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Synthesis and Characterization of New Anhydrous Cadmium Iodate zeta polymorph ζ-$Cd(IO_3)_2$

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Abstract

Two methods of preparation with different routes to obtain a new anhydrous cadmium iodate ζ-Cd(IO3)2 are presented in this paper. This polymorph has been isolated and characterized by powder XRD device, indexed in monoclinic system, with unit cell a=8.4672 Å, b=11.4365 Å, c=14.4432 Å, β=91.12°.

1. Introduction

The metal iodates are of great importance in the investigation of nonlinear optical and dielectric materials [1-21]. Since 1838, anhydrous cadmium iodate was known by Rammelsberg, it is synthesized by precipitation from hot concentrated solution of sodium iodate and cadmium nitrate [22]. Single crystal of $Cd(IO_3)_2$ with small size of few mm in all directions was grown by evaporation of an aqueous solution containing 60% HNO_3 at a temperature of 343 K. The structure was reported by Bach and Kuppers in 1978 [23], called later δ-$Cd(IO_3)_2$ [24][25]. Bentria and al. found that the use of KIO_3 in an aqueous solution gives cadmium iodate monohyadrate, $Cd(IO_3)_2H_2O$[26]. In 2005 the investigation of $CdCl_2$-HIO_3 system in aqueous or nitric acid solutions of different concentrations revealed that anhydrous cadmium iodate presents a marked polymorphism, four $Cd(IO_3)_2$ polymorphs have been isolated and characterized (α, β, γ, and ε) two of which γ and ε showing second harmonic generation (SHG) activity, γ-$Cd(IO_3)_2$ is thermally stable up to 380°C then transforms to ε-$Cd(IO_3)_2$[24][27]. In 2014 Yang B.P and al. have revealed two compounds with a mixed ligand the Chloro cadmium iodate $CdIO_3Cl$ and hydroxy cadmium iodate $CdIO_3OH$ [28]. In 2016 a chemical preparation of $CdIO_3Cl$ are given by using γ-$Cd(IO_3)_2$ [29].In the present paper two methods of preparation routes are presented to obtain a new anhydrous cadmium iodate polymorph, ζ-$Cd(IO_3)_2$ showing second harmonic generation activity.

2. Experimental

2.1. *Preparation*

All reagents were purchased from Sigma–Aldrich, $CdCl_2$ (99%), KIO_3 (99.5%), and used without further purification. X-ray powder diagram were recorded on Philips-Xpert pro (λ=1.54Å) sample content analysis was based on close examination of X-ray diagrams by comparison with diagram repertory in publication [24] figure 1.Search and cell refinement were carried out using Treor [30] and Celerf [31] programs. Heat treatment of compound were carried out in furnace under (standard) atmosphere with a following rates 15°/min up ward 2

hours, at fixed temperature then 5°/min down ward to ambient temperature. The second harmonic generation (SHG) efficiency of the polymorph was evaluated by the Kurtz and Perry powder test [32].

2.2 Synthesis of ζ-$Cd(IO_3)_2$

The first method, 2 mmol of anhydrous cadmium chloride and 1mmol potassium iodate was dissolved in 20ml of deionised water. The solution was evaporated slowly at room temperature. After two days transparent and colorless prismatic of $Cd(IO_3)_2H_2O$ crystals are filtered from the solution.

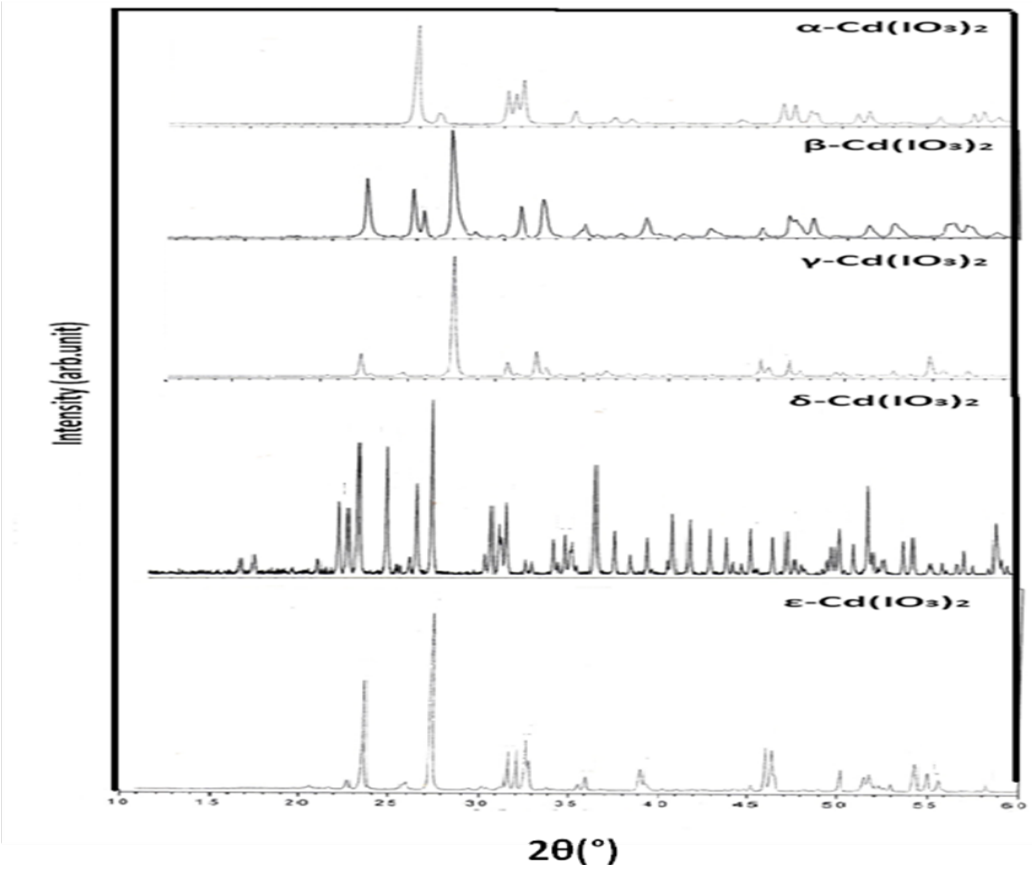

Figure 1: X-ray powder diagram of $Cd(IO_3)_2$ polymorphs.

The solution was evaporated slowly at room temperature again, after four days, ζ-$Cd(IO_3)_2$ precipitates as colorless crystalline powder. They were filtered, washed with deionised water, and dried at room temperature (yield 30%).The second method consists to prepare the polymorph γ-$Cd(IO_3)_2$ 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 1mmol of KIO_3,. The ζ-$Cd(IO_3)_2$, was obtained by heating γ-$Cd(IO_3)_2$ at 450°C for two hours.

2.3 *Characterization of ζ-$Cd(IO_3)_2$*

2.3.1. *XRD analysis*

The X-ray powder diagram of this novel compound prepared by the first method is illustrated in figure 2, the analysis shows that is a polymorph different than α,β,γ,δ, and ε polymorphs, his diagram characterized by the main peak d=3.14 Å.

For the second method, figure 3 shows the powder diagram of γ-$Cd(IO_3)_2$ polymorph before the thermal treatment characterized by the main peak d=3.22 Å , after heating (figure 4), a mixture of powders was obtained, the polymorph zeta (ζ-$Cd(IO_3)_2$) in the main phase and epsilon (ε-$Cd(IO_3)_2$) in the second phase, the latter is characterized by its broad peak d= 3.25 Å.

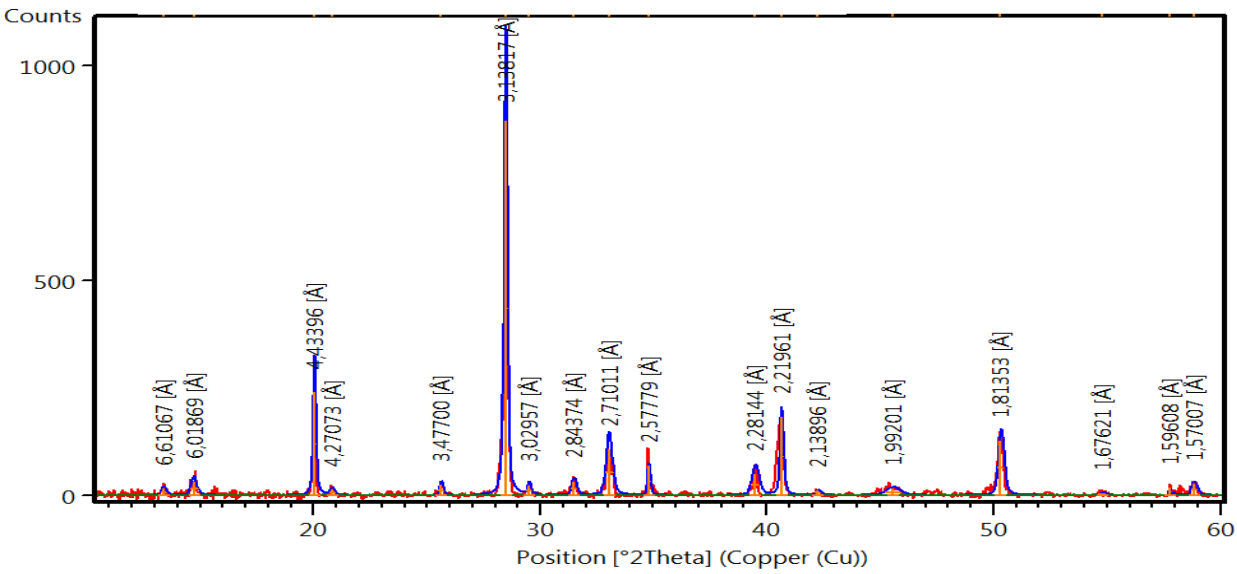

Figure 2 : X-ray powder diagram of ζ-$Cd(IO_3)_2$ polymorph (obtained by the first method).

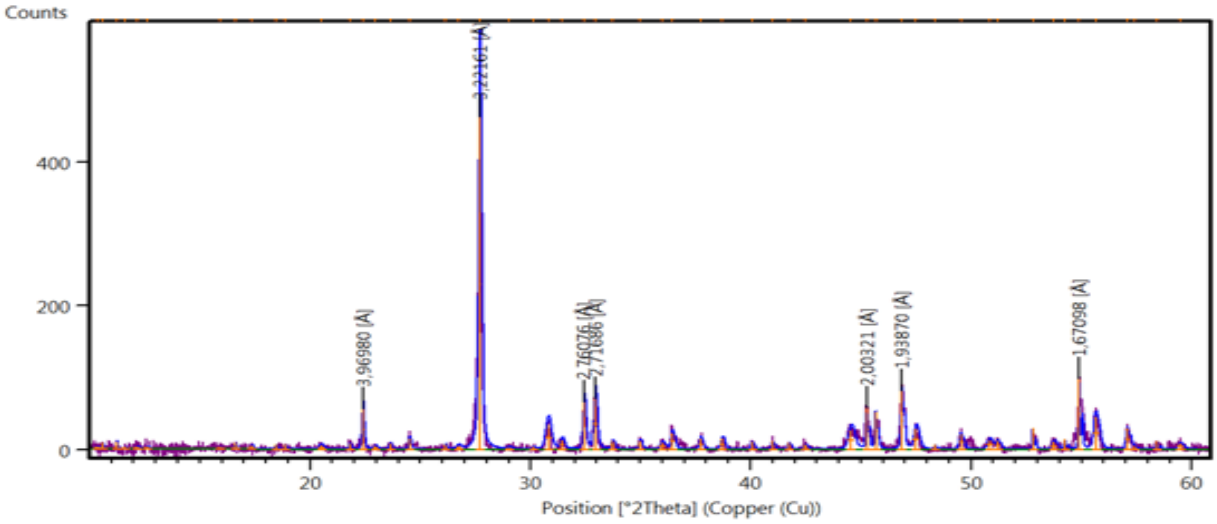

Figure 3: X-ray powder diagram of γ-$Cd(IO_3)_2$ polymorph before heating.

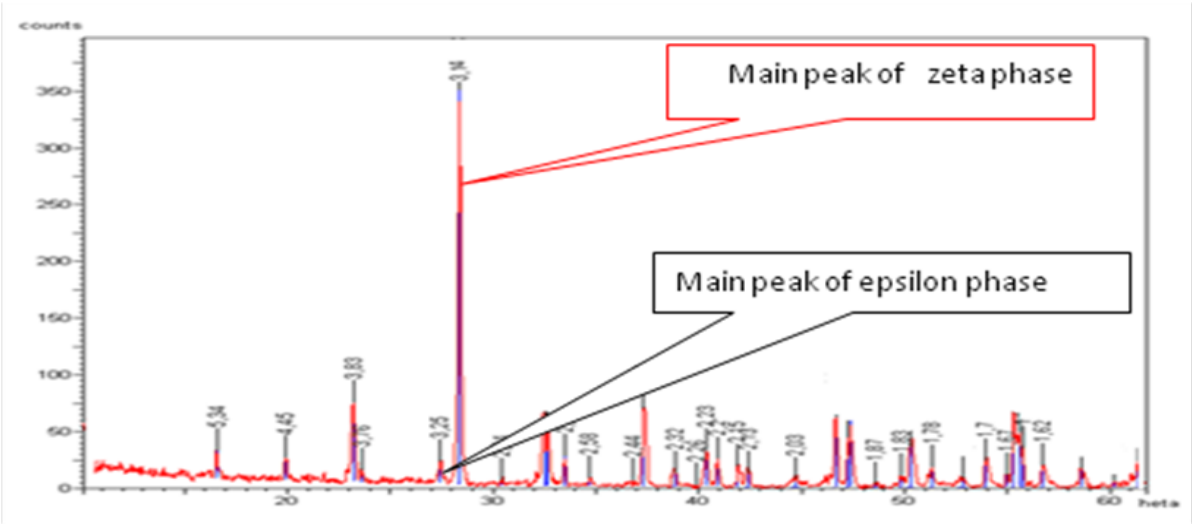

Figure 4: X-ray powder diagram of ζ-$Cd(IO_3)_2$ polymorph(obtained by the second method).

3. Results and Discussion

We have used the powder diagram of the first preparation for peak indexing (table 1). 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**=8.4672Å ,**b**=11.4365 Å, **c**=14.4432 Å, β=91.12° (agreement factor R=0.057 for all 16 peaks). The two only peaks which do not fit with this cell are positioned at 2θ= 20.796° and 2θ= 31.474° with the relative intensity I=1.649 % and I=5.4 % respectively. The table 2 show comparative study between the parameter cell of the different polymorphs α, β, γ, δ, ε and the new polymorph ζ-$Cd(IO_3)_2$ and illustrate that all the polymorphs crystallizes in monoclinic system only δ, and ε-$Cd(IO_3)_2$ in orthorhombic system.

Table1: Indexed reflections, standardized intensities and 2θ values (°) of ζ-$Cd(IO_3)_2$ polymorph used for cell determination.

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

Table2: The parameter cell of the different polymorphs

	a(Å)	b(Å)	c(Å)	β(°)	Reference
α -$Cd(IO_3)_2$	10.630	4.907	5.251	90.96	[24]
β-$Cd(IO_3)_2$	5.773	18.910	5.210	89.87	
γ-$Cd(IO_3)_2$	14.522	5.315	13.451	91.570	
δ-$Cd(IO_3)_2$	5.854	17.485	5.587	---	
ε-$Cd(IO_3)_2$	17.605	5.501	11.177	---	
ζ-$Cd(IO_3)_2$	8.4672	11.4365	14.4432	91.12	

Second harmonic generation at 1.064μm was used as an indicator for the lack of a center of symmetry as well as for indicating optical nonlinear device potential. This ζ-$Cd(IO_3)_2$ polymorph exhibits a noticeable SHG activity which shows that it crystallizes in an acentric space group.

Conclusions

The present study provides two methods of preparation routes to obtain anhydrous cadmium iodate and shows existence of new polymorph anhydrous cadmium iodate ζ-$Cd(IO_3)_2$, characterized by X-ray powder and indexed in monoclinic system, the powder of ζ-$Cd(IO_3)_2$ exhibits a noticeable second harmonic generation activity which shows that it crystallizes in an acentric space group. Anhydrous cadmium iodate crystallizes in six different structures two of which (δ and ε-$Cd(IO_3)_2$) in the orthorhombic system[24], and the four polymorphs (α, β, γ, and ζ-$Cd(IO_3)_2$) in monoclinic system.

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