

X-RAY STUDIES ON Tl_2HgI_4 , $PbHgI_4$, $CdHgI_4$ AND Au_2HgI_4
INORGANIC COMBINATIONS

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ABSTRACT

The parameters of the crystalline elementary cells were calculated starting from the diffraction X-ray spectra obtained on microcrystalline powders of compounds with thermochromic and semiconductor properties. The respective cell/units belong to the tetragonal system and have the following values: $a=6.450$ A, $c=3.14$ A for the Tl_2HgI_4 compound; $a=6.875$ A, $c=13.110$ A for the $PbHgI_4$ compound; $a=6.40$ A, $c=13.12$ A for the Au_2HgI_4 compound. The wet synthesis method is described for the $CdHgI_4$ compounds.

RESUMO

Os parâmetros das células unitárias cristalinas foram calculados a partir de espectra de difração de raios-x obtidos de pós microcristalinos dos compostos que exibem propriedades termocrômicas e semicondutoras. As respectivas células unitárias pertencem ao grupo tetragonal e tem os seguintes valores: $a=6.450$ A, $c=3.14$ A para Tl_2HgI_4 ; $a=6.875$ A, $c=13.11$ A para o composto $PbHgI_4$; $a=6.40$ A, $c=13.12$ A para o composto Au_2HgI_4 . A síntese via úmida dos compostos do grupo $CdHgI_4$ é descrita.

KEYWORDS: X-Ray diffraction, tetraiodomercurates, thermochromic properties, semiconductor properties, cell parameters.

INTRODUCTION

Barlot and all¹ supplied (1921) the first information regarding to the physico-chemical properties of the Tl₂HgI₄ compound, specifying that these properties are much different to that of the Ag₂HgI₄ and Cu₂HgI₄ compounds. No details regarding this compound were known since 1973, when Halmos and al² had synthesised and studied the Tl₂HgI₄ and PbHgI₄ compounds. They expressed the electrical conductivity versus the temperature and the differential thermal analysis, with no details regarding the type and the parameters of the crystalline lattice. It was 1975 when Joy³ performed the X-ray diffraction spectra on the Tl₂HgI₄ compound, without establishing its structure. Ammlung and all contributors⁴ in 1979, measured the electrical conductivity of the Tl₂HgI₄ compound, at 250°C, a much lower temperature than the corresponding ones for the M₂HgI₄ homologues (M⁺ = Ag⁺, Cu⁺), as a result of the decreased mobility of the Tl⁺ ion, compared with Ag⁺ and Cu⁺ ions. The dependence of the Raman spectra for the Tl₂HgI₄ and PbHgI₄ compounds on pressure, was studied in 1983 by Adams and all⁵, obtaining information about the existence of the phase transitions for these compounds, under the pressure effect. The thermoanalytic behaviour of the Tl₂HgI₄ and PbHgI₄ compounds was studied in 1986 by Negoiu and all⁶, in order to clear up the thermocronic transitions temperatures. Two compounds were also added to the M_xHgI₄ complex combination class, (M⁺ = Ag⁺, Cu⁺, Tl⁺, Pb²⁺), namely CdHgI₄ and Au₂HgI₄. These last compounds haven't been described in the speciality literature and data confirming the formation of the respective compound or other information referring to its physico-chemical properties are not known yet.

The aim of this paper is to establish and finalise the crystalline structure of the mentioned combinations. In order to provide a comparison basis, the authors considered necessary to synthesise the Cu₂HgI₄ and Ag₂HgI₄ compounds and to study the X-ray diffraction spectra on the powders of these compounds. The diffractometric data, compared to the one existing in the literature, is represented in table 3 and 4.

EXPERIMENTAL PART

The Tl_2HgI_4 and $PbHgI_4$ combinations have been obtained through the wet synthesis described by Well and all⁷, otherwise applied by Adams too, in 1983. This method isn't much different to the one used for obtaining the Ag_2HgI_4 .

The same technique has been generally applied for the $CdHgI_4$ and Au_2HgI_4 compounds. A CdI_2 (0,5 M) and a $AuCl$ (0,5 M) solution respectively were added to a K_2HgI_4 (4 M) solution, until the stoichiometric ratio is reached. The solution obtained by this method were slowly heated at 75 - 80°C. Carmin-red, respectively redish-golden precipitates were formed, containing crystals with metallic-reflexion. The precipitates were then washed with water in order to remove the possible soluble impurities, were dried under vacuum on phosphorus pentoxide for 60 h, at the room temperature, and then kept in containers, until being used for investigation.

The compounds obtained by this method have been characterised by elementary analysis, as follows:

* Mercury was determined through atomic absorption spectrophotometry method, described by El-Awady and all¹¹ and completed by Luca and all¹².

Thus, the $CdHgI_4$ and Au_2HgI_4 combinations were decomposed by the wet way, into an aq. HNO_3 solution (1 N), through slowly heating. Then, the mercury was brought back by the elementary state using Sn^{2+} chloride and drowe through the cell of an atomic absorbtion spectrophotometer. The absorbtion of the radiation was determined at $\lambda = 253.7$ nm.

The standard Hg (II) solution with a 1000 $\mu g/ml$ concentration, was obtained by dissolving the necessary pure mercuric chloride quantity into distilled water. The mercury quantity within the complex samples (table 1 and 2) was calculated using the calibration curve.

* Cadmium was determined according with the method described by Fries and Getrost¹³, using diphenilthyocarbazone, the solution to be analysed being brought to pH = 7-8. At pH = 7-8 the cadmium ions form, in the presence of the diphenilthyocarbazone a macromolecular complex, which exhibits a maximum absorbtion of the light radiation at $\lambda = 520$ nm.

The standard Cd (II) solution, with 1000 $\mu g/ml$ concentration was obtained by diluting the necessary quantity of pure CdI_2 into the distilled water. The calibration curve Abs ($\lambda = 520$ nm) versus the standard Cd (II) concentration initially traced and the Cd^{2+} quantity within the samples taken in work was calculated by extrapolating the calibration curve.

* Gold was determined to the method described by Fries and Getros¹⁴ using tetraethylrodamine, the analysed solution being brought to a pH = 5. In the presence of the B rhodamine, the gold ions form a macromolecular complex which is extracted in diisopropylic ether. The formed complex exhibits a maximum absorbtion of the light radiation at $\lambda = 565$ nm.

The standard Au (I) solution with a 100 $\mu g/10$ ml concentration was obtained by diluting the necessary pure $AuCl$ quantity in distilled water. The Au^+ ions were complexed at once with B rhodamine, and the form compound was separated in diisopropylic ether. The calibration curve Abs ($\lambda = 565$ nm) versus the standard Au (I)

concentration was then traced. The Au⁺ quantity was calculated by extrapolating this curve and using the samples taken in work.

* Jodine was determined by difference, accordingly to the quantities of samples taken in work.

Tables 1 and 2 contain results obtained using five different complex of the CdHgI₄ and Au₂HgI₄ compounds.

All the obtained results confirm the formation of the CdHgI₄ and Au₂HgI₄ inorganic combinations.

The Tl₂HgI₄, PbHgI₄, CdHgI₄ and Au₂HgI₄ compounds obtained through this method are microcrystalline powders, in the following colours: yellow, orange, carmine-red and respectively, redish-golden.

The complex were dry ground to a mean size particles (aprox. 15 μ) in order to perform X-ray diffraction studies. Determinations were performed at room temperature.

The diffraction spectra were obtained between 15 and 35° Bragg using a TUR-M-62 HZG apparatus equiped with 3 diffractometer. The CuK_α radiation (λ = 1.54051 Å) was used, the radiation was filtered through a Ni sheet; the rate of the counter was 0.5 /min.

RESULTS AND DISCUSSION

Tables 3 - 8 contain the "d" lines positions expressed in Å and the relative intensities I/I₁ of these lines, beside the same properties experimental obtained from diffraction spectra of the respective complex combinations.

This thing was carried out because it is not known quite if the conditions of the used preparation methods lead either to pure equilibrium compounds or to mixtures of non-equilibrium compounds and reactants.

Anyway, for the indexation, the diffraction lines of the reactants were as much as possible not taken in consideration.

In order to index the diffraction spectra on powders, the recurrent formulae given within the international crystallography tables of the cubic, tetragonal and rhombic systems were used. This thing was performed because the preliminary microscopic studies have shown that the crystalline shape of this compounds can be defined within one of this systems.

It has been proven that all the four compounds: Tl₂HgI₄, PbHgI₄, CdHgI₄ and Au₂HgI₄, beside the Ag₂HgI₄ and Cu₂HgI₄ compounds belong to the tetragonal system, having the "d" parameter values and the hkl index shown in tables 3-8.

Tables 3 - 8.

Table 9 exhibits the crystalline elementary cells parameters of the M_xHgI₄ synthesised complex combinations, compared to the existent literature data. These parameters were calculated using the diffraction patterns obtained on the microcrystalline powders of the compounds. At the room temperature, a single tetragonal structural phase (named β phase) exists for the up to date known M_xHgI₄ substances class (M = Ag, Cu, Tl, Pb, Cd, Au).

Table 9.

As observed in table 9, the crystalline elementary cells parameters of the Ag₂HgI₄ and Cu₂HgI₄ compounds are likewise those presented within the literature⁴.

Table 1. Some Properties of the CdHgI_4 Compound.

Table 1

No.	CdHgI_4 g/50ml	Cd^{2+} , g/50ml		Hg^{2+} , g/50ml		I, g/50ml	
		theoretical	exp.	theoretical	exp.	theoretical	exp.
1.	0.11095	0.0150	0.0148	0.0270	0.0258	0.0675	0.0689
2.	0.1460	0.0200	0.0199	0.0357	0.0350	0.0903	0.0911
3.	0.1826	0.0250	0.0250	0.0446	0.0452	0.1130	0.1124
4.	0.2191	0.0300	0.0301	0.0535	0.0543	0.1356	0.1347
5.	0.2556	0.0350	0.0340	0.0625	0.0630	0.1681	0.1586

Table 2. Some Properties of the Au_2HgI_4 Compound.

Table 2

No.	Au_2HgI_4 g/50ml	Au^+ , g/50ml		Hg^{2+} , g/50ml		I, g/50ml	
		theoretical	exp.	theoretical	exp.	theoretical	exp.
1.	0.0140	0.0050	0.0048	0.0025	0.0028	0.0065	0.0064
2.	0.0210	0.0075	0.0078	0.0038	0.0041	0.0097	0.0091
3.	0.0285	0.0100	0.0098	0.0052	0.0055	0.0133	0.0132
4.	0.0350	0.0125	0.0122	0.0064	0.0060	0.0161	0.0168
5.	0.0420	0.0150	0.0147	0.0076	0.0071	0.0194	0.0202

Table 3. X-Ray diffraction spectrum on Ag_2HgI_4 powder, compared to literature data

$\gamma - \text{AgI}^*$			Ag_2HgI_4 [16]			$\beta - \text{Ag}_2\text{HgI}_4$ [17]			Ag_2HgI_4 [19]			$\text{Ag}_2\text{HgI}_4^{**}$			
d, Å	I/I ₁	hkl	d, Å	I/I ₁	hkl	d, Å	I/I ₁	hkl	d, Å	I/I ₁	hkl	d _{exp} , Å	I/I ₁	hkl	d _{theoretical} , Å
			6.27	2	200	-	-	-	6.33	Fs	100	6.2668	14	002	6.2668
			5.64	3	210	5.47	25	101	5.69	Fs	101	5.6253	19	101	5.6364
			4.47	3	220	4.42	25	110	4.49	Fs	110	4.4622	16	110	4.4622
3.75	100	111	-	-	-	-	-	-	-	-	-	3.7384	19	-	-
			3.65	100	222	3.65	90	112	3.61	I	112	3.6390	100	112	3.6349
			3.50	2	320	3.50	25	103	3.58	Fs	103	3.4941	16	103	3.4836
			-	-	-	3.14	20	004,200	-	-	-	-	-	-	-
			2.82	3	420	2.83	45	202	2.84	S	210	2.8184	16	202	2.8182
			2.76	4	421	2.80	55	211	2.77	Fs	211	2.7525	15	211	2.7532
			2.57	2	422	2.57	45	114	-	-	-	2.5728	14	212	2.5733
			2.48	1	510	-	-	-	-	-	-	-	-	-	-
			2.34	2	F.II	2.34	40	105,213	2.36	Fs	213	2.3433	14	213	2.3386
2.30	60	220	-	-	-	-	-	-	-	-	-	2.2905	16	-	-
			2.23	50	440	2.228	100	204,220	2.24	K	220	2.2317	49	220	2.2311
			2.10	2	600,442	2.109	40	006,222	2.11	Fs	222	2.1040	16	222,300	2.1035
			2.08	2	610	-	-	-	2.08	Fs	301	-	-	006,214	2.0889
1.96	30	311	1.90	30	622	1.90	100	116,312	1.91	K	312	1.9239	28	312	1.9015
			1.88	1	630,543	-	-	-	-	-	-	1.9034	28	116	1.8919

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Table 4

Table 4. X-Ray diffraction spectrum on Cu_2HgI_4 powder, compared to literature data

HgI_2^*			$\beta\text{-Cu}_2\text{HgI}_4$ [17]				$\beta\text{-Cu}_2\text{HgI}_4^{**}$		
d, Å	I/I_1	hkl	d, Å	I/I_1	hkl	$d_{\text{exp}}, \text{Å}$	I/I_1	hkl	$d_{\text{theoretical}}, \text{Å}$
6.22	55	002	-	-	-	6.2056	12	-	-
-	-	-	5.42	25	101	5.4399	14	101	5.4399
4.12	70	101	-	-	-	4.1106	16	-	-
3.58	100	102	-	-	-	3.5699	31	-	-
-	-	-	3.52	100	112	3.5172	100	112	3.5116
-	-	-	3.43	25	103	3.3857	14	103	3.3744
3.11	3	004	-	-	-	-	-	-	-
3.09	2	110	-	-	-	-	-	-	-
-	-	-	3.05	15	200;004	-	-	200;004	3.0407
3.01	40	103	-	-	-	3.0034	14	-	-
2.768	30	112	2.72	10	202	2.7592	10	104;202	2.7207
-	-	-	-	-	-	-	-	-	2.7199
-	-	-	2.67	30	211	2.6542	12	211	2.6542
2.534	7	104	2.52	10	114	-	-	-	-
-	-	-	2.27	35	105	2.2618	10	105;213	2.2595
-	-	-	-	-	-	-	-	-	2.2589
2.192	60	114	-	-	-	-	-	-	-
2.186	55	200	-	-	-	2.1881	12	-	-
2.163	15	105	2.15	100	220;204	2.1562	24	220;204	2.1501
-	-	-	-	-	-	-	-	-	2.1506
-	-	-	-	-	-	2.1454	20	115;221	2.1180
-	-	-	-	-	-	-	-	-	2.1173
2.074	15	006	2.04	10	226;006	2.0651	8	224;006	2.0272
-	-	-	-	-	-	-	-	-	-

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Table 5. X-Ray diffraction spectrum on $PbHgI_4$ powder

HgI_2^*			PbI_2^{**}			$PbHgI_4^{***}$ powder			
d, Å	I/I ₁	hkl	d, Å	I/I ₁	hkl	d _{exp} , Å	I/I ₁	hkl	d _{theoretical} , Å
			6.98	25	001	6.964	100	-	-
			-	-	-	6.553	10	002	6.552
6.22	55	002	-	-	-	6.188	30	-	-
			-	-	-	-	-	111	4.558
			-	-	-	4.2913	10	003	4.370
4.12	70	101	-	-	-	4.1106	9	-	-
			3.9456	16	100	4.022	8	112	3.905
3.58	100	102	-	-	-	3.5728	13	-	-
			3.489	4	002	3.4767	10	-	-
			3.435	100	101	3.4340	7	-	-
			-	-	-	3.3330	15	201	3.325
			-	-	-	3.2804	13	004	3.278
3.01	40	103	-	-	-	2.994	9	-	-
2.768	30	112	-	-	-	2.7658	14	-	-
			-	-	-	2.6992	10	203	2.703
			-	-	-	2.6345	8	005	2.622
			2.614	55	102	2.6062	10	-	-
			-	-	-	2.4012	7	221	2.390
			2.327	6	003	2.3251	17	-	-
			2.278	65	110	-	-	-	-
2.192	60	114	-	-	-	-	-	-	-
2.186	55	200	-	-	-	2.1821	9	-	-
2.163	15	105	2.166	14	111	2.1580	7	-	-
			-	-	-	2.1415	9	311	2.145
2.074	15	006	-	-	-	2.0705	12	-	-
1.874	15	6	2.0052	16	103	-	-	-	-
1.865	15	212	1.7496	6	004	1.7433	15	-	-
1.654	3	214	-	-	-	1.6856	7	-	-

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Table 6. X-Ray diffraction spectrum on Tl_2HgI_4 powder

d, Å	HgI_2^*		d_{exp} , Å	Tl_2HgI_4 - powder **		$d_{theoretical}$, Å
	I/I_1	hkl		I/I_1	hkl	
-	-	-	6.5823	19	002	6.5700
6.22	55	002	6.2056	133	-	-
-	-	-	4.6091	15	102	4.6027
-	-	-	4.1990	15	111	4.3087
4.12	70	101	4.1068	28	-	-
3.58	100	102	3.5643	41	103	3.6235
-	-	-	3.3309	20	004	3.2850
3.11	3	004	3.1120	100	201	3.1320
3.09	2	110	-	-	-	-
3.010	40	103	3.0114	26	-	-
-	-	-	2.9838	61	104	2.9300
-	-	-	2.9227	15	202	2.9000
2.768	30	112	2.7625	19	211	2.9174
2.634	-	-	2.6110	13	203	2.5970
-	7	104	2.5100	13	-	-
-	-	-	2.4870	13	105	2.4370
-	-	-	2.3563	19	213	2.4090
-	-	-	2.3120	22	204	2.3013
-	-	-	2.2727	17	115	2.2770
-	-	-	2.2222	17	221	2.2468
2.192	60	114	2.1912	24	006	2.1900
2.186	55	200	-	-	-	-
2.163	15	105	2.1591	17	300;222	2.1218
-	-	-	2.1100	17	301	2.1218
2.074	15	006	2.0750	39	106	2.0737
-	-	-	1.9993	13	311	2.0155
-	-	-	1.9233	13	303	1.9300

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Table 7. X - Ray diffraction spectrum on $CdHgI_4$ powder

d, A	HgI_2^*		d_{exp} , A	$CdHgI_4$ - powder**		$d_{theoretical}$, A
	I/I_1	hkl		I/I_1	hkl	
6.220	55	002	6.2317	83	002	6.220
4.120	70	101	4.1106	76	101	4.122
3.580	100	102	3.5756	100	102	3.575
3.110	3	004	3.1120	21	004	3.110
3.090	2	110	-	-	-	-
3.010	40	103	3.0014	48	103	3.008
2.768	30	112	2.7625	41	112	2.767
2.534	7	104	2.5265	24	104	2.534
2.192	60	114	2.1902	55	114	2.192
2.186	55	200	2.1871	59	200	2.185
2.163	15	105	2.1581	28	105	2.162
2.074	15	006	2.0695	31	006	2.070
2.062	7	202	-	-	002	2.0612
1.931	9	211	1.9285	28	211	1.930
1.874	15	106	1.8732	31	106	1.873
1.865	15	212	1.8609	31	212	1.874

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Table 8. X-Ray diffraction spectrum on Au_2HgI_4 powder

d, A	HgI_2^*		d_{exp}, A	Au_2HgI_4 - powder**		
	hkl	hkl		hkl	hkl	$d_{\text{theoretical}}, \text{A}$
6.220	55	002	6.5620	74	002	6.5622
4.120	70	101	4.0865	67	101	4.0987
3.580	100	102	3.5443	12	102	3.6035
3.110	3	004	3.1019	39	004	3.1315
3.090	2	110	-	-	-	-
3.010	40	103	3.0001	32	103	3.0080
2.768	30	112	2.7425	100	112	2.7430
2.534	7	104	2.5011	15	104	2.5240
2.192	60	114	2.1712	46	114	2.1725
2.186	55	200	2.1670	50	200	2.1682
2.163	15	105	2.1592	19	105	2.1588
2.074	15	006	2.0650	22	006	2.0683
2.062	6	202	-	-	202	2.0568
1.931	9	211	-	-	211	1.9460
1.874	15	106	1.8232	22	211	1.8252
1.865	15	212	1.8110	22	211	1.8110

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Table 9. The parameters of the "a" and "c" crystalline lattice (Å), expressed for the M_xHgI_4 studied compounds

Compound	$r_{M^{n+}}$, Å	Lattice parameters		References
		a, Å	c, Å	
Ag_2HgI_4	1.26	6.353	6.340	15
		12.62	12.62	16
		6.31	12.63	17
		6.322	12.605	18
		6.33	12.66	19
Cu_2HgI_4	0.96	6.3105	12.5336	**
		6.09	12.23	17
Tl_2HgI_4	1.40	6.0814	12.1683	**
		6.450	13.140	**
$PbHgI_4$	1.20	6.875	13.110	**
$CdHgI_4$	0.97	4.3693	12.4399	**
Au_2HgI_4	1.37	6.4010	13.1250	**

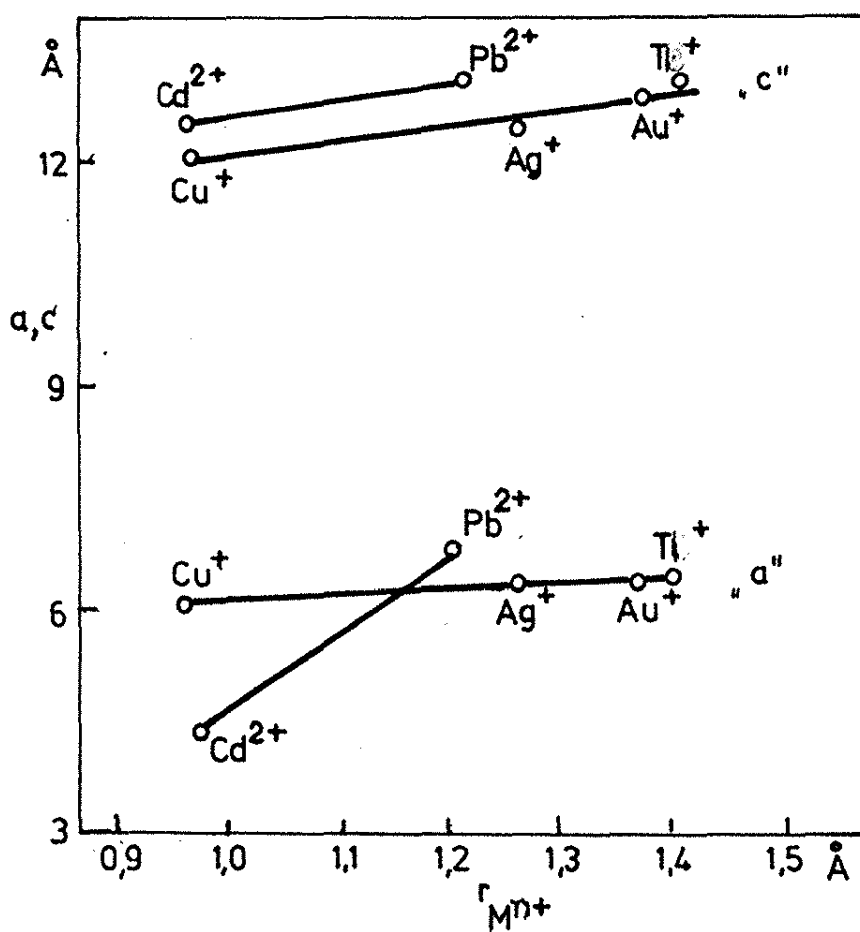


Fig.1. Relationships between the ionic rays and the tetragonal elementary cells parameters, within the M_xHgI_4 system

It is also observed that the elementary cell parameter increases with the increasing of the metallic radius ion, without the alteration of the crystallisation system.

For the M_2HgI_4 compounds, the increasing of the reticulate parameter with the metallic radius ion (M^+) is more emphasised on the "c" direction than on the "a" direction and for the $MHgI_4$ compounds, with metallic bivalent ions (M^{2+}), the increasing is more emphasised on the "a" direction than on the "c" direction. These relationships are presented in figure 1.

This fact would prove that, at least for the presented cases, the ellipsoidal deformation of the metallic ion is possible in the presence of the HgI_4^{2-} anion field.

Considering the monovalent ions cases, the ellipsoidal has the large axis on the "a" direction and in the bivalent ions cases, the ellipsoidal has the large axis on the "c" direction. The spherical symmetry of the M^{n+} ions gets an ellipsoidal shape under the influence of the crystalline field. The d_{z^2} orbital is extended either on the "c" or on the "a" direction, same way with the increasing of the cellular unit parameter in "c" or "a" direction⁴.

CONCLUSIONS

The inorganic $CdHgI_4$ and Au_2HgI_4 combinations were synthesized.

The reticulate parameters and the crystalline systems of the Tl_2HgI_4 , $PbHgI_4$, $CdHgI_4$ and Au_2HgI_4 not known until now, were determined.

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