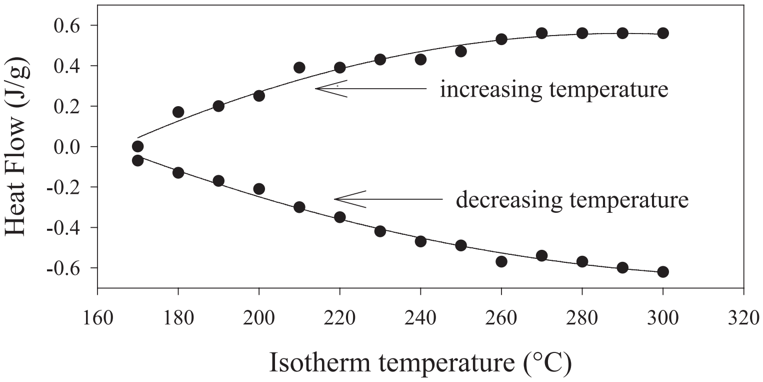


Fig. 8. Evolution of the differential enthalpy versus $T_{\max}^{(n)}$ isotherm temperature of the $RbCdCl_3$ A-crystal.

transition (i.e. the cubic-tetragonal transition identified through X-ray diffraction): at 110.7 (1) °C, the differential enthalpy is equal to $-0.07(1)$ J/g (see Fig. 7). Results for all the other cycles are summarised in Figure 8. Above 250 °C, the differential enthalpy corresponding to the cubic-tetragonal transition observed at 110.7(1) °C becomes practically constant and equal to $-0.60(1)$ J/g (Fig. 8): the points on this figure correspond to the values of the differential enthalpy observed both in heating runs (20 °C $\rightarrow T_{\max}^{(n)}$) and cooling runs ($T_{\max}^{(n)} \rightarrow$ 20 °C) for different isotherm $T_{\max}^{(n)}$temperatures ($n = 1-13$). Two important results can be deduced from this experiment. The first one is that between 160 °C and 250 °C there is coexistence of two phases (orthorhombic and cubic) and the second one is that, above 250 °C, the orthorhombic phase is entirely transformed into a cubic phase.

Another important point concerns the presence (or absence) of water. In order to clarify this subject of controversy, T.G.A. experiments have been performed on different $RbCdCl_3$ samples. For each recording, the weight variation was negligible (the weight loss is insignificant). This result, at variance with that of Bohac et al. [3], allows us to conclude that $RbCdCl_3$ A-crystals do not contain water. Considering that the tetragonal state is metastable and the speed of reaction of the system is weak, this strongly suggests that the tetragonal – orthorhombic transformation occurs progressively without the involvement of water.

3.3 Discussion

The phase transition sequence of the $RbCdCl_3$ compound depends on which way the sample is grown. The results obtained via X-ray diffraction and D.S.C. measurements are summed up in Table 1.

The M-sample grown from the melt exhibits a cubic-tetragonal phase transition at 110 °C. These two phases are structurally similar: only a slight contraction of parameters is observed: 1.2% for the a and b parameters; 0.5% for the c parameter.

The behaviour of the A-sample grown from aqueous solution is more complicated: it depends on the direction of the temperature change. Thus during the first increase of temperature a direct orthorhombic – cubic phase transition occurs at 240 °C. This transition seems to require a significant activation energy since it is accompanied by a breaking of the single crystal. The condensation of a zone-boundary mode associated with the rotational vibrations of the $CdCl_6$ octahedra are the cause of this phase transition. The distortion of the $CdCl_6$ octahedra seen in the orthorhombic phase [14] vanishes progressively when the temperature increases: these octahedra progressively organize each other in order to reach the cubic structure.

Moreover, there is a coexistence of the orthorhombic and cubic phases between 160 °C and 240 °C. On decreasing temperature the behaviour is different: a cubic-tetragonal phase transition appears at 110 °C. The two phases involved in this cooling process of the A-crystal powder are rigorously the same as those observed in the $RbCdCl_3$ M-sample grown from the melt in situ. To summarize comparatively, it is found that, whereas the dynamical behaviours of the two A and M samples are identical during the cooling steps, they are quite different during the heating ones.

After some time, for both types of crystal, i.e. crystal grown from the melt and crystal grown from aqueous solution, the tetragonal phase has been observed to convert into the orthorhombic one. This conversion is not due to the possible presence of water as suggested by Bohac et al. [12]: our T.G.A. experiments have definitely rejected this hypothesis.

For both crystals the room temperature phase at the end of the first thermal cycle (and subsequent ones) is tetragonal. However, this phase converts slowly into an orthorhombic phase: room temperature X-ray diffraction measurements carried out on these crystals every hour after the end of the cycles show the progressive appearance of peaks characteristics of the orthorhombic phase that superimpose on the tetragonal phase pattern. After about one day, the conversion is practically complete. It is clear now that the tetragonal phase is a metastable phase. The stable equilibrium state of the $RbCdCl_3$ formula unit at room temperature is orthorhombic although it seems to have to pass through a tetragonal metastable state before it is stabilized.

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