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Cadmium Iodate Syntheses and Characterization

Zoulikha Hebboul

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Abstract

Six polymorphs of anhydrous cadmium iodate are characterized, three of which showing second harmonic generation activity (SHG). Single crystals of $\text{Cd}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ are obtained by slow evaporation of aqueous solutions of CdCl_2 and KIO_3 . This compound crystallizes in the triclinic space group $P1\bar{1}$, $a = 7.119(2)$, $b = 7.952(2)$, $c = 6.646(2)\text{\AA}$, $\alpha = 102.17(2)^\circ$, $\beta = 114.13(2)^\circ$, and $\gamma = 66.78(4)^\circ$. Three chemical routes of preparation of chloro cadmium iodate CdIO_3Cl are given. The prepared material was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystal structure has been determined by single-crystal X-ray diffraction methods; the unit cell is orthorhombic with $a = 7.270(0)\text{\AA}$, $b = 15.995(0)\text{\AA}$, $c = 7.1980(0)\text{\AA}$, $V = 837.009(1)\text{\AA}^3$, and $Z = 8$. The space group is CmCa . The cadmium hydroxy-iodate CdIO_3OH is synthesized in the form of transparent platelets in the same way as CdIO_3Cl ; the unit cell is orthorhombic with $a = 11.5245(11)\text{\AA}$, $b = 6.7985(7)\text{\AA}$, $c = 4.7303(4)\text{\AA}$, $V = 304.31(1)\text{\AA}^3$, and $Z = 4$.

Keywords: cadmium, iodate, XRD, SHG, polymorphism, mixed ligand

1. Introduction

Cadmium is a chemical element with symbol Cd and atomic number 48. This soft, bluish-white metal is chemically similar to the two other stable metals in group 12, zinc and mercury. Like zinc, it demonstrates oxidation state +2 in most of its compounds, and like mercury, it has a lower melting point than the transition metals in groups 3 through 11. Cadmium and its congeners in group 12 are often not considered transition metals, in that they do not have partly filled *d* or *f* electron shells in the elemental or common oxidation states. The average concentration of cadmium in Earth's crust is between 0.1 and 0.5 parts per million (ppm). It was discovered in 1817 simultaneously by Stromeyer and Hermann, both in Germany, as an impurity in zinc carbonate.

Despite cadmium being a hazardous heavy metal and toxic to almost all living organisms, it is used in batteries, electroplating, nuclear reactors, and semiconductors. In 2009, 86% of cadmium was used in batteries, predominantly in rechargeable nickel-cadmium batteries. Nickel-cadmium cells have a nominal cell potential of 1.2 V. The cell consists of a positive nickel hydroxide electrode and a negative cadmium electrode plate separated by an alkaline electrolyte (potassium hydroxide) [1]. Cadmium electroplating, consuming 6% of the global production, is used in the aircraft industry to reduce corrosion of steel components [2]. It is used too in the control rods of nuclear reactors, acting as a very effective “neutron poison” to control neutron flux in nuclear fission [2]. When cadmium rods are inserted in the core of a nuclear reactor, cadmium absorbs neutrons preventing them from creating additional fission events, thus controlling the amount of reactivity. The pressurized water reactor designed by Westinghouse Electric Company uses an alloy consisting of 80% silver, 15% indium, and 5% cadmium [2]. The cadmium oxide was used in black and white television phosphors and in the blue and green phosphors of color television cathode ray tubes [3]. Cadmium sulfide (CdS) is used as a photoconductive surface coating for photocopier drums [4]. Various cadmium salts are used in paint pigments, with CdS as a yellow pigment being the most common. Cadmium selenide is a red pigment, commonly called cadmium red. To painters who work with the pigment, cadmium provides the most brilliant and durable yellows, oranges, and reds—so much so that during production, these colors are significantly toned down before they are ground with oils and binders or blended into watercolors, gouaches, acrylics, and other paint and pigment formulations. Because these pigments are potentially toxic, users should use a barrier cream on the hands to prevent absorption through the skin [5] even though the amount of cadmium absorbed into the body through the skin is reported to be less than 1% [6]. In PVC, cadmium was used as heat, light, and weathering stabilizers [2, 7]. Currently, cadmium stabilizers have been completely replaced with barium-zinc, calcium-zinc, and organo-tin stabilizers. Cadmium is used in many kinds of solder and bearing alloys, because of a low coefficient of friction and fatigue resistance [2]. It is also found in some of the lowest-melting alloys, such as Wood’s metal [8].

The SHG is a nonlinear optical (NLO) process, in which two photons with the same frequency interacting with a nonlinear material are effectively “combined” to generate new photons with twice the energy and therefore twice the frequency and half the wavelength of the initial photons. Second harmonic generation, as an even-order nonlinear optical effect, is only allowed in media without inversion symmetry [9]. It is a special case of sum frequency generation. Half-harmonic generation (a special case of spontaneous parametric down-conversion) is its reverse process where one photon leads to a pair of photons with half the energy and occurs in parallel of the SHG with a lower probability though [10]. The second-order nonlinear susceptibility of a medium is responsible for the creation of SHG, which can convert a small or a large part of the excitation wave depending on some interference conditions that can happen in the medium. It, often called frequency doubling, is also a process in radio communication; it was developed early in the twentieth century and has been used with frequencies in the megahertz range. It is a special case of frequency multiplication.

Metal iodates are of great importance in the investigation of nonlinear optical (NLO) materials. Owing to the presence of stereochemically active lone-pair electrons on IV ions, the IO_3 unit is

a favorable NLO-active anionic group with large microscopic second-order NLO susceptibility. The alignment of IO_3 units in polar or non-centrosymmetric (NCS) crystal structures may result in materials with excellent second harmonic generation (SHG) properties [11]. Recently, a few effective routes have been developed for the synthesis of novel NLO iodates, such as the introduction of mixed ligand Cl^- , F^- , and OH^- . These research efforts afforded a large number of metal iodates with excellent SHG properties, including $\text{Bi}(\text{IO}_3)_2$ [11] and $\text{Zn}(\text{IO}_3)\text{OH}$ [12].

Cadmium iodate $\text{Cd}(\text{IO}_3)_2$ is a chemical compound of cadmium and iodate ligand. It is notable for its crystal structure. In 1838, Rammelsberg synthesized anhydrous cadmium iodate by hot mixing concentrated solutions of sodium iodate and cadmium nitrate [13]. A century later in 1940, Oelke and Wagner studied the solubility of this compound in water [14] and thermal behavior [15]; the first diffraction pattern was presented in 1968 [16]. In 1978 the structure of anhydrous cadmium iodate is described as a single orthorhombic phase $\text{P2}_1\text{2}_1\text{2}_1$ [17, 18], later called $\delta\text{-Cd}(\text{IO}_3)_2$. But in 1980, Liang et al. [19] gave powder diffraction results that do not correspond to this compound [20]. Work carried out in 2005 revealed a polymorphism of anhydrous $\text{Cd}(\text{IO}_3)_2$ iodate. The $\text{CdCl}_2\text{-IO}_3$ system has shown that there are no less than five polymorphic phases for cadmium— $\alpha\text{-Cd}(\text{IO}_3)_2$, $\beta\text{-Cd}(\text{IO}_3)_2$, $\gamma\text{-Cd}(\text{IO}_3)_2$, $\delta\text{-Cd}(\text{IO}_3)_2$, and $\varepsilon\text{-Cd}(\text{IO}_3)_2$ —obtained according to the synthesis conditions [13, 21, 22], and finally in 2017, Hebboul provides existence of a new polymorph $\zeta\text{-Cd}(\text{IO}_3)_2$ [23]. This is a complex chemical system that has a large polymorphism that makes these materials very difficult to develop as crystals for optics, and obtaining large crystals was a problem because of the complexity of the system [20, 24, 25]; all these polymorphic phases are not acentric; those are $\gamma\text{-Cd}(\text{IO}_3)_2$, $\varepsilon\text{-Cd}(\text{IO}_3)_2$, and $\zeta\text{-Cd}(\text{IO}_3)_2$; of course $\delta\text{-Cd}(\text{IO}_3)_2$ has a signal of second harmonic generation (SHG) but lower than that of LiIO_3 [13]. Ravi Kumar et al. optimized the growth conditions of the $\delta\text{-Cd}(\text{IO}_3)_2$ crystal that was grown from an aqueous solution by employing the slow-cooling technique. The structure was confirmed by single-crystal XRD analysis. $\text{Cd}(\text{IO}_3)_2$ is transparent from 350 to 2000 nm, thus confirming its wider optical transmission range to extend its applications in the entire visible and NIR region. The optical band gap is found to be 3.85 eV from the Tauc's plot. As an inorganic material, the developed crystal has moderate SHG efficiency, good thermal stability, and mechanical strength, and $\text{Cd}(\text{IO}_3)_2$ has the promise to be utilized for NLO applications and photonic device fabrications. The results of optical band gap, mechanical, dielectric, and electrical properties of $\text{Cd}(\text{IO}_3)_2$ are reported for the first time in 2008 [22].

This chapter will investigate the bibliography on synthetic methods and powder spectra for various $\text{Cd}(\text{IO}_3)_2$ polymorphs and monohydrate cadmium iodate. Moreover, bibliography on the two cadmium mixed ligand compounds, cadmium chloro-iodate CdIO_3Cl and cadmium hydroxy-iodate CdIO_3OH .

2. Synthesis methods and powder spectra for various $\text{Cd}(\text{IO}_3)_2$ polymorphs and monohydrate cadmium iodate

At 20°C and constant concentration of cadmium, it is possible to precipitate in sequence; this fact is used to assign a name—the first polymorph that precipitates is called $\alpha\text{-Cd}(\text{IO}_3)_2$, the

(1) Variable cadmium concentration at fixed temperatures and time ($T = 20^{\circ}\text{C}$, $t = 4$ hours)				
Concentration	$C_1 = 94.510^{-3} \text{ mol/l}$	$C_2 = 56.810^{-3} \text{ mol/l}$	$C_3 = 35.510^{-3} \text{ mol/l}$	$C_4 \leq 25.810^{-3} \text{ mol/l}$
Polymorphs present in the precipitate	$\alpha \sim \beta \sim \gamma$	$\beta \sim \delta > \alpha \sim \gamma$	$\gamma > \beta \sim \alpha$	$\gamma > > \alpha$
(2) Variable reaction time with fixed cadmium concentration ($T = 20^{\circ}\text{C}$, $C_{Cd} = 94.510^{-3} \text{ mol/l}$)				
Reaction time	$t = 10 \text{ min}$	$t = 1 \text{ h}$	$t = 4 \text{ h}$	$t = 7 \text{ h}$
Polymorphs present in the precipitate	α	$\alpha > > \beta$	$\alpha \sim \beta \sim \gamma$	$\alpha \geq \gamma > > \delta$
(3) Variable reaction time with fixed cadmium concentration ($T = 60^{\circ}\text{C}$, $C_{Cd} = 94.510^{-3} \text{ mol/l}$)				
Reaction time	$t = 10 \text{ min}$	$t = 1 \text{ h}$	$t = 4 \text{ h}$	$t = 7 \text{ h}$
Polymorphs present in the precipitate	$\alpha \geq \gamma$	$\gamma > \alpha \geq \delta$	$\gamma > > \delta > > \alpha$	$\gamma > > \delta > > \alpha$

Table 1. Summary of various results obtained according to synthesis conditions [20].

following $\beta\text{-Cd}(\text{IO}_3)_2$, then $\gamma\text{-Cd}(\text{IO}_3)_2$, and finally $\delta\text{-Cd}(\text{IO}_3)_2$ —heating these four polymorphs or working in nitric acid at 30°C can lead to $\varepsilon\text{-Cd}(\text{IO}_3)_2$ [20]. The kinetic study of the $\text{CdCl}_2\text{-HIO}_3$ [13] system in aqueous solution is extremely complicated and very sensitive to the procedure. A thorough study of this system by systematically varying the operating conditions was carried out. **Table 1** summarizes the different results obtained according to the four studied items:

1. Variable cadmium concentration at fixed temperature and time
2. Variable reaction time at fixed cadmium concentration and at $T = 20^{\circ}\text{C}$
3. Variable reaction time with fixed cadmium concentration and at $T = 60^{\circ}\text{C}$
4. The synthesis in a concentrated nitric acid medium

From acid solutions Abrahams and Nassau have shown that the transition metal iodate d or f could be obtained in the anhydrous state from nitric acid solutions [26–32]. Nitric acid is the medium used by Bach for the polymorph crystallogenesi s of the $\delta\text{-Cd}(\text{IO}_3)_2$ [18].

The fifth polymorph ε can be prepared under the same previous conditions but in the 30% nitric acid medium [13, 20].

The comparison of all results shown in the literature shows that the XRD diagram of the polymorph ε has been already published in 1980 without being identified [19].

2.1. Preparations and characterizations of pure phases

2.1.1. The polymorph $\alpha\text{-Cd}(\text{IO}_3)_2$

This product precipitates in the form of a very fine white powder from a solution of cadmium chloride and the highly concentrated iodic acid, $C_1 = 94.510^{-3} \text{ mol/l}$; all very slow evaporation efforts in order to obtain single crystals for structural study proved vain. The powder diagram of this variety is shown in **Figure 1** indicating that the spectrum of polymorph α is characterized by the main peak $d = 3.5784 \text{ \AA}$ [13].

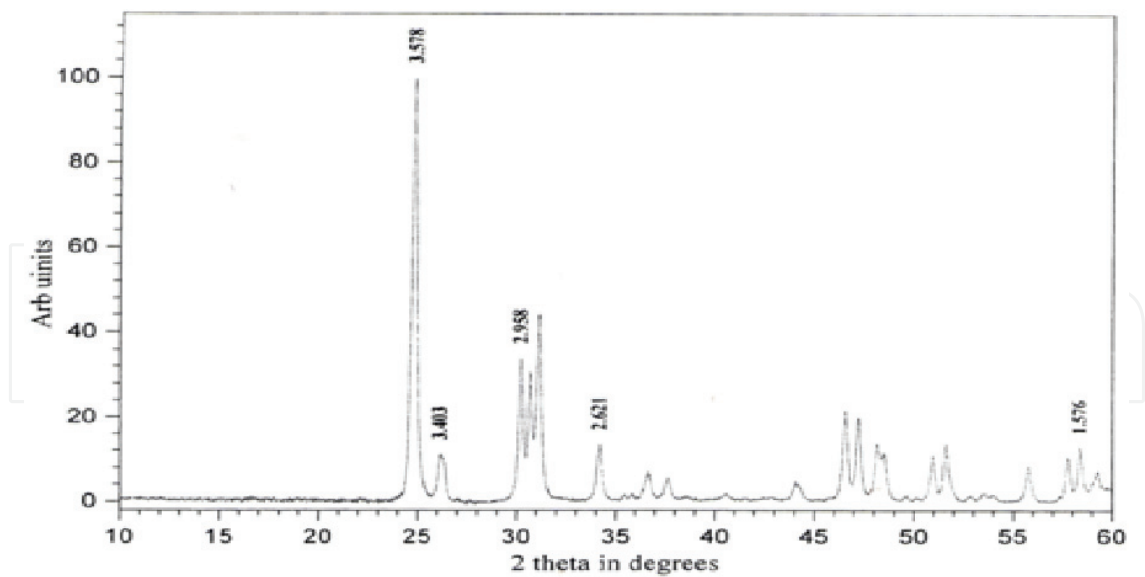


Figure 1. Diffraction diagram of α - $\text{Cd}(\text{IO}_3)_2$ [20].

2.1.2. The polymorph β - $\text{Cd}(\text{IO}_3)_2$

The polymorph β is obtained in its pure state when heating, at 250°C , the product obtained after a few days of the reaction of cadmium chloride (0.26 g) with lithium iodate (0.5 g) in 70 ml of water. The powder diagram of this variety is shown in **Figure 2** and shows that the spectrum of the polymorphic β is characterized by the main peak $d = 3.296 \text{ \AA}$ [13].

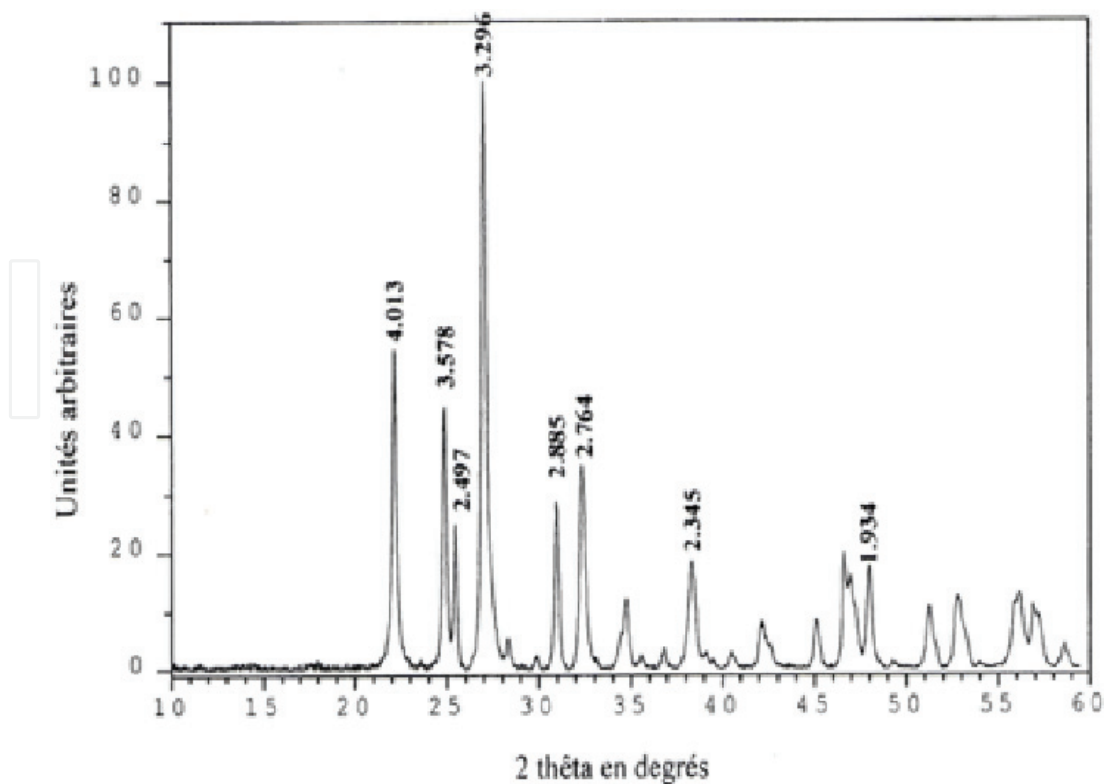


Figure 2. Diffraction diagram of β - $\text{Cd}(\text{IO}_3)_2$ [20].

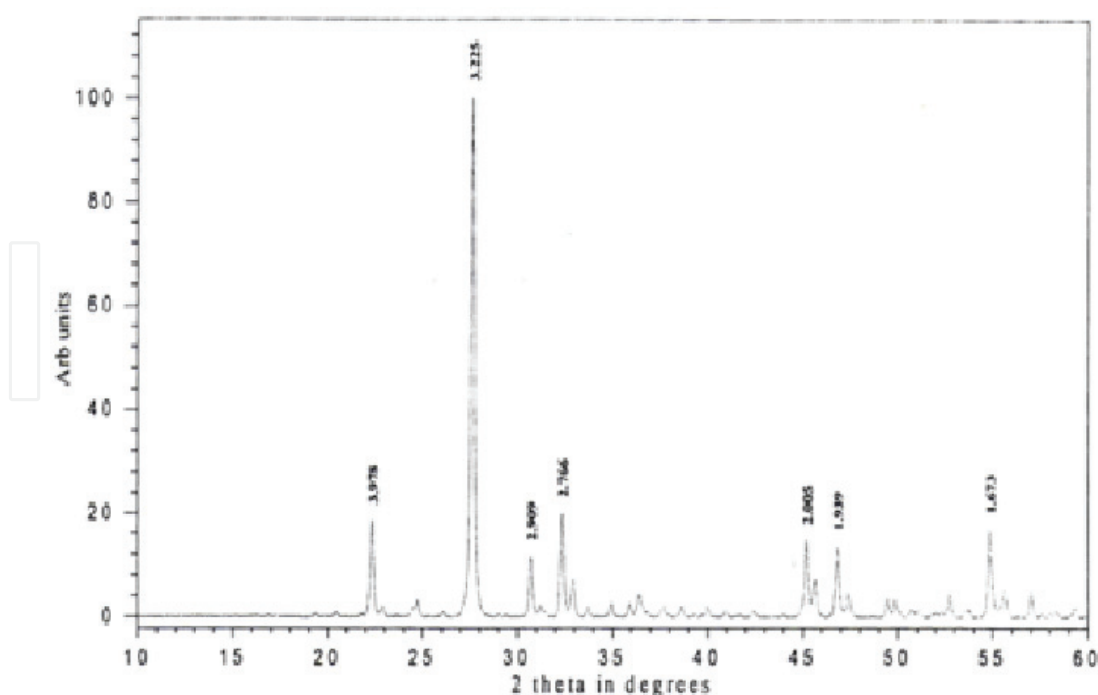


Figure 3. Diffraction diagram of $\gamma\text{-Cd}(\text{IO}_3)_2$ [20].

2.1.3. The polymorph $\gamma\text{-Cd}(\text{IO}_3)_2$

This polymorph can be obtained in its pure state, in the form of a well-crystallized powder, by two different methods: by evaporation at 60°C of a dilute aqueous solution of cadmium chloride and iodic acid ($C_{\text{Cd}} < 25 \cdot 10^{-3} \text{ mol/l}$) and by evaporation at 70°C of a dilute aqueous solution of cadmium chloride 0.26 and 0.607 g of potassium iodate in 100 ml of water. The crystallogensis efforts on this compound have not succeeded. It should be noted that this compound remains stable up to 380°C [13, 20, 25] and crystallizes in the non-centro-symmetric space group, because the optical activity test in second harmony generation (Kurtz and Perry test [33]) is positive and visually inferior to that of LiIO_3 [13, 20, 24, 25]. The X-ray diffraction pattern shown in **Figure 3** shows a perfectly crystallized product that is not listed in the JCPDS database. It should be noted that in the $2\theta = 10^\circ\text{--}60^\circ$ range of its powder spectrum, there are 44 low-intensity peaks compared to the main peak $d = 3.22 \text{ \AA}$.

2.1.4. The polymorph $\delta\text{-Cd}(\text{IO}_3)_2$

A solution containing (0.2 g) of $\gamma\text{-Cd}(\text{IO}_3)_2$ and 30 ml (60%) HNO_3 gives after slow evaporation (70°C) a prismatic transparent crystals, slightly yellow [13, 20]. A monocrystal of $11 \times 10 \times 2 \text{ mm}^3$ shown in **Figure 4** was obtained [22] from a saturated solution of a white powder of $\text{Cd}(\text{IO}_3)_2$ in a 60% nitric acid medium of HNO_3 at $T = 60^\circ\text{C}$; the total crystallogensis time is 20–25 days. The white powder used is the product of the reaction of cadmium chloride and iodic acid (1/2) in an aqueous medium.

Unlike other polymorphs, the spectrum of $\delta\text{-Cd}(\text{IO}_3)_2$ shown in **Figure 5** of $2\theta = 10^\circ$ to $2\theta = 60^\circ$ is characterized by several peaks because it contains more than 60 peaks, six among which are intense ($d = 3.93 \text{ \AA}$, $d = 3.66 \text{ \AA}$, $d = 3.44 \text{ \AA}$, **$d = 3.32 \text{ \AA}$** , $d = 2.49 \text{ \AA}$, and $d = 1.77 \text{ \AA}$).

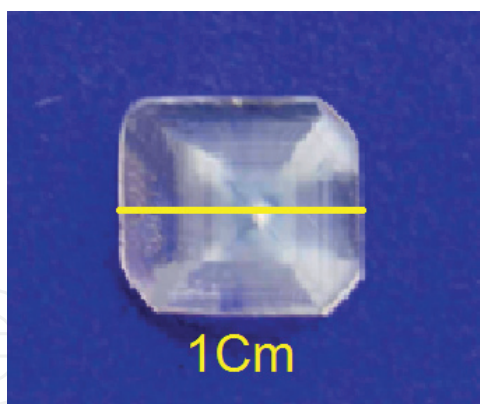


Figure 4. δ -Cd(IO₃)₂ morphology [22].

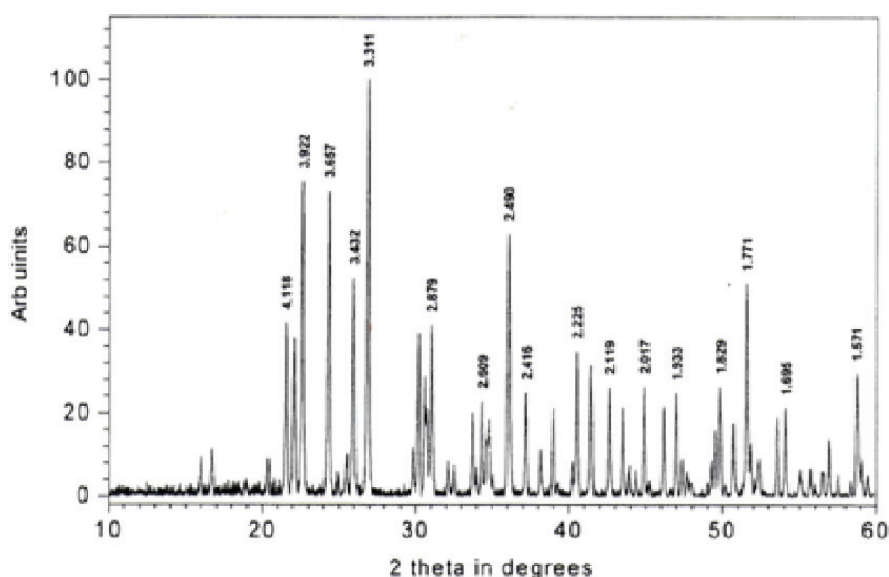


Figure 5. Diffraction diagram of δ -Cd(IO₃)₂ [20].

2.1.5. The polymorph ε -Cd(IO₃)₂

This polymorph constitutes the final product of the thermal evaluation, before the decomposition, of all the polymorphs described previously [20]. This polymorph can be obtained in solution by slow evaporation at 70°C of a solution containing 0.2 g of γ -Cd(IO₃)₂ in 30 ml of 30% HNO₃ [13].

Clear colorless needles, about 0.2 mm shown in **Figure 6**, are used to solve the crystalline structure of this polymorph which crystallizes in the centro-symmetric group Pca2₁, thus inactive in GSH but thermally stable up to 550°C. The powder diagram is given in **Figure 7** characterized by the main peak $d = 3.26$ Å.

2.1.6. The polymorph ζ -Cd(IO₃)₂

2 mmol of anhydrous cadmium chloride and 1 mmol potassium iodate were dissolved in 20 ml of deionized water. The solution was evaporated slowly at room temperature. After 2 days

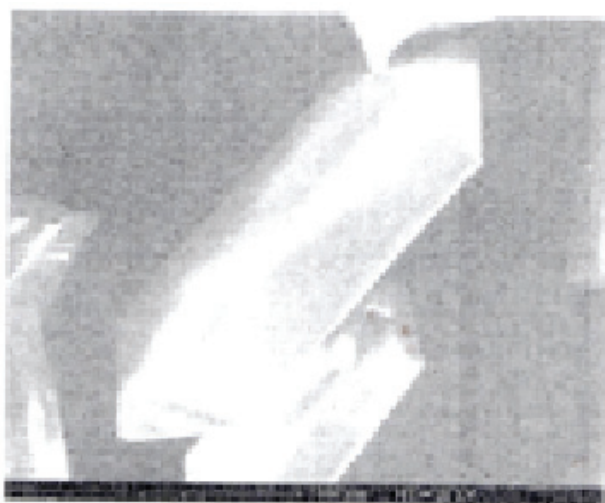


Figure 6. SEM view on the polymorph ϵ - $\text{Cd}(\text{IO}_3)_2$ [20].

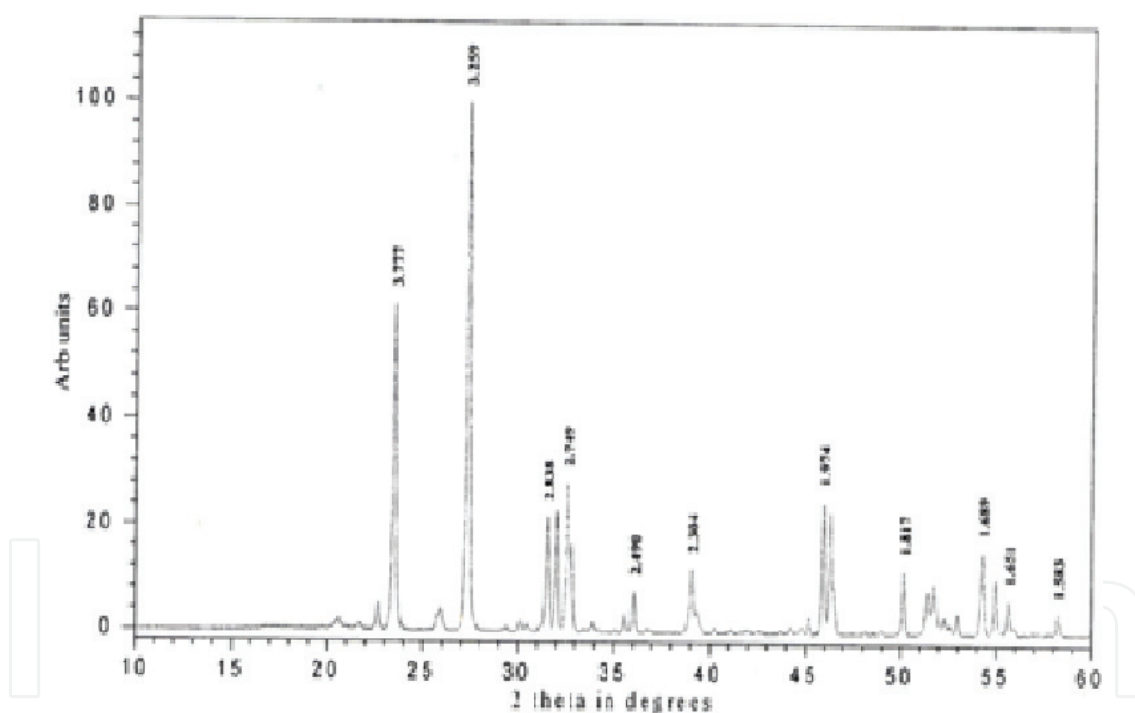


Figure 7. Diffraction diagram of ϵ - $\text{Cd}(\text{IO}_3)_2$ [20].

transparent and colorless prismatic of $\text{Cd}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ crystals is filtered from the solution. The solution was evaporated slowly at room temperature again; after 4 days, ζ - $\text{Cd}(\text{IO}_3)_2$ precipitates as colorless crystalline powder. They were filtered, washed with deionized water, and dried at room temperature (yield 30%). The second method consists of preparing the polymorph γ - $\text{Cd}(\text{IO}_3)_2$ in one step. This compound precipitates at a temperature of 60°C , as colorless crystalline powder from low concentrated aqueous solution of 2 mmol CdCl_2 and 1 mmol of KIO_3 . The ζ - $\text{Cd}(\text{IO}_3)_2$ was obtained by heating γ - $\text{Cd}(\text{IO}_3)_2$ at 450°C for 2 hours [23].

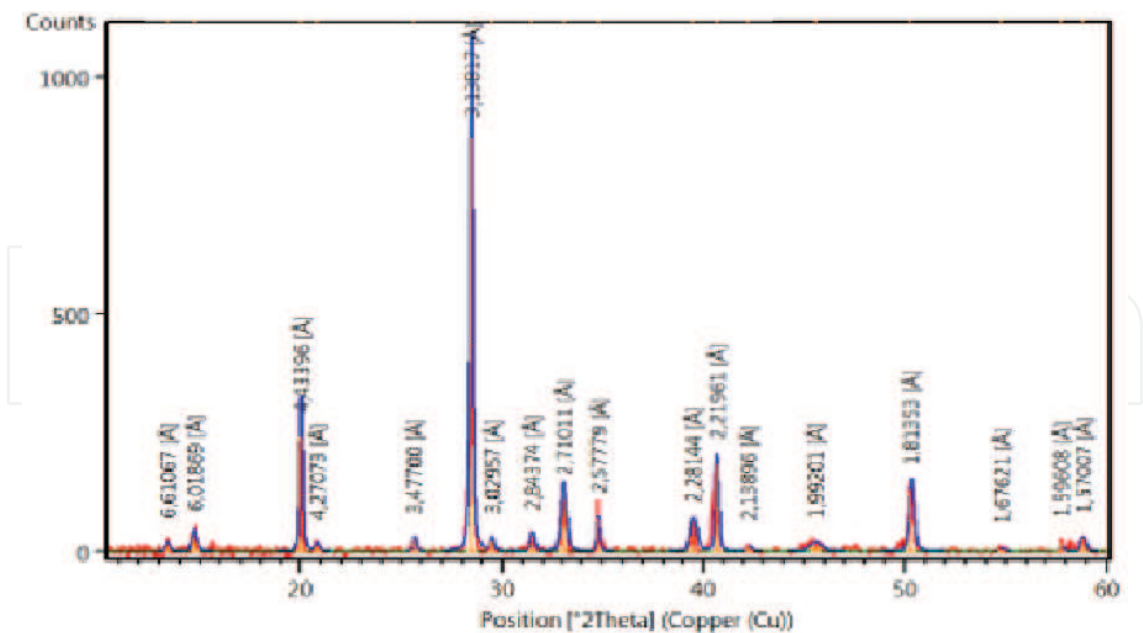


Figure 8. X-ray powder diagram of ζ-Cd(IO₃)₂ polymorph [23].

h	k	l	Int	2θ(obs)	2θ(cal)	diff
0	1	3	25.69	20.0196	20.0145	0.0051
*	*	*	1.649	20.7960	*****	*****
1	3	0	2.22	25.6282	25.6287	−0.0005
−1	3	2	100	28.4564	28.4086	0.0478
2	1	3	1.36	29.4866	29.4287	0.0579
*	*	*	5.40	31.4740	*****	*****
1	4	0	10.87	33.0587	33.0709	−0.0122
−3	1	2	7.519	34.8143	34.8034	0.0109
−1	1	6	6.959	39.4989	39.5209	−0.0220
3	2	3	20.99	40.6123	40.5692	0.0431
1	2	6	1.013	42.2563	42.3072	−0.0509
3	0	5	3.915	45.3698	45.3740	−0.0042
−1	4	5	2.662	45.7851	45.7821	0.0030
4	3	1	1.739	49.7340	49.7907	−0.0567
3	0	6	15.11	50.3116	50.3107	0.0009
−1	7	1	1.832	57.8014	57.8082	−0.0068
2	2	8	0.583	58.2564	58.2407	0.0157
−4	3	5	3.258	58.8234	58.8067	0.0167

* Peak wich do not fit with this cell.

Table 2. Indexed reflections, standardized intensities, and 2θ values (°) of ζ-Cd(IO₃)₂ polymorph used for cell determination [23].

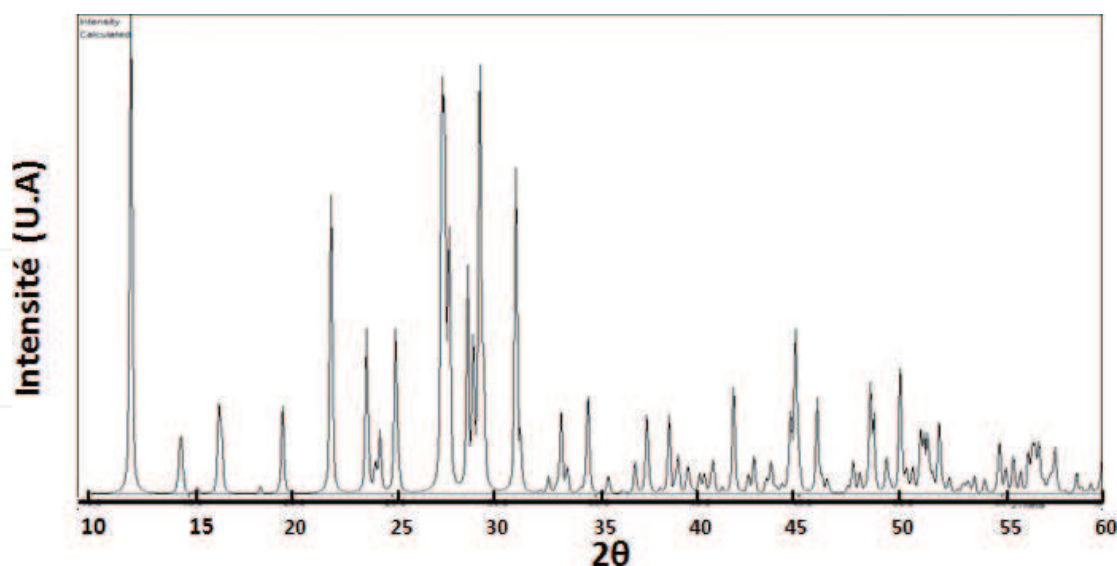


Figure 9. Theoretical powder diagram of $\text{Cd}(\text{IO}_3)_2\text{H}_2\text{O}$.

The X-ray powder diagram of this novel compound prepared by the first method is illustrated in **Figure 8**; the analysis shows that it is a polymorph different than α , β , γ , δ , and ϵ polymorphs; this diagram is characterized by the main peak $d = 3.14 \text{ \AA}$. We have used the powder diagram for peak indexing (**Table 2**). In the 15° – 60° range, 18 peaks have a relative intensity greater than 0.58%; 16 peaks can be indexed using the following monoclinic cell: $a = 8.4672 \text{ \AA}$, $b = 11.4365 \text{ \AA}$, $c = 14.4432 \text{ \AA}$, and $\beta = 91.12^\circ$ (agreement factor $R = 0.057$ for all 16 peaks). The two only peaks which do not fit with this cell are positioned at $2\theta = 20.796^\circ$ and $2\theta = 31.474^\circ$ with the relative intensity $I = 1.649$ and 5.4% , respectively. This ζ - $\text{Cd}(\text{IO}_3)_2$ polymorph exhibits a noticeable SHG activity which shows that it crystallizes in an acentric space group [23].

2.2. Synthesis method and the powder spectrum for monohydrate $\text{Cd}(\text{IO}_3)_2\text{H}_2\text{O}$ iodate

The slow evaporation of a very dilute solution of CdCl_2 (0.26 g) and 0.607 g of KIO_3 in 100 ml of distilled water gives, after a few days, clear transparent crystals of prismatic shape and millimetric size of $\text{Cd}(\text{IO}_3)_2\text{H}_2\text{O}$. This compound is characterized by its theoretical powder diagram retraced by the Poudrix software [34] (**Figure 9**). This compound crystallizes in the triclinic space group $P1^-$ $a = 7.119(2)$, $b = 7.952(2)$, $c = 6.646(2) \text{ \AA}$, $\alpha = 102.17(2)^\circ$, $\beta = 114.13(2)^\circ$, and $\gamma = 66.78(4)^\circ$ [20].

3. Synthesis method and the powder spectra for the two mixed cadmium-based ligand compounds: cadmium chloro-iodate CdIO_3Cl and cadmium hydroxide-iodate CdIO_3OH

In 2014, the cadmium chloro-iodate compound CdIO_3Cl in the form of a prism is synthesized by Yang and Mao. The mixture of 1 mmol of CdCl_2 and 0.5 mmol of I_2O_5 and 1 ml of water sealed in an autoclave equipped with teflon liner (23 ml) at 200°C for 4 days and then cooled to

30°C at 6°C/h. The crystal structure has been determined by single-crystal X-ray diffraction methods; the unit cell is orthorhombic with $a = 7.293(6)$ Å, $b = 16.04(2)$ Å, $c = 7.207(5)$ Å, $V = 843(1)$ Å³, and $Z = 8$. The space group is $CmCa$ [35].

The cadmium hydroxy-iodate $CdIO_3OH$ is synthesized in the form of colorless platelike in the same way as $CdIO_3Cl$ except that they have used the starting reagents: 0.25 mmol of $Cd(CH_3COO)_2 \cdot 2H_2O$, 2.5 mmol I_2O_5 , and 0.625 mmol of K_2CO_3 in a volume of 3 ml of distilled water [35]. The powder diagram for both compounds is shown in **Figure 10**. The crystal structure has been determined by single-crystal X-ray diffraction methods; the unit cell is orthorhombic with $a = 11.5245(0)$ Å, $b = 6.7985(7)$ Å, $c = 4.7303(4)$ Å, $V = 304.31(1)$ Å³, and $Z = 4$. The space group is $Pnma$ [35].

In 2016, two new production methods were published by Hebboul [36] to obtain the $Cd(IO_3)Cl$ compound; the first method (Procedure 1) is a synthesis by double decomposition; it consists of dissolving the KIO_3 in nitric acid 16 N, the same for the $CdCl_2$ whose molar ratio is 2:1; then the reaction mixture is conducted into ambient. In the first minute, the solution becomes opaque, seen by optical microscope after 24 h; it shows the formation of very small needles,

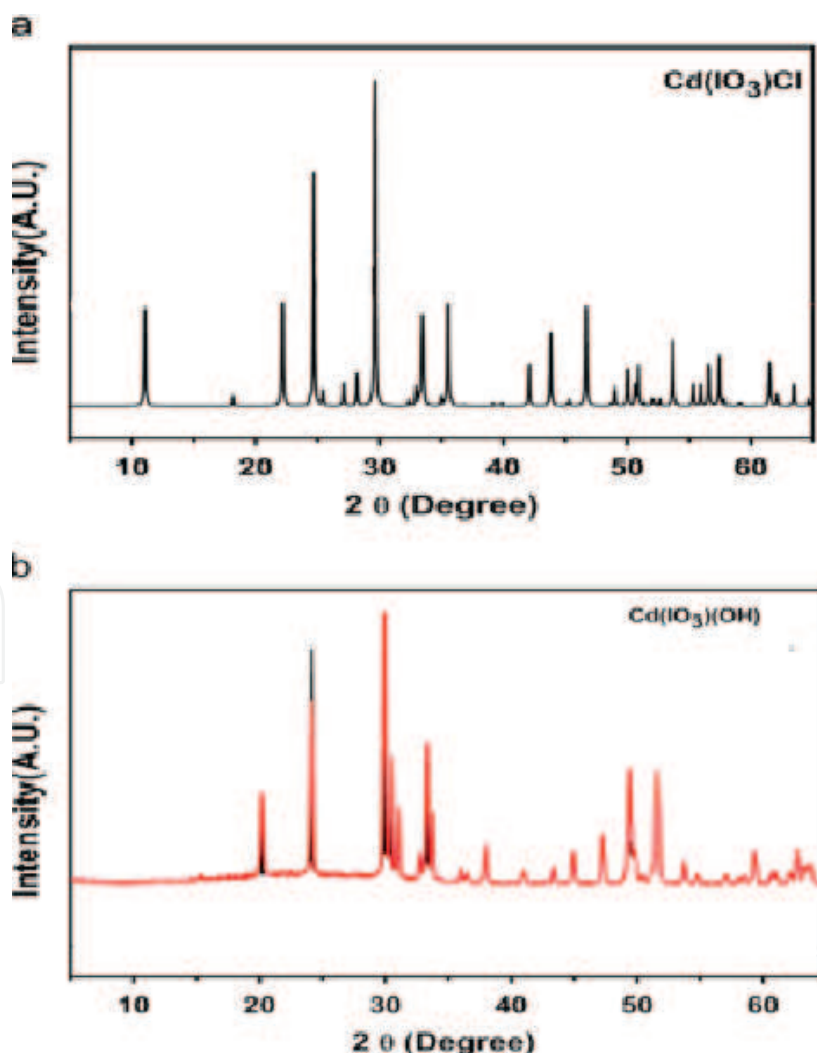


Figure 10. Mixed ligand compound powder diagram [35]. a- $Cd(IO_3)Cl$ and b- $Cd(IO_3)OH$.

but after 7 days, we noticed the increase in the size of the crystals in the form of spherulite needles (**Figure 11**).

The time at which the crystals appear in solution depends strongly on the concentration of nitric acid. Thus, a weakly concentrated solution of nitric acid requires almost dry evaporation, while a more concentrated solution, such as 7 M, allows crystallization when half of the solvent has evaporated. These crystals are filtered, rinsed with distilled water, and then dried at 60 °C in a drying oven. The molar yield of the reaction is around 90%.

The second method (Procedure 2) is a synthesis by substitution of one of the two groups $[\text{IO}_3^-]$ of the polymorph $\gamma\text{-Cd}(\text{IO}_3)_2$ by a chloride $[\text{Cl}^-]$. Iodic acid HIO_3 (0.148 g) and cadmium chloride CdCl_2 (0.48 g) are solubilized in 20 ml of distilled water; then the reaction mixture is brought into ambient; after a few days, we notice the formation of a mixture of two phases, crystals in the form of rods and white powder.

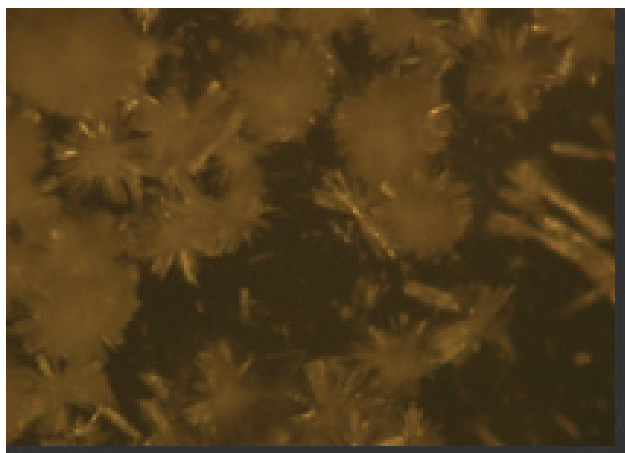


Figure 11. A view taken by the optical microscope after 7 days [37].

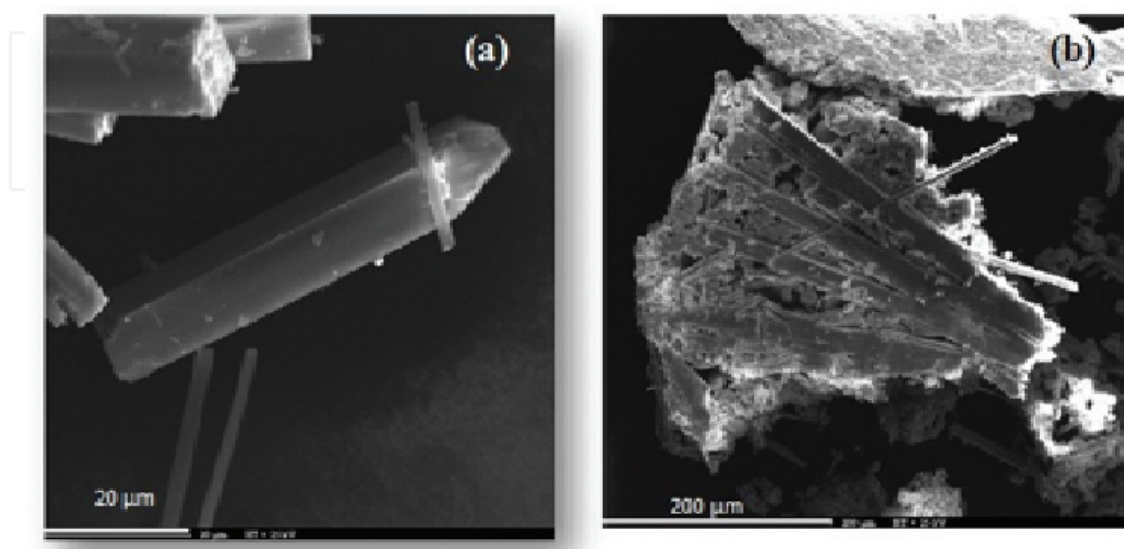


Figure 12. Morphology of the produced samples [36]. a- CdIO_3Cl and b- $\text{CdCl}_2\text{H}_2\text{O}$ et $\gamma\text{-Cd}(\text{IO}_3)_2$.

The mixture thus produced is heated at 400°C in a muffle furnace for 2 hours. Finally, the desired compound is obtained in the form of a powder with some trace of residual cadmium chloride which can be removed through washing by using distilled water.

3.1. CdIO₃Cl compound characteristics

The SEM image of **Figure 12a** shows the crystalline appearance of CdIO₃Cl compound obtained by method 1; the crystal has needle morphology. **Figure 12b** shows the morphology of the mixture produced by method 2; a powder of γ -Cd(IO₃)₂ is stuck to the CdCl₂H₂O rods

A monocrystalline needle is obtained by Procedure 1 of dimensions 0.09 × 0.03 × 0.03 mm³ and was chosen and then mounted on a goniometric head. The conditions of the intensity collection and the refinement parameters of the structure are given in **Table 3**. The CdIO₃Cl

Formula	CdIO ₃ Cl
Shape color	Colorless needle
Crystal size (mm ³)	0.09 × 0.03 × 0.03
Molecular weight (g.mol ⁻¹)	322.75
Crystalline system	Orthorhombic
Temperature (K)	293
λ (Ag) (Å)	0.56087
Space group (n°)	CmCa(64)
<i>a</i> (Å)	7.270(0)
<i>b</i> (Å)	15.995(0)
<i>c</i> (Å)	7.1980(0)
<i>V</i> (Å ³)	837.01
<i>Z</i>	8
<i>D_x</i> (g.cm ⁻³)	5.122
Absorption factor (mm ⁻¹)	6.897
<i>F</i> (000)	1136
Scan area in/θ (°)	3.00 – 21.38
Indication limits (h k l)	–9 ≤ 9; –20 ≤ 20; –9 ≤ 9;
Measured reflections	16,006
Independent reflections	522
Number of refined parameters	33
<i>R</i> _{int}	0.0457
<i>R</i> ₁	0.0385
ω <i>R</i> ₂	0.0888
Refinement quality (S)	1.247
ρ _{max} /ρ _{min} (e.Å ⁻³)	1.406/–1.565

Table 3. Crystallographic data and structural refinement of CdIO₃Cl [36].

crystallizes in the orthorhombic system, CmCa space group (No. 64) with the following mesh parameters: $a = 7.270(0) \text{ \AA}$, $b = 15.995(0) \text{ \AA}$, $c = 7.1980(0) \text{ \AA}$, $V = 837.009 \text{ \AA}^3$, and $Z = 8$.

The powder spectrum of **CdIO₃Cl** (Figure 13) was recorded and compared to the spectrum calculated with the Poudrix program [34]. The similarity of the diagrams shows that the phase obtained is pure.

The experimental diagrams (Procedure 2) are refined with the High Score Plus software; the identification of the presented phases is carried out by comparing the obtained experimental diagram with the reference file. The analysis gave us the types of the prepared phases

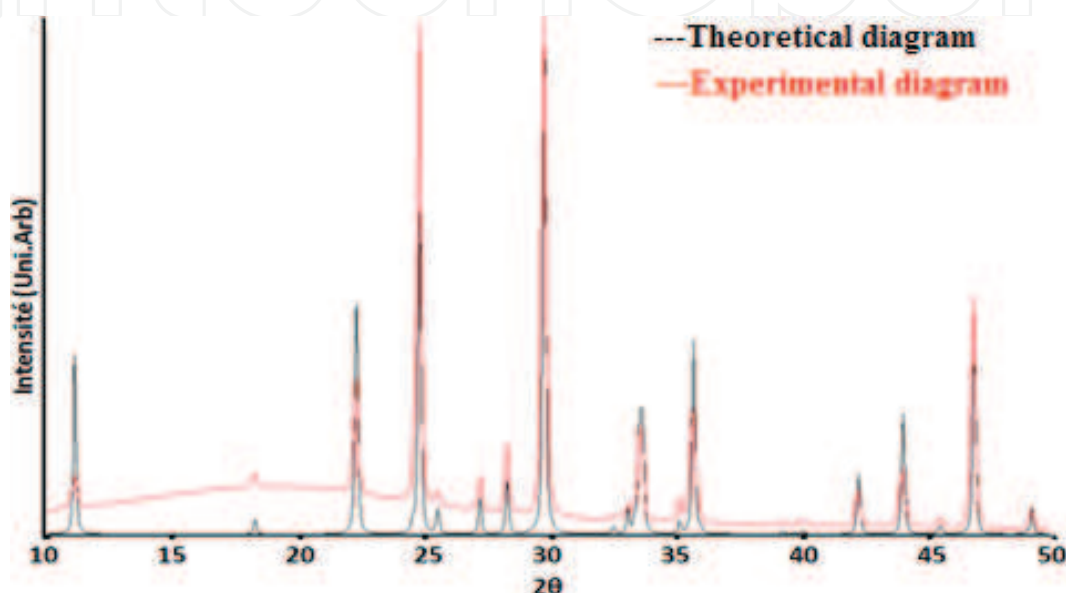


Figure 13. (XRD) Experimental and calculated powder spectra of the CdIO₃Cl compound [36].

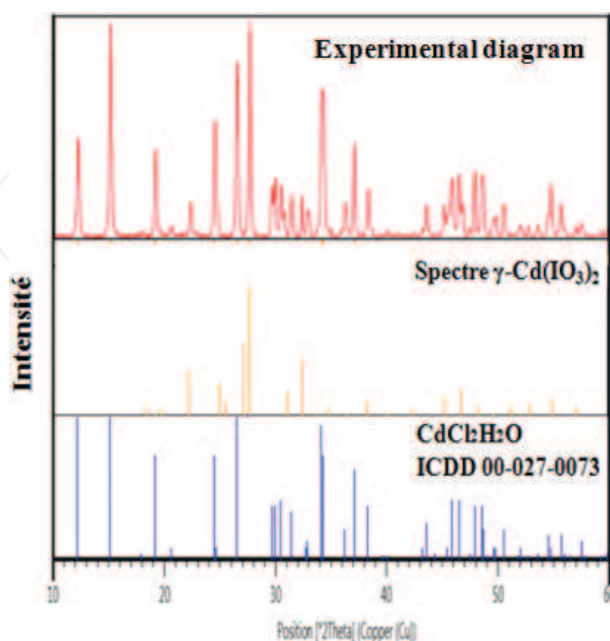


Figure 14. DRX spectrum of the produced mixture [36].

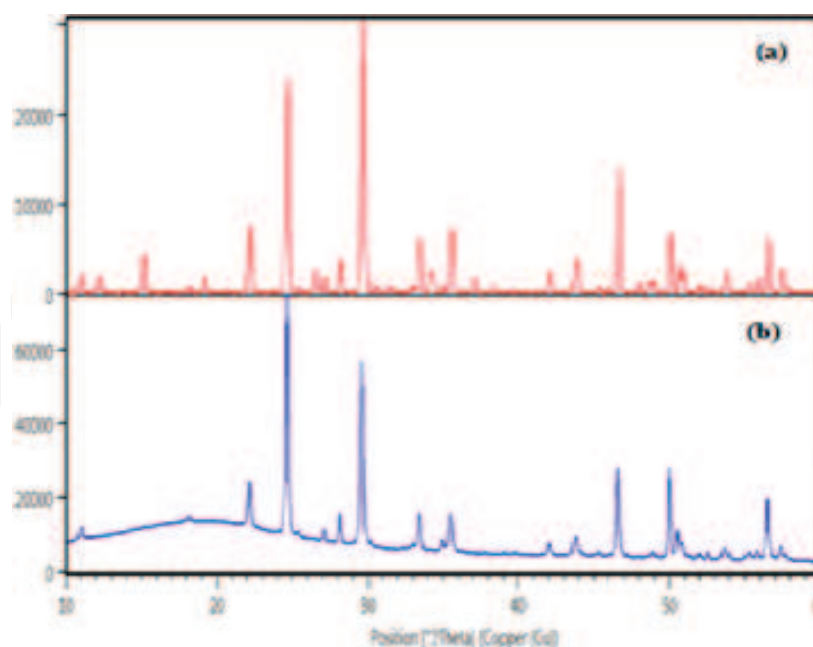


Figure 15. CdIO₃Cl DRX spectrum [36]. a-Before washing and b-After washing.

(Figure 14); the comparison with the JCPDS files shows that one of the phases is hydrate cadmium chloride CdCl₂·H₂O No.00-027-0073; the other is not listed, but a simple comparison with the powder spectra published on the polymorphs of cadmium iodate [13] confirms the formation of γ-Cd(IO₃)₂. After the heat treatment, the powder diagram analysis before and after the washing (Figure 15a) and (Figure 15b) shows the formation of the CdIO₃Cl good phase.

4. Conclusion

It is still a great challenge to summarize the relationships between structures or chemical compositions of the materials with their NLO properties. It is possible for compounds with the same chemical composition to exhibit several different phases with different structures. In this chapter, we provided the conditions for obtaining six polymorphs of anhydrous cadmium iodate in their pure state, as well as their powder diffractograms, whose three of which showing second harmonic generation activity (SHG), based on the work of Sciences Fondamentales Laboratory, University of Laghouat, in collaboration with Crystallography Laboratory, CNRS Grenoble, France, carried out between 2001 and 2005 and then the work of crystallogenesis by Ravi Kumar et al., in 2008; finally the work was realized in 2017 (LPCM, University of Laghouat), and we described the conditions for obtaining the triclinic single crystal of Cd(IO₃)₂·H₂O. Three chemical routes of preparation of chloro-cadmium iodate CdIO₃Cl are given. The prepared material was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The crystal structure has been determined by single-crystal X-ray diffraction methods. The hydroxy-cadmium iodate CdIO₃OH is synthesized in the form of colorless platelike. The crystal structure has been determined by single-crystal X-ray diffraction methods.

Author details

Zoulikha Hebboul

Address all correspondence to: z.hebboul@lagh-univ.dz

Physico-Chimie des Matériaux Laboratory (LPCM), University of Amar Telidji, Laghouat, Algeria

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