Crystalline forms of silver iodide II. Determination of phase transformations

MARIJA R. VUKIĆ[1*#], DRAGAN S. VESELINOVIĆ[2#] and VESNA G. MARKOVIĆ[3]

[1]*Institute "Kirilo Savić" a. d., Vojvode Stepe 51, 11000 Belgrade,*
[2]*Faculty of Physical Chemistry, Studentski trg 12, P.O.Box 550, 11000 Belgrade and*
[3]*ITNMS, Franchet d'Esperey Str. 86, 11000 Belgrade, Serbia*

Abstract: In order to obtain appropriate forms of AgI (β- and γ-), a procedure was developed to synthesize AgI at room temperature (23 °C), whereby samples of varying crystallographic purity and of varying crystallographic contents of the different forms were obtained. This paper presents the results of investigations of the influence of the manner of preparation of β-AgI and γ-AgI samples and the sample heating rate on the phase transformations and their temperatures. During the heating of non-ground, ground and pressed synthesized AgI samples, the phase transformations and the corresponding temperatures for one β-AgI and four γ-AgI samples with different β-AgI contents (representing a crystallographic impurity) were identified. The following phase transformations were observed for the non-ground AgI samples: β-AgI → α-AgI at 149.6 °C (for the β-AgI sample) and γ-AgI → α-AgI at 148.7 °C or 148.2 °C for the γ-AgI samples with a minimum content of β-AgI (less than 7 %), as a crystallographic impurity. The phase transition γ-AgI → α-AgI was irreversible because β-AgI was obtained whenever the samples were heated up to 260 °C. Manual sample grinding, as well as pressing at p_1 = 650 MPa and p_2 = 900 MPa resulted in the β-AgI → γ-AgI phase transition in all the investigated cases.

Keywords: silver iodide, heat treatment, mechanical treatment, phase transformation, DSC, X–ray diffractometry

INTRODUCTION

Silver iodide exists in three different crystalline phases.[1–4] According to literature data,[4] at ambient conditions, AgI usually exists as a two-phase mixture of the cubic zinc blende-structured γ-phase (F–43m, a = 6.495 Å, Z = 4)[5] and the hexagonal wurtzite-structured β-phase (P6₃mc, a = 4.592 Å, c = 7.510 Å, Z = 2).[6,7] At room temperature, the predominant phase is γ-AgI phase with the zinc-blende face-centered-cubic structure F–43m*,* although some β-AgI is also usually present with the wurtzite hexagonal structure P6₃mc.[8] β-AgI becomes the more stable phase above 384 K although the coexistence of the phases may still occur.[7]

Both phases transform to body-centered-cubic α-AgI at 420 K,[4,8,9] which is stable above this temperature and is the superionic phase.[10–12]

The literature reveals disagreement among authors about phase transformations of some forms AgI during heating. Parsonage and Staveley[13] consider that there is only one phase transition at a temperature of 147 °C in the course of heating or cooling, *i.e.*, β-AgI into α-AgI and, *vice versa*, α-AgI into β-AgI, respectively. The authors were of the opinion that a considerable segment of the phase transition is isothermal and that γ-AgI and β-AgI have lattices of very similar thickness and energy and transform into α-AgI at the same temperature (146 – 148 °C). Alpha silver iodide is stable only above 147 °C and transforms very quickly to the beta phase during cooling down to room temperature.[14,15] According to published data,[3] γ-AgI is thermodynamically stable at room temperature and pressure and up to 413 K and 588 MPa; β-AgI is formed above 413 K and pressures of 883 MPa.

It used to be considered that at approximately 410 K (137 °C), β-AgI form transforms into γ-AgI, but this phenomenon was questioned in the literature.[16] Perrott and Fletcher[17] claimed that this phase transformation was absent in samples deviating from stoichiometry by only 1 mol %. Transition temperatures given in the literature[18] are somewhat different and depend on the applied methods and preparation of the samples, which may affect the quality of the nature of the phase transition. Values for phase transformation given in the literature[19] are: β-AgI → α-AgI: $t = 147$°C and $\Delta H = 26.21$ J g^{-1}.

Hanaya *et al.*[20] observed a thermal anomaly in the DSC curves at around 150 °C during heating due to the phase transition from β/γ-AgI to α-AgI, as in the case of bulk crystalline AgI ($t = 147$ °C). However, the transition temperature from α-AgI to β/γ-AgI during cooling decreased remarkably with decreasing pore size from 50 to 10 nm.

Previous investigations defined the conditions for obtaining stable samples of γ-AgI with an as low percent as possible of the accompanying β-AgI and of β-AgI containing a low percent of γ-AgI.[21–23]

The goal of this study was to contribute to the solution of certain dilemmas of the type, number and temperature of the phase transformations occurring during heating and spontaneous cooling, and the effects of grinding/pressing the AgI samples.

<div align="center">EXPERIMENTAL</div>

Synthesis of AgI samples

The synthesis process of both crystallographic forms of AgI, and the employed apparatus were described in detail in earlier papers[22,23] and only the data of significance for this paper are presented here.

While adding the AgNO$_3$ solution into the KI solution,[24] the reaction of the chemical synthesis occurs in an excess of I$^-$ ions,[21-23] hence β-AgI (with a hexagonal structure) is the dominant crystal shape obtained in the sample. While adding the solution in the reverse order, the reaction occurs in an excess of Ag$^+$ ions and γ-AgI (with a cubic, face-centered structure) is obtained as the dominant crystal shape, with different amounts of β-AgI (from 3.3 to 16.0 %). The

percent of β-AgI in the γ-AgI depends on the addition rate and the ratio of the concentrations of the solutions, as well as on the method of drying the sample.[22,23]

All the procedures were performed almost in darkness, at room temperature under conditions (solution volume and concentration, and dropping rate) defined in previous papers.[22,23] The amounts of other crystal forms in the synthesized crystalline forms of AgI are given in Table I.

TABLE I. The amount of other crystal form in synthesized crystalline forms of AgI[22,23]

Crystalline form	No. of the sample	Amount of other crystal form, $I(I_{max})^{-1}$ / %
β-AgI	1	2.4 γ-AgI
γ-AgI	3	9.9 β-AgI
	4	10.2 β-AgI
	5	16.0 β-AgI
	6	15.6 β-AgI
	7	6.6 β-AgI
	8	3.2 β-AgI
	9	4.2 β-AgI

X–Ray diffraction analysis showed that rather pure crystallographic forms of silver iodide (the β-AgI had a crystallographic purity of 97.6 % and the γ-AgI samples between 84 % and 96.8 %), being simultaneously thermodynamically stable (over a certain time period),[22,23] were obtained by the developed synthesis procedures.

Methods

The aim of this study was to test the behavior of the synthesized samples of β-AgI and γ-AgI (before and after grinding) on heating from 0 °C to 260 °C and spontaneous cooling back to room temperature, in order to enable adequate conclusions on the thermal stability of such forms to be drawn. Also, the influence of grinding on the changes within the structures of these forms, namely on changes in the behavior at their phase transformations, was studied.

The influence of heating, grinding and pressing of the samples on the stated phenomenon was studied by the following methods: a) crystal powder diffraction (X–ray) and b) differential scanning calorimetry (DSC).

AgI crystal forms were identified by the X–ray diffraction method,[25-27] and the obtained results were compared with data published in JCPDS cards.[28] These investigations consisted of heating non-ground and ground synthesized to a desired temperature and analyzing the obtained diffractograms.

The most adequate method for structural analysis of crystals of polycrystalline samples is the crystal powder diffraction method. The distance between the level *d*, the parameter of the grid *a* in a cubic lattice (from the general technical term of Hull and Davey),[26] that is, the parameters *a* and *c* of a hexagonal lattice (for each pair of 2θ reflections), are given by well-known expressions. The mean values *a* and *c* were obtained from the previously calculated single values.

The investigations using the DSC method were performed by heating the synthesized samples (before and after grinding) within the 0–250 °C temperature interval, at heating rates of 1, 2 and 3 °C min^{-1}. Some of the samples were also monitored after the "heating–spontaneous cooling" process.

Apparatus

For testing the influence of heating and grinding of the AgI samples on the change of their structure and on the phase transformations, the following instruments were employed:

a) Philips APD 1700 Diffractometer with a PW 1820 vertical goniometer and a graphite mono-chromator, equipped with a computer system which provides direct value procurement for 2θ, *d* and I/I_0;

b) DSC (differential scanning calorimeter) V2. 2A Du Pont 9900.

X–Ray sample characterization was performed both with and without previous mechanical treatment of the samples using the following recording parameters:
   – Generator settings: 35 kV and 50 mA;
   – Cu–alpha 1, 2 wavelength: 1.54060 Å and 1.54439 Å;
   – Step size, sample time: 0.020 step, 0.50 s, 25.00 s per step;
   – Monochromator used: Yes;
   – Divergence slit: Constant (1 step);
   – Analysis program number: 40;
   – Peak angle range: (4.010 – 59.990) step;
   – Range in D spacing: (1.54083 – 22.0169) Å;
   – Cryst. peak width range: (0.00 – 2.00) step;
   – Minimum peak significance: 0.75.

The DSC instrument was employed for monitoring the heat flow during the heating of the non-ground and ground silver iodide samples, *i.e.*, for identifying the influence of grinding on their structural changes and phase transitions.

RESULTS AND DISCUSSION

The influence of heating rate on the phase transformations

The DSC curves shown in Fig. 1 were obtained by heating non-ground sample 1 (curve **a**) and ground sample 1 (curve b) at a heating rate of 2 °C min^{-1} (see part c).
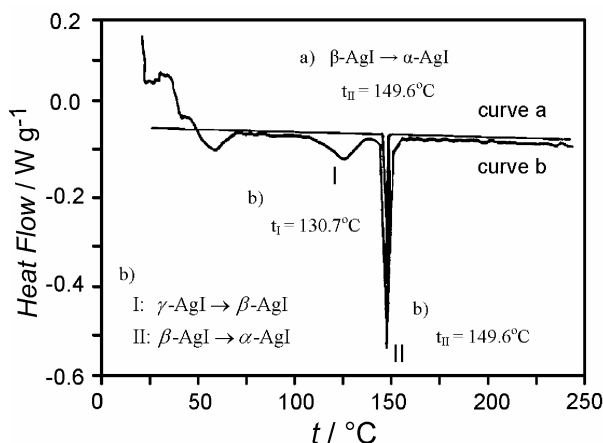

Fig. 1. DSC Curves of β-AgI (sample 1) recorded at a heating rate of 2 °C min^{-1}: a) non-ground synthesized powder (hexagonal structure) and b) after grinding (cubic, face-centered structure).

Figure 1 (curve a) shows the presence of only one phase transformation at a temperature of 149.6 °C (β-AgI → α-AgI) for sample 1 (with the maximum amount of 97.6 % β-AgI and 2.4 % γ-AgI, as a crystallographic impurity). This phase transformation temperature of 149.6 °C deviates from the values given in the literature.[13] This was the motivation to study the dependence of the phase transformation temperature on the sample heating rate (for sample 1, β-AgI). The results obtained for the thermal stability testing of β-AgI at different heating rates (1, 2 and 3 °C min^{-1}) are given in Table II.

From the results given in Table II, it is obvious that reducing the sample

heating rate (from 3 to 1 °C min^{-1}) lowered the values of the phase transition temperature (from 151.8 °C to 148.6 °C). This leads to the conclusion that this may be the reason for the different values of the phase transition temperature given in the literature.

TABLE II. Dependence of phase transformation (β-AgI → α-AgI) temperatures on rate of heating of non-pulverized sample 1[22,23]

Sample heating rate, v / °C min^{-1}	Phase transformation temperature t / °C
1.0	148.6
2.0	149.6
3.0	151.8

The influence of thermal treatment on the phase transformations

Determination of phase transitions temperatures was performed by differential scanning calorimeter (DSC) on non-ground samples 1 (β-AgI), and 3, 5, 7 and 9 (γ-AgI), at a heating rate of 2 °C min^{-1}. The curves obtained for samples 1, 3 and 9 are shown in Figs. 1,2 and 3 (curves a), while the corresponding data for the phase transition temperatures and other characteristics of the tested samples are given in Table III.
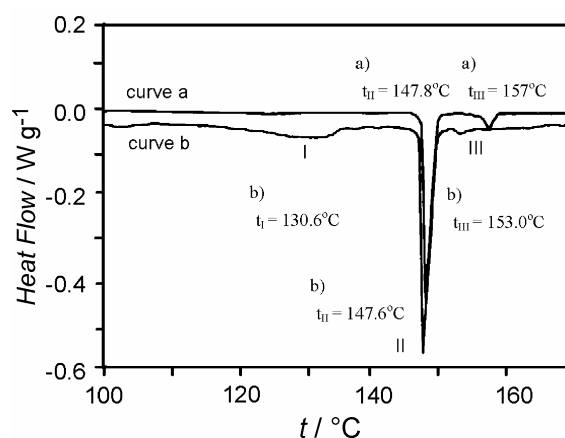

Fig. 2. DSC Curves of γ-AgI (sample 3); a) non-ground synthesized powder and b) after grinding.

The obtained results indicate that sample 1, with the maximum content β-AgI (97.6 %), exhibited only one phase transition at 149.6 °C over the whole range of investigated temperatures (from room temperature to 180 °C). For the samples 7 and 9, with the maximum content of γ-AgI and the minimum content of β-AgI (6.6 % and 4.2 %, respectively), a transition was observed at 148.7 °C, respectively 148.2 °C (over the same temperature range). However, with samples 3 and 5, which contained a larger percent of β-AgI (9.9 % and 16.0 %, respectively) compared with samples 7 and 9 (Tables I and III), two peaks appeared on the DSC

curves, as can be seen in Fig. 2 (curve a) for sample 3. The more expressed maximum were at 147.8 °C (sample 3, curve a in Fig. 2) and 148.5 °C (sample 5, curve a in Fig. 5), and the lower maximum were at 157.0 °C (sample 3, curve a in Fig. 2) and 154.1 °C (sample 5, curve a in Fig. 5).
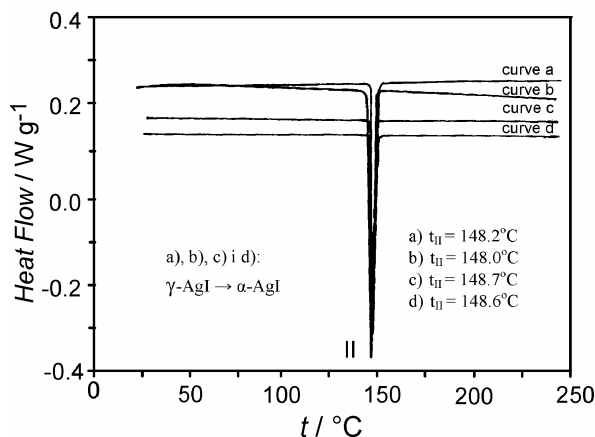

Fig. 3. DSC Curves of γ-AgI (sample 9); a) non-ground synthesized powder, b) after grinding, c) pressed at a pressure p_1 = 650 MPa and d) pressed at a pressure p_2 = 900 MPa.

TABLE III. Phase transformations and their temperatures* for adequate crystallographic forms** of AgI obtained from DSC method, without and after mechanical and heat treatment of samples (heating rate, v = 2 °C min^{-1})[22]

Sample No.	Crystallographic form before heating	Content of β-AgI %	Phase transformations during mechanical and heat treatment		
			γ-AgI → β-AgI	1) β-AgI → α-AgI 2) γ-AgI → α-AgI 3) β-AgI → M-AgI[e]	M-AgI[e] → α-AgI
			t_I / °C	t_{II} / °C	t_{III} / °C
1	β-AgI[a]	97.6	–	1) 149.6	–
	γ-AgI[b]	22.09	130.7	1) 149.6	–
3	γ-AgI[a]	9.9	125.0	3) 147.8	157.0
	γ-AgI[b]	36.59	130.6	3) 147.6	153.0
5	γ-AgI[a]	16.0	122.3	3) 148.5	154.1
	γ-AgI[b]	–	–	2) 148.6	–
7	γ-AgI[a]	6.6	–	2) 148.7	–
	γ-AgI[b]	–	–	2) 148.5	–
9	γ-AgI[a]	4.2	–	2) 148.2	–
	γ-AgI[b]	–	–	2) 148.0	–
	γ-AgI[c]	–	–	2) 148.7	–
	γ-AgI[d]	–	–	2) 148.6	–

[a]Non-pulverized; [b]pulverized; [c]pressed at a pressure p_1 = 650 MPa; [d]pressed at a pressure p_2 = 900 MPa; [e]M = α+β+γ (a mix of all three forms)

  * The temperatures of phase transformations correspond to the peak positions on obtained DSC diagrams.
** The crystalline form of samples at certain temperatures was defined by diffractographic method.

A series of X-ray diffraction patterns were therefore recorded at different temperatures, *i.e.*, at 23, 123, 140, 152 and 160 °C or 170 °C, as well as at 23 °C after cooling.

The presence of the different forms of AgI at these temperatures are given in Table IV for samples 1, 3, 5 and 9 and in Fig. 4 for sample 5 only.

TABLE IV. Phase compositions of synthesised AgI samples at different temperatures recorded on diffractograf[22]

Sample No.	Composition before heating	Composition						Composition after cooling to 23 °C
		t / °C						
		23	123	140	152	160	170	
1	β-AgI with 2.4 % γ-AgI	β*+γ	β*+γ	β*+γ	α*	α*	α*	β*+γ
3	γ-AgI with 9.9 % β-AgI	γ*+β	γ*+β	γ*+β	–	α*	–	β*+γ
5	γ-AgI with 16.0 % β-AgI	γ*+β	γ↓+β↑	β*+γ+α	α*	–	α*	β*+γ
9	γ-AgI with 4.2 % β-AgI	γ*+β	γ↓+β↑	β*+γ+α	M**	–	α*	β*+γ

* Prevailing structure; ↓ reduced content; ↑ increased content; ** M = β + γ + α (a mix of all three forms)

The diffraction patterns of sample 5 at five different temperatures are presented in Fig. 4. Pattern a was obtained at 23 °C and corresponds to the initial γ-AgI form with the maximum content of the accompanying β-AgI form (16.0 %), while pattern b obtained at 123 °C shows the presence of two forms of AgI (the dominant γ-AgI with an increased content of β-AgI). The patterns c and d, recorded at 140 °C and 152 °C, respectively, exhibit reflections showing the presence of all three forms of silver iodide (α, β and γ) in the samples at these temperatures, implying that a mixture of all three forms of the salt was obtained. At the temperature of 170 °C (pattern e), only α-AgI was present.

With sample 3 (γ-AgI with 9.9 % β-AgI), only was present at 152 °C and with sample 9 (γ-AgI with 4.2 % β-AgI), α-AgI was present at 160 °C. In the other cases, the other two forms (β-AgI and γ-AgI) were present, but their relative amounts at 123 °C was changed compared to those in the initial sample (obtained by means of synthesis). Such a situation was registered with samples containing greater amounts of the accompanying β-AgI form in mainly γ-AgI.

The obtained results show that the initial content of β or γ form of AgI in a mixture has an influence on the phase content and the phase transitions of AgI at the investigated temperatures.

It was concluded that the basic criteria for the explanation of such a phenomenon is the percent β-AgI, as a crystallographic impurity, in γ-AgI.[22,29] The conducted studies showed that samples of γ-AgI containing a higher percent of β-AgI (samples 3 and 5, with 9.9 – 16 % of β-AgI) underwent the phase transformation γ-AgI → β-AgI, whereas such a transformation did not occur to a significant extent in samples 7 and 9 (with a β-AgI content within the range 4.2 – 6.6 %). It is assumed that a higher content of β-AgI (> 7 %) in γ-AgI represents a "germ"

that, along with the heating process, causes an easier transformation of the γ form into the β form, resulting in such a transformation to occur in the temperature range from 122.3 °C to 125.0 °C (Table III). In our opinion, the content of β-AgI is relatively low (< 7 %) in the γ-AgI samples 7 and 9 and is not sufficient to act as a "germ" for the phase transition γ-AgI → β-AgI on heating. For this reason, only the direct phase transformation γ-AgI → α-AgI occurred at the temperatures 148.2 °C and 148.7 °C, respectively (Table III).
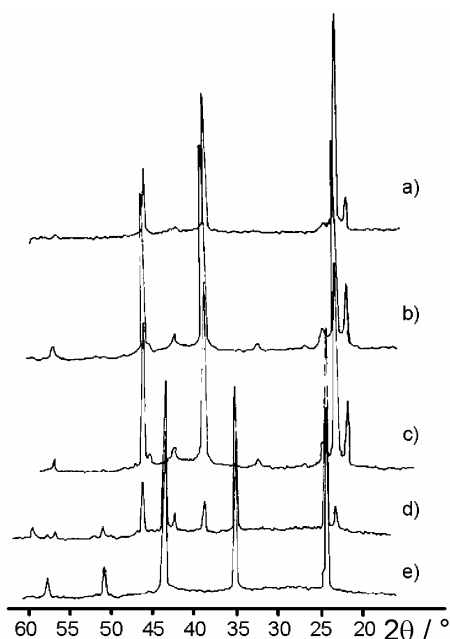

Fig. 4. X-Ray diffraction patterns of sample 5 (γ-AgI) obtained at different temperatures:
a) 23 °C – γ-AgI,
b) 123 °C – (γ+β)-AgI,
c) 140 °C – (γ+β+α)-AgI,
d) 152 °C – (γ+β+α)-AgI and
e) 170 °C – α-AgI.

It can be seen from the data in Table III, that the transition temperature at 149.6 °C (sample 1) corresponds to the phase transition β-AgI → α-AgI, and that the temperatures 148.7 °C and 148.2 °C (the mean temperature 148.5 °C) for the samples 7 and 9, respectively, correspond to phase transition γ-AgI → α-AgI. The literature data[19] for the transitions β-AgI → α-AgI and γ-AgI → α-AgI gives a value of 147 °C, which is near the values for experimentally obtained phase transitions of 147.8 °C for sample 3 (Table III). The more expressed maximum at 147.8 °C and 148.5 °C for samples 3 and 5, respectively, correspond to the phase transitions γ-AgI → (γ+β+α)-AgI, and the lower maximum at 157.0 °C and 154.1 °C, respectively, could probably correspond to the transitions (γ+β+α)-AgI → α-AgI because it was determined by X-ray diffraction analysis (Table IV) that all three forms of AgI were present at 152 °C. This also means that in the transition γ-AgI → β-AgI. This also confirms the previous assumption that the γ-AgI form is the metastable state of this salt. Simultaneously, the very small differences in the temperatures of phase transitions explain the facts that transition γ-AgI in β-AgI

is not clearly defined in the literature.[13,17] For these reasons, the less expressed peaks on the diagrams for samples 3 (Fig. 2, curve a) and 5 may not be the result of a new phase transition but also the result of other processes during the larger representation of β, γ and α form AgI.

The influence of sample treatment on phase transition temperature is in accordance with literature data,[20] *i.e.,* on the crystallite size. In all cases, as was already stated in previous papers,[22,23] after spontaneous cooling of the heated samples to 23 °C, β form AgI was obtained, which indicates that the transition γ-AgI → β-AgI is irreversible, namely that γ-AgI is a metastable state of this compound. This is an additional reason for the greater stability of β-AgI. Thus, the previous statements[13] that only one phase transition exists in case of β-AgI (β-AgI → α-AgI) were confirmed.

It was also proved that in neither case does the phase transition β-AgI → γ-AgI appear, which has also been discuss by other authors.[16]

The influence of the manual pulverization on phase transformation

The influence of grinding of β-AgI and γ-AgI on the appearance of the different phase transitions was also studied in this work.

The effects of grinding on the phase transitions was followed by the DSC method (heating from 0 to 250 °C at a heating rate of 2 °C min^{-1}), for sample 1 (β-AgI) and samples 3, 5, 7 and 9 (γ-AgI).

DSC Curve with one phase transition (β-AgI → α-AgI) was obtained heating non-ground sample 1, which was proved by X-ray diffraction analysis to have a hexagonal structure (β-AgI) after synthesis (Fig. 1, curve a).

The structure of the sample was changed to γ-AgI by manual grinding of the sample 1 (β-AgI) in an agate mortar and by repeated recording of the DSC curves over the temperature interval from 0 to 250 °C, whereby a change of the phase transformations occurred. In this case, the DSC curve exhibited two phase transitions, *i.e.,* γ-AgI → β-AgI and β-AgI → α-AgI, at the temperatures of 130.7 °C and 149.6 °C, respectively, which is illustrated in Fig. 1 by curve b. Thus, the X-ray diffraction results of the influence of grinding β-AgI on the structural change were also confirmed by DSC.

The samples 3, 5, 7 and 9 (γ-AgI, containing the amounts of β-AgI given in Table I) were treated in the same way as the sample 1 (β-AgI).

No change of the structure of the dominant γ-form into the β-form was observed with samples 7 and 9 (containing 6.6 % and 4.2 % of β-AgI, respectively), but a reduction of the amount of β-AgI (due to already discussed influence of grinding on the structural change of β-AgI) was registered. Hence, after mechanical treatment of these samples, DSC curves with only one peak, corresponding to the phase transition γ-AgI → α-AgI, were obtained. This is illustrated in Fig. 3 by curves a and b using sample 9 as an example. Using the results of previous

studies,[22,29] and the demonstrated influence of the amount of β-AgI, as a crystallographic impurity in the dominating γ-AgI form, it can be concluded that grinding does not influence the phase transitions if the content of β-AgI is less than 7 %.

The DSC curves for samples 3 and 5 (containing 9.9 % and 16.0 % of β-AgI, respectively) with two or three phase transitions were obtained for the ground and non-ground samples[22,29](Figs. 2 and 5).
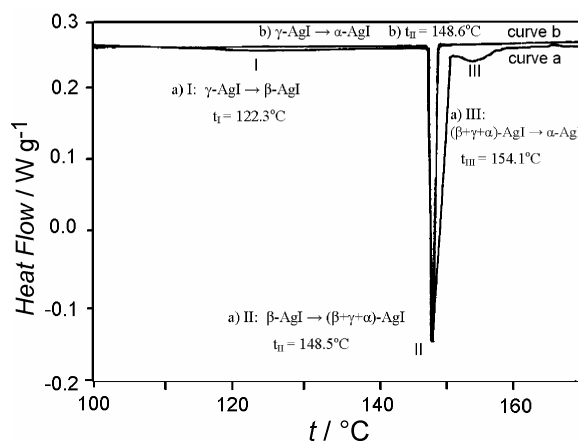

Fig. 5. DSC Curves of γ-AgI (sample 5); a) non-ground synthesized powder
(curve a) and b) after grinding (curve b).

In a previous study,[22] the influence of larger amounts of β-AgI, shown to be an impurity in the dominating γ-AgI, on the appearance of the two or three transitions during the thermal treatment of non-ground samples was investigated. X-Ray diffraction analysis (Fig. 4, Tables III and IV) showed that the three peaks on the DSC curve (Fig. 5, curve a) for non-ground sample 5 correspond to the phase transitions γ-AgI → β-AgI (at t_I = 122.3 °C), β-AgI → (β+γ+α)-AgI (at t_{II} = 148.5 °C) and (β+γ+α)-AgI → α-AgI (at t_{III} = 154.1 °C). Grinding of this sample in an agate mortar caused the already discussed change of β-AgI into γ-AgI, which lead to the reduction of the content of this form in the dominating form γ-AgI and the elimination of the so-called "germ", which resulted in the appearance of only the one-phase transition γ-AgI → β-AgI (at t_I) and (β+γ+α)-AgI → α-AgI (at t_{III}). For this reason, after grinding and heating of sample 5 (from 0 to 250 °C), the peaks I and III were absent on the DSC curve (Fig. 2, curve b), which means that the grinding of γ-AgI containing more than 7 % β-AgI has an influence on the phase transitions. The final result of grinding in this case is the complete absence of the phase transition γ-AgI → β-AgI, so that the immediate phase transition γ-AgI → α-AgI developed.

An interesting phenomenon was registered with sample 3 (γ-AgI containing 9.9 % of β-AgI). On the DSC curve of the non-ground sample (Fig. 2 curve a),

two peaks at 147.8 and 157.0 °C corresponding to the phase transitions β-AgI → (β+γ+α)-AgI and (β+γ+α)-AgI → α-AgI, respectively, are clearly manifested. After the sample had been ground, a peak corresponding to the phase transition γ-AgI → β-AgI appeared at 130.6 °C, whereas the peak at 153.0 °C almost completely disappeared (curve b, Fig. 2). Considering the previously established influence of mechanical grinding on the structural change of β-AgI into γ-AgI, a decrease of the amount of β-AgI in the dominantly γ-AgI sample would also have occurred in this case after grinding. However, quantitative X-ray diffraction analysis showed that the content of β-AgI in the dominant γ-AgI had increased from 9.9 to 16.5 % after grinding. This result was evidenced for sample 3 only.

After having analyzed all the results, the conclusion was reached that the peak at 153 °C corresponds to a sample structure which is a combination of all three crystallographic forms (γ+β+α)-AgI. Only after heating above 160 °C is the α-AgI form obtained (BCC).

The influence of the pressure on the structure and phase transitions

The influence of pressing on the structure and the phase transitions was studied with the sample 9 (γ-AgI, with 4.2 % of β-AgI). The experiment consisted of pressing the sample at two different pressures (p_1 = 650 MPa and p_2 = 900 MPa). X-Ray diffraction analysis showed that in this case a transformation of β-AgI into γ-AgI occurs, resulting in a reduction of amount of β-AgI in the dominating γ-AgI, but that there is no influence on the phase transition γ-AgI → α-AgI (which was present with the as synthesized sample, without the influence of the mechanical treatment or the increased pressure). Considering that this sample contained a small amount of β-AgI (smaller than 7 %), only one peak for the phase transition γ-AgI → α-AgI (Fig. 3, curves c and d) were observed on the DSC curves, practically at the same temperature as for the non-ground ground samples (Fig. 3, curve a and b, respectively).

It is assumed that β-AgI was transformed under pressure into cubic γ-AgI and, hence, the peak for the phase transformation γ-AgI → β-AgI was completely absent direct transformation of γ-AgI into α-AgI occurred.

ИЗВОД

КРИСТАЛОГРАФСКИ ОБЛИЦИ СРЕБРО ЈОДИДА II.
ОДРЕЂИВАЊЕ ФАЗНИХ ПРЕЛАЗА

МАРИЈА Р. ВУКИЋ[1], ДРАГАН С. ВЕСЕЛИНОВИЋ[2] и ВЕСНА Г. МАРКОВИЋ[3]

[1]Иститӯт “Кирило Савић”д.д., Војводе Сте̄пе 51, 11000 Беоīрад, [2]Факултет за физичку хемију, Студентски тр̄ī 12, 11000 Беоīрад и [3]ИТНМС, Франше Депереа 86, 11000 Беоīрад

У циљу добијања одговарајућих облика сребро јодида (β-AgI и γ-AgI) развијене су методе њихове синтезе на собној температури од 23 °C, при чему су добијени узорци различите кристалографске чистоће и састава. У овом раду су приказани резултати испитивања утицаја начина припреме и брзине загревања узорака β-AgI и γ-AgI на фазне прелазе и

њихове температуре. При загревању неспрашених, спрашених и пресованих испитиваних син-тетизованих узорака AgI идентификовани су фазни прелази и њихове температуре за један узорак β-AgI и четири узорка γ-AgI са различитим садржајем β-AgI у себи (као криста-лографске нечистоће). Евидентирани су следећи фазни прелази за неспрашене узорке AgI: β-AgI → α-AgI на 149,6 °C и γ-AgI → α-AgI на 148,7 °C односно 148,2°C за узорке γ-AgI са минималним садржајем β-AgI (до 7 %), као кристалографске нечистоће. Прелаз γ-AgI → α-AgI је иреверзибилан, јер се при хлађењу узорака, загрејаних до 260 °C, добија увек β-AgI. Ручно спрашивање узорака, као и пресовање на $p_1 = 650$ MPa и $p_2 = 900$ MPa, доводи до фазног прелаза β-AgI → γ-AgI у свим испитиваним случајевима.

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