

# Thermal and Mechanochemical Initiated Phase Transformations in Silver Carboxylates

B. B. Bokhonov,<sup>\*</sup> A. A. Sidelnikov, M. R. Sharafutdinov, and B. P. Tolochko,

*Institute of Solid State Chemistry SB RAS, Novosibirsk, Russia*

L. P. Burleva and D. R. Whitcomb<sup>▲</sup>

*Eastman Kodak Company, Oakdale, Minnesota, USA*

Small-angle X-ray scattering, electron and optical microscopy, and thermal analytical investigation of the structure and morphology changes in silver laurate, myristate, palmitate, and stearate show that these fatty acid silver salts undergo an irreversible Martensitic phase change in the 110 – 120°C temperature range. This phase change is characterized by the formation of a more symmetrical phase, compared to the initial crystalline silver carboxylate. The formation of the high temperature phase proceeds according to a Martensitic transition mechanism, which is a diffusionless transformation by a large number of atoms in a cooperative movement. An ordered orientation is observed that separates Martensitic layers in the matrix of the initial crystalline silver carboxylate. Along with this first phase transition, a micro-twin structure on the basal plane of the crystal is formed. Increasing the temperature above 120°C leads to a decrease in the distance between silver layers in the high temperature phase structure, which is a result of the disordering of the carbon chains of the molecule.

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## Introduction

Silver carboxylates of the general formula  $[\text{Ag}(\text{O}_2\text{C}_n\text{H}_{2n-1})_2]$ , where  $n = 12 - 22$ , are one of the basic components in thermographic and photothermographic (PTG) materials that provide the source of silver ions in the thermal development process.<sup>1,2</sup> Despite the large amount of work reported on the investigation of the properties of photothermographic materials and the individual components included in this material, questions remain open regarding the effect of the phase transformations originating in the silver carboxylates in the heating process.<sup>1</sup> It is known that the temperature of the first phase transition for long-chain silver carboxylates lie in the 110 – 120°C range,<sup>3,4</sup> and it is in this temperature interval that the thermal development process of photothermographic materials is carried out.

X-ray investigations of silver carboxylates with 2 to 22 carbon atoms have shown that they all belong to the triclinic crystal class<sup>5,6</sup> and contain two molecules in a unit cell. Among the basic properties of the silver carboxylate crystal structure is the characteristic, significant anisotropy in the physical and chemical properties. This anisotropy can be directly attributed to the layered structure in which two layers of silver ions are sepa-

rated by two layers of long methylene chains. A refinement of the structure of silver stearate shows that the silver molecules are composed of dimers,  $[\text{Ag}(\text{O}_2\text{C}_n\text{H}_{2n-1})_2]$ .<sup>7</sup> However, there is now contradictory information in the literature regarding the tilt angles of long hydrocarbon ends of the molecule in the silver ion plane (*ab*). According to one model, the hydrocarbon chain is 90°,<sup>7</sup> and according to other models, the long hydrocarbon axis of the molecular (*ab*) plane is 70–80°.<sup>5</sup>

Thermal analysis and NMR data on the phase transitions in silver carboxylates have been reported.<sup>3</sup> Based on that data, the temperatures of the phase transitions were determined for various silver carboxylates. It was shown that the silver carboxylate transition from the crystalline state to the isotropic liquid state undergoes 6 or 7 phase transformations. As a rule, these phase transitions follow the sequence: crystalline state (curd); super curd (SUC); sub-waxy (SW mesomorphic state); waxy (W); super waxy (SUW); sub-neat (SN); neat (N); and liquid state (IL isotropic liquid). It should be noted that the phase transition from the crystalline state to the super-curd (SUC) or sub-waxy phase (SW mesomorphic state) in silver carboxylates occurs in the region of 100 – 120°C. Accordingly, the paraffin chain is in motion in the sub-waxy mesomorphic state.<sup>3</sup>

In other work,<sup>8,9</sup> the X-ray, calorimetric, and IR data were obtained during the investigation of the structure changes in the silver stearate crystalline lattice. It was shown that the silver stearate transformations proceed through a series of mesomorphic states on heating. The first phase transition appears at 122°C and is related to disorder in the packing of the aliphatic chain, which is

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▲ IS&T Member

\* Corresponding Author; e-mail: bokhonov@solid.nsk.su

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apparent by the significant decrease in the distance between silver ion layers. Increasing the temperature above 130°C leads to gradual disordering and breakup of the silver ion layer and is responsible for the onset of the thermal decomposition reaction of the silver stearate.

The structural transformation of polycrystalline silver behenate during the *in situ* heating process in the X-ray diffractometer has also been reported.<sup>10</sup> In contrast to the previous work,<sup>8,9</sup> where the process of heating silver stearate was accompanied by a decreasing interlayer spacing, these authors<sup>10</sup> observed that the heated silver behenate crystals increased its interlayer spacing. In this report, heating the silver behenate to 120°C leads to an irreversible transition from the crystalline to an amorphous state. Further, at 138–142°C the first phase transition is observed, as indicated by the appearance of a diffraction peak with a smaller Bragg 2θ angle, which corresponds to an increase of interlayer spacing in the silver behenate. Heating the silver behenate crystals above 145°C results in a phase transition into the liquid crystalline state (smectic A). The formation of the metallic state occurs at 180°C. The authors further propose that the initial stages of heating are accompanied by disorder in the aliphatic chain of the silver behenate. However, despite the analogy to the described structural changes originating in the silver behenate<sup>10</sup> and silver stearate,<sup>8,9</sup> both show significant decomposition in the sequence of structure changes and phase transformations. Therefore, heating silver stearate is accompanied by a sharp decrease in the interlayer spacing,<sup>8,9</sup> but heating silver behenate crystals after proceeding through amorphous structures, is reported to result in an increased interlayer spacing.<sup>10</sup> The contradiction between the silver behenate and silver stearate crystals on heating is surprising because the silver behenate and silver stearate structures are so similar that the thermal phase changes should lead to similar physical and chemical effects.

In addition, a new report labeling the thermally induced formation of silver behenate phases from type I (less than 130°C) to type II (130–156°C) to type III (156–180°C) has appeared.<sup>11</sup> Those phases reportedly can be stabilized and remain observable at room temperature if certain compounds, such as glutaric acid, benzo[e][1,3]-oxazine-2,4-dione, phthalazinone, and polyvinyl butyral, were added to the formulation. Phase II was shown to be consistent with a smectic A composition, but neither of the high temperature phases were further characterized structurally.

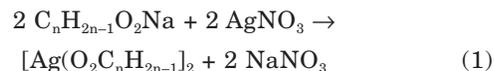
Another question becomes relevant with regard to possible changes in the silver carboxylate structure that occur prior to the heating process, during the preparation of the photothermographic formulation. Preparation of these materials includes homogenizing mixtures of components that are added to the PTG formulation. For example, some photothermographic dispersions are prepared with mechanical processing in a ball mill for three hours.<sup>12</sup> However, mechanical effects on the component purity of mixtures of organic and/or inorganic materials have been reported to initiate changes in their structures as well as to enhance additional reactivity.<sup>13,14</sup> The main cause of changes of this sort is the formation of various types of point and extended defects in the material. The following changes were noted to occur in mechanical activation of organic compounds: molecular crystals became more amorphous and exhibited polymorphic transitions; the formation of more disorganized structures and conformational transformations occurred;

breaking of C–C bonds, formation of radicals, and breakup of weak intermolecular interactions also occurred; and polymerization reactions initiated.<sup>13,14</sup> Unfortunately, despite the commercial importance of mechanical dispersion, there is no data in the literature regarding the structural changes that may be occurring in silver carboxylates as the result of mechanical processing.

In this work, we have tried to make up for the lack of experimental data regarding the thermal and mechanical initiation of phase changes in silver carboxylates. The solution to this problem may be accomplished with a comparative investigation of the thermal and mechanical effects on a series of silver carboxylates with various aliphatic chain lengths. Such a systematic investigation enables the general mechanism to be established and resolves literature conflicts regarding the structural transformations observed in the silver carboxylates during heating and mechanical processes.

## Experimental

The synthesis of silver carboxylates (laurate, myristate, palmitate, and stearate) was carried out by the general reaction between sodium salts of the corresponding acid and silver ion:



The sodium carboxylates were prepared by mixing 0.01 M aqueous emulsion of the organic acid with an equimolar amount of NaOH solution. The temperature of the solution was typically 5°C higher than the melting point of the corresponding acid. Next, the temperature of the solution was lowered to ~50°C and the silver nitrate solution was added. The crystalline precipitate was filtered, washed with water and ethanol, and air dried. Single crystals of silver stearate were grown by slow cooling of a saturated (from 50°C) ethanol-pyridine solution of the silver carboxylate as described in the literature.<sup>15</sup>

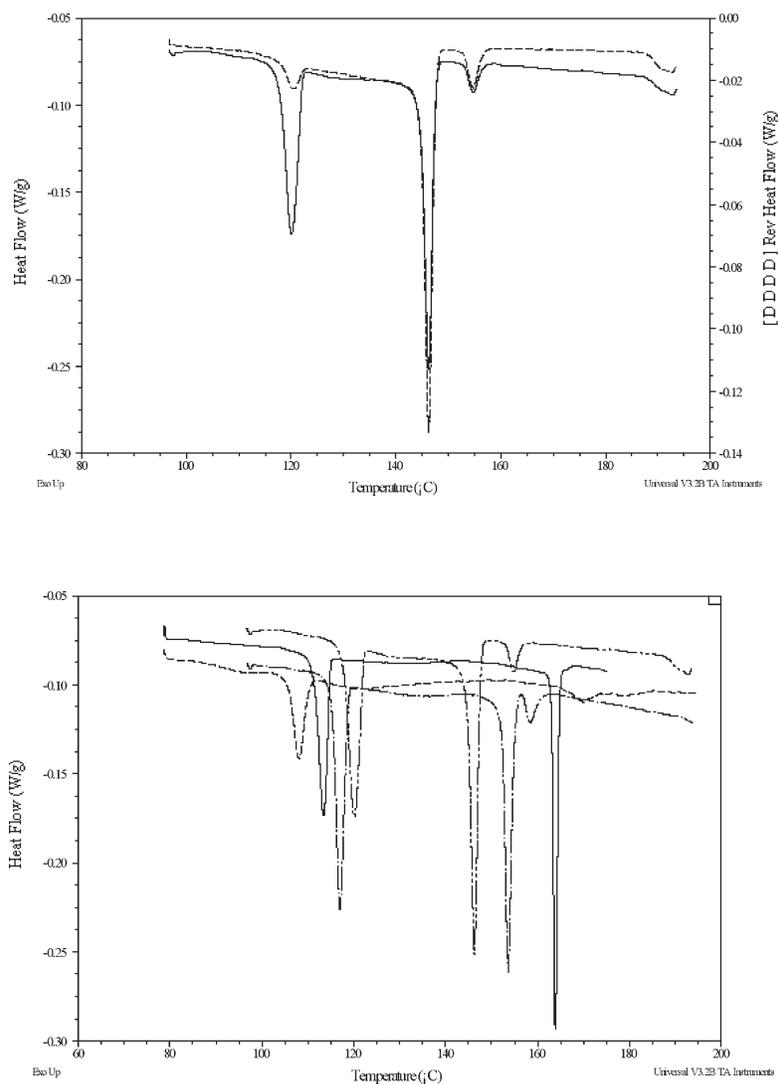
Optical microscopy investigations were carried out in polarized light with a polarizing-interference microscope BIONAR. Heating samples were carried out in a special thermally stabilized vessel. For improved thermal contact, the single crystals were immersed in silicone oil. The precision of the thermal measurements was ±2°C.

Electron microscope investigations were carried out with a JEM-2000FX II electron microscope with 200 KV acceleration voltage. In order to prevent heating of the polycrystalline carboxylate, samples were placed in a special cooling sample holder, EM-SCH3.

Mechanochemical activation (without solvent) of silver carboxylates was carried out in a centrifuging planetary mill, AGO-3, in a steel cylinder with steel balls (0.5 cm) with a 20 g acceleration. The sample-to-ball-mass ratio was 1:5.

Diffraction measurements were carried out at the synchrotron radiation diffractometer at the VEPP-3 storage ring (Novosibirsk, Russia). The silver carboxylate samples were placed in the diffractometer in a high temperature chamber. The diffraction patterns were continuously recorded in transmission mode with a position-sensitive detector, OD-3.3, in the 2θ region of 0 – 20°, heating from 20 – 175°C.

Modulated differential scanning calorimetry (MDSC) was carried out with a TA Instruments 2920 MDSC under nitrogen flow. The heating rate was 0.50°C/min,



**Figure 1.** DSC of  $\text{AgC}_{18}$  (heating and cooling), top, DSC of  $\text{AgC}_{12}$ - $\text{AgC}_{18}$ , dash, solid, dash-dot, dash-dot-dot, respectively, bottom.

**TABLE I. Phase Transition Peak Temperatures**

Silver carboxylate	Peak 1	% Reversible	Peak 2	% Reversible
$[\text{C}_{12}\text{H}_{23}\text{O}_2\text{Ag}]_2$	108.1 <sup>a</sup>	1	169.9	58
$[\text{C}_{14}\text{H}_{27}\text{O}_2\text{Ag}]_2$	113.4	3	163.9	72
$[\text{C}_{16}\text{H}_{31}\text{O}_2\text{Ag}]_2$	117.1	5	153.6	71
$[\text{C}_{18}\text{H}_{35}\text{O}_2\text{Ag}]_2$	120.1	7	146.4	69

<sup>a</sup> small peak at 99.6°C also observed

modulated 0.08°C every 60 sec, which ensured 4 – 5 full cycles during each phase transition.

## Results

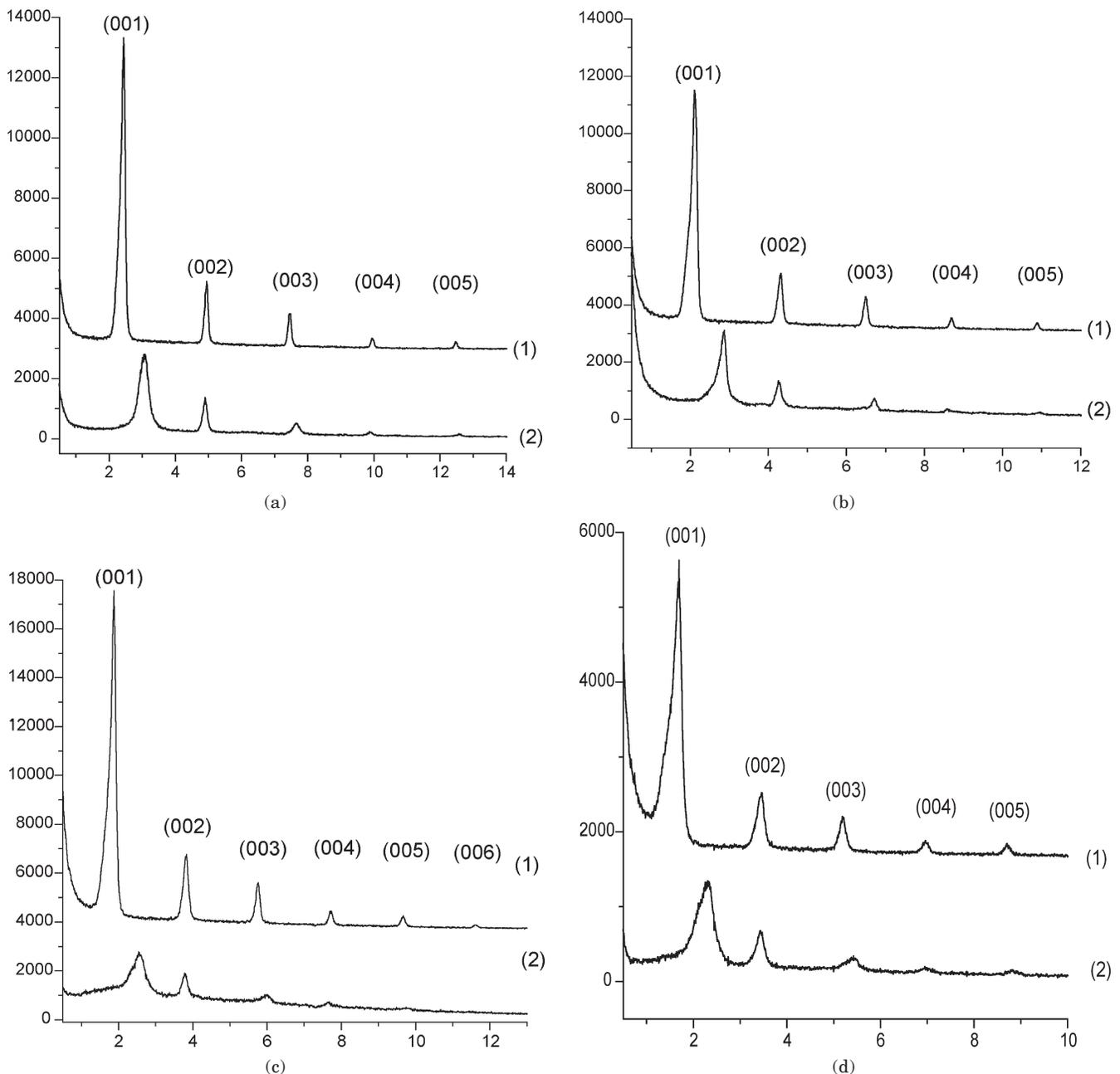
### *Phase Transitions in Silver Laurate, Myristate, Palmitate, and Stearate. The Effect of Preheating and Mechanical Activation on the Phase Transformation*

An example of the typical MDSC thermograms of the silver carboxylates is given for silver stearate in Fig. 1, which shows the thermally reversible component of the

phase changes. The phase transition temperatures of the investigated silver carboxylates from 20 – 175°C are given in Table I. Keeping in mind that some differences can be expected depending on the silver soap preparation conditions,<sup>1</sup> the phase transition temperatures observed are in general agreement with those reported in the literature.<sup>4</sup>

According to the terminology adopted in Ref. 3, the first phase transition is related to the transformation of the crystalline silver carboxylate in the mesomorphic, sub-waxy (SW) phase.

Our investigations showed that preheating and mechanical processing of silver carboxylates results in the same change in the thermodynamic characteristics; so, in all cases, heating silver myristate, palmitate, and stearate to 175°C leads to a nearly complete loss of the first phase transition. Analogous changes in the loss of the first phase transition are observed after short mechanical activation of these silver carboxylates (up to 5 min of activation). However, the endothermic phase changes at the higher temperatures still occur.



**Figure 2.** X-ray of patterns (relative intensity versus  $2\theta$ ); (a)  $\text{AgC}_{12}$ ; (b)  $\text{AgC}_{14}$ ; (c)  $\text{AgC}_{16}$ ; (d)  $\text{AgC}_{18}$ ; (pre- and post-heating), left to right, top to bottom.

***X-Ray Investigation of the Structural Changes of Silver Laurate, Myristate, Palmitate, and Stearate After Heating and Mechanical Activation***

The interplanar distance calculated from the X-ray data of the initial polycrystalline samples of silver laurate, myristate, palmitate, and stearate are in good agreement with previously reported data.<sup>8</sup> However, it is clear that the peak shapes of the diffraction lines for carboxylates at small angles, characteristic of the (001) layer reflection, are asymmetric (Fig. 2 a-d). The longer the chain length, the larger the asymmetry.

Preliminary heating of samples of silver carboxylates to 150°C or mechanical activation (processing time up to 5 min) leads to a decreasing intensity of all reflections (Fig. 2 (a)-(d)). Diffraction reflections in the small-angle region, characteristic of the distance between the

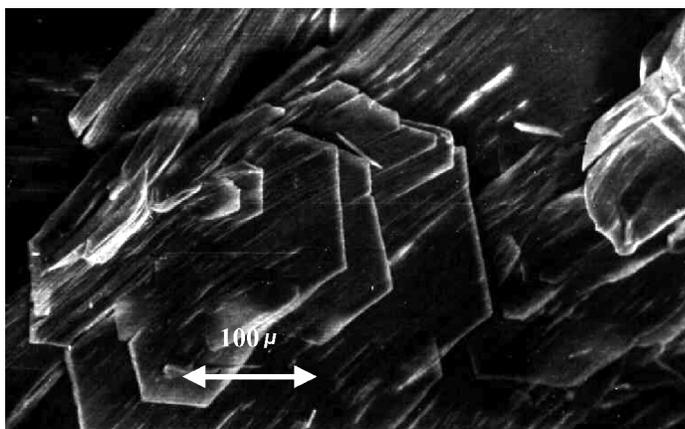
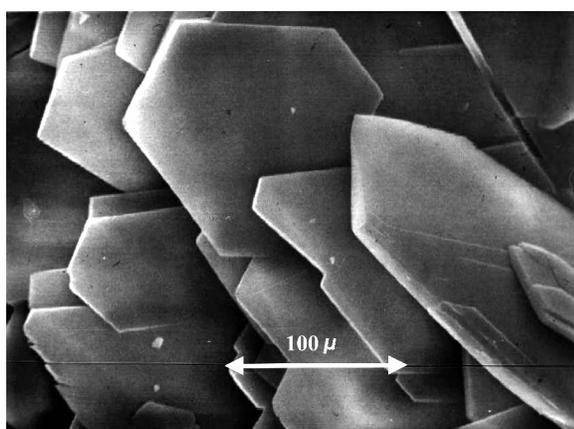
silver layers in the silver carboxylate structure, become more symmetric. It should be noted that the diffraction lines, the (001) indices, after first heating (mechanical activation) are not uniformly shifted and indicate the complexity of the changes in the structures of the silver carboxylates. The diffraction lines in the  $2\theta > 20^\circ$  angle range are significantly broadened, and some are completely gone.

***In-Situ Optical-Microscope Investigation of Silver Carboxylate First phase Transitions During the Heating Process***

The optical microscope investigation of the phase transformations in single crystals of silver stearate showed that the phase transition temperature from the crystalline state to the first high temperature phase is



**Figure 3.** Optical micrograph of silver stearate single crystal during the first phase transition.



**Figure 4.** SEM micrograph of (a) initial silver stearate crystal, left and (b) after the first phase transition, right.

in good agreement with the data obtained by the DTA experiments. A periodic formation and rapid growth of a new lamellar phase at the basal plane (001) of single silver carboxylate crystals is observed, which is oriented relative to the crystallographic axis of the initial crystal (Fig. 3). Taking into account the data in Ref. 15, in which the habit of a silver laurate single crystal was determined, we observe that growth of the first high temperature phase occurs in the [010] direction. In the process of phase transformation to the high temperature phase, a double reflection is observed that is characteristic of a regularity present in the structure of the forming phase. Cooling the high temperature phase to below the temperature of the phase transition does not result in the re-appearance of the initial crystalline phase, which confirms the irreversibility of the phase transition. It should be further noted that the phase transition is accompanied by a change in the physical length of the silver stearate single crystal; a significant increase in the crystal size in the direction perpendicular to the direction of the crystal growth of the new plate-like phase is observed.

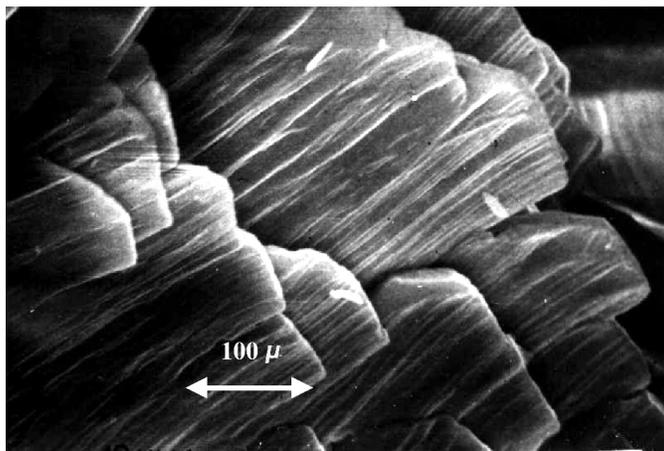
It is clear that the unique morphology of the observed phase transition has all the appearances of a Martensitic transformation.<sup>16</sup> The Martensitic transformation pro-

cess normally leads to the formation of a phase having higher symmetry relative to the starting phase.

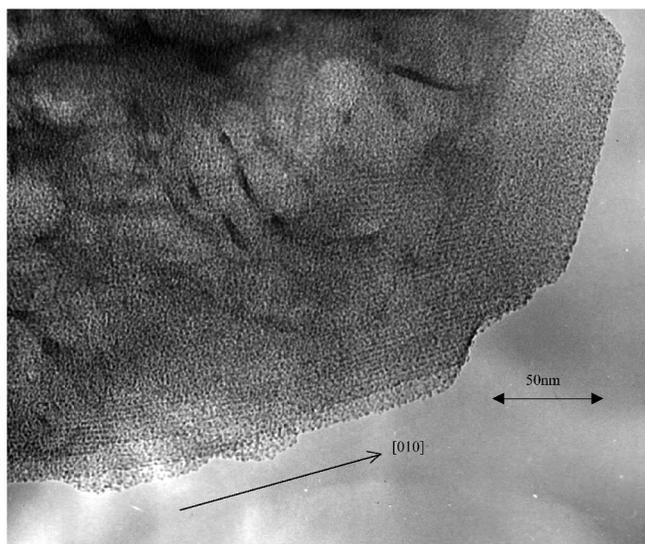
#### ***SEM and TEM Investigation of the Morphology Changes of Silver Stearate Single Crystals During Heating***

The results of the electron micrographic investigation of silver stearate single crystals annealed at 120 – 125°C revealed that the initial heating leads to the formation of a disordered spacing of the fractured basal plane (001) of the single crystals – the fractures are arranged in the direction parallel to the [010] axis of the single crystal. The formation of these fractures in all the single crystals is the same (Fig. 4). Increasing the temperature higher than the second phase transition (154°C) leads to deformation of the single crystals and the appearance of contours on the surface (Fig. 5).

The TEM investigation of the polycrystalline silver carboxylates, first heated to a temperature above the first phase transition, showed formation of an ordered twin boundary on the base plane of the silver carboxylate crystals, precisely orientated relative to the crystallographic axis of the initial silver carboxylate crystal (Fig. 6). It is known that the appearance of an ordered twin boundary is a characteristic indication of the Mar-



**Figure 5.** SEM of silver stearate single crystals after the second phase transition.



**Figure 6.** TEM of silver carboxylate after heating to 135°C.

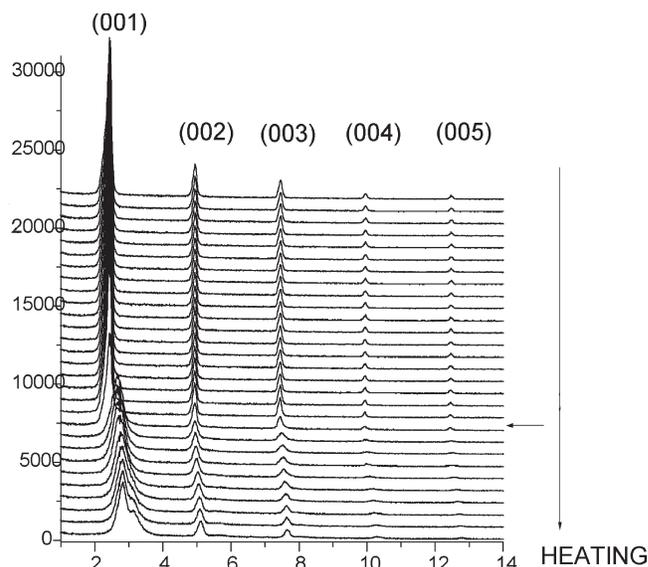
tensitic transition.<sup>16</sup> The twinning parameters of the high temperature phases are 37 Å for silver stearate and 25 Å for silver laurate, and correlate with the long aliphatic chain of the silver carboxylate.

#### ***In-Situ SAXS Investigation of the Structural Transitions of Silver Carboxylates via Synchrotron Radiation***

The in situ X-ray diffraction study of the phase transitions of silver carboxylates during heating showed that, despite some specific features for all the silver carboxylates, similar types of changes occur in the diffraction patterns. The fundamental changes in the spectra of the small angle scattering for various silver carboxylates are discussed below.

#### **Structure Changes in Silver Laurate Phase Transformations**

The in situ SAXS investigation showed that the heating process of silver laurate to 102°C did not produce any significant change in the intensity or position of the diffraction maxima (Fig. 2(a) and Fig. 7). Raising the temperature above 102°C creates a noticeable broaden-

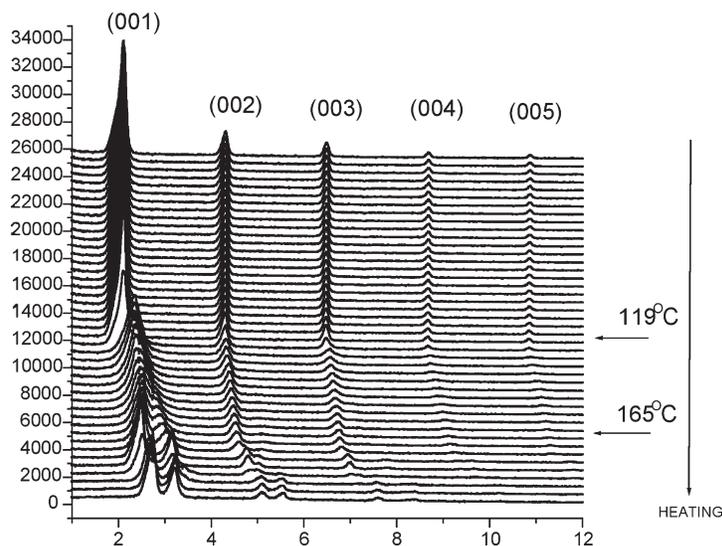


**Figure 7.** SAXS pattern, relative intensity versus  $2\theta$ , of  $\text{AgC}_{12}$  changes during heating. The arrow indicates 120°C.

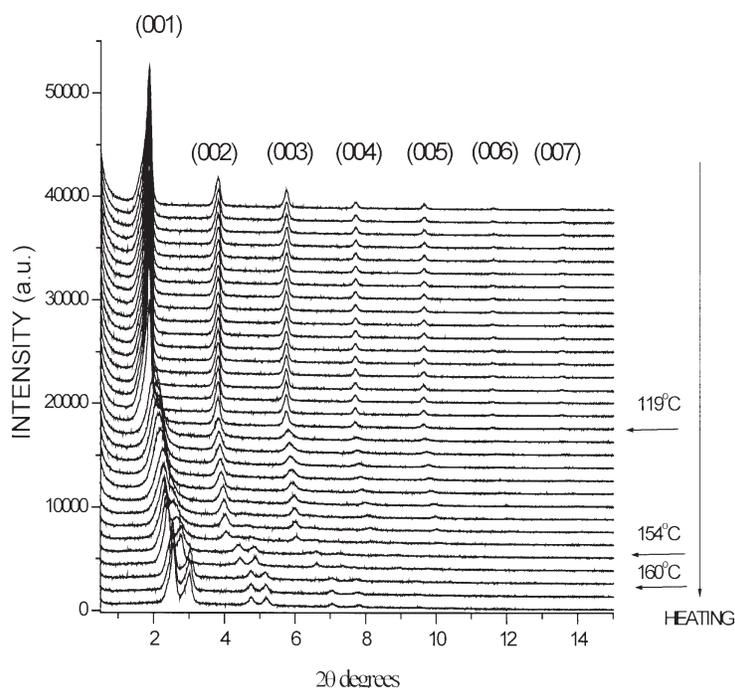
ing of the (001) diffraction reflection, a shift of this reflection to higher angles, and a decrease in its intensity. It should be noted that at this temperature, the remaining layer reflections show no change in their position, and they exhibit only a broadening and decreasing intensity. Subsequent heating of the polycrystalline silver laurate to 110°C leads to a synchronous shift of all the layer reflections in the high diffraction angle region. Simultaneously, an additional diffraction reflection with a small interplanar distance is observed in silver laurate. Increasing the temperature above 110°C leads to an increase in the observed reflection intensity, but the remaining layer reflections, except for the (003) reflection, remain unchanged in position and intensity, once again shifted to the small angle region. A stable diffraction picture is observed, unchanging either on heating to 140°C or on cooling to room temperature.

#### **Structure Changes In Silver Myristate Phase Transformations**

The structural changes in silver myristate in the 20 – 170°C range are even more complicated than in the silver laurate. This could be the result of a larger number



**Figure 8.** SAXS pattern, relative intensity versus  $2\theta$ , of  $\text{AgC}_{14}$  changes during heating.



**Figure 9.** SAXS pattern, relative intensity versus  $2\theta$ , of  $\text{AgC}_{16}$  changes during heating.

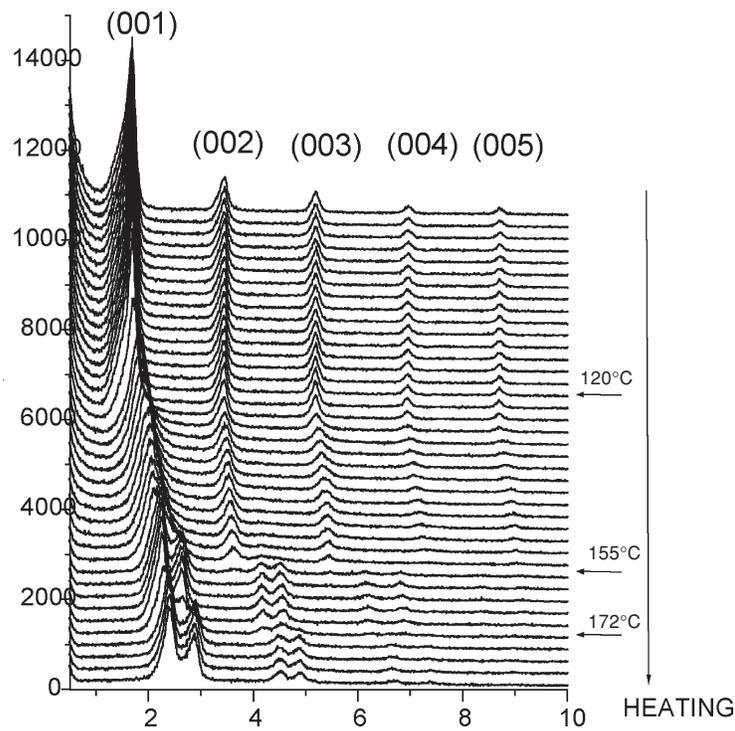
of phase transformations in this temperature range than for silver laurate. Nevertheless, the initial stages of all of these changes and the first phase transition in silver laurate and myristate are accompanied by similar changes in the SAXS.

Therefore, heating silver myristate to  $110^\circ\text{C}$  does not lead to any significant change in the diffraction reflection half-widths of the layer reflections, Fig. 2(b) and Fig. 8. Only a small decrease in the intensity of the first diffraction line (001) is observed. At  $115^\circ\text{C}$ , the (001) reflection intensity decreases and, at the same time, a new reflection appears at slightly higher angles. At  $117^\circ\text{C}$ , the (001) layer reflection disappears and the intensity of the new peak increases. It should be noted that the remaining series of reflections only decrease in intensity and shift to small angles to a significantly lesser degree than that observed for the first series of reflections. Further heat-

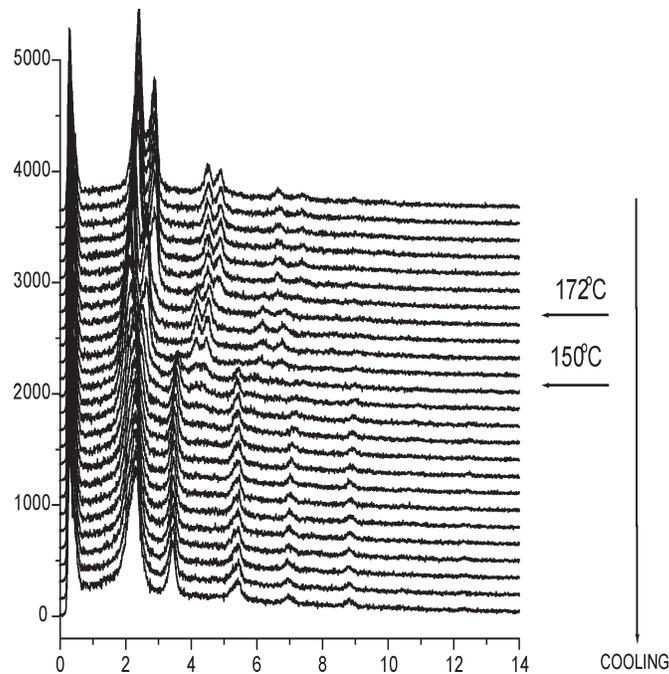
ing of the silver myristate crystals from  $120$ – $155^\circ\text{C}$ , as followed by the synchrotron, decrease intensity, and a shift of all reflections to larger angles is observed. The structural character of silver myristate upon heating above  $162^\circ\text{C}$ , when the material undergoes the second phase transition, is confirmed with the SAXS X-ray data by the appearance of additional reflections.

#### Structure Changes in the Phase Transformations of Silver Palmitate

The diffraction characteristics observed for silver palmitate during heating are the same as those seen for silver myristate. Thus, upon heating to  $119^\circ\text{C}$ , the positions and intensities of the layer line diffractions observed are unchanged. Increasing the temperature above  $119^\circ\text{C}$  leads to a significant decrease in the first layer reflection (001) (Fig. 2(c) and Fig. 9). At the same time, a new reflection



**Figure 10.** SAXS pattern, relative intensity versus  $2\theta$ , of  $\text{AgC}_{18}$  changes during heating.



**Figure 11.** SAXS pattern, relative intensity versus  $2\theta$ , of  $\text{AgC}_{18}$  changes during cooling.

is observed for the (001) series in the high-diffraction angle region. At  $123^\circ\text{C}$ , the (001) reflection disappears, and the intensity of the new reflection increases. Further heating to  $160^\circ\text{C}$  is accompanied by a synchronous shift of all layer reflections to higher angles. Further heating above  $160^\circ\text{C}$ , reveals a series of additional layer lines having a larger interlayer spacing in the X-ray data.

#### Structure Changes in the Phase Transformations of Silver Stearate

Upon heating, changes in the diffraction patterns of silver stearate are very similar, as expected, to those occurring in silver myristate and silver palmitate (Fig. 2(d) and Fig. 10). Thus up to  $\sim 115^\circ\text{C}$ , the position and intensities of the layer lines remain unchanged. In-

ing the temperature leads to a decrease in the layer line intensity for the (001) peak. At the same time, in addition to the (001) reflection, a new diffraction line is observed at a slightly higher angle. At 123°C, the (001) reflection disappears, and the intensity of the new reflection increases. Further heating to 160°C is accompanied by a synchronous shift of all the layer lines in the large angle region. Upon heating the silver stearate crystals higher than 160°C, a series of additional reflections having a significantly smaller interlayer parameter is observed in the X-ray diffraction along with the shift in layer spacing. Cooling the silver stearate crystals below 160°C leads to the same spectrum in the small-angle scattering characteristic of the 110–160°C region observed during the heating process (Fig. 11). Cooling to room temperature does not result in the restoration of the initial X-ray spectrum of the silver stearate crystal. After cooling the sample from 160°C, a diffraction picture characteristic of the phases above 110°C is observed, which confirm the irreversibility of the first phase transition.

## Discussion

The investigation of the transformations occurring in the phase changes of silver carboxylates enables general rules to be established that are characteristic of all silver carboxylates:

1. The first phase transition is accompanied by a shift of the first (001) reflections and reveals a diffraction reflection with smaller parameters.
2. The first phase transition for all the investigated carboxylates is irreversible. The first heating of the silver carboxylate to 119–160°C leads to stabilization of the high temperature phase.
3. Heating polycrystalline silver carboxylates to temperatures above the first phase transition (120–140°C) is accompanied by a shift in all of the layer reflections to higher angles.
4. The second phase transition leads to the formation of a phase characterized by an additional series of diffraction reflections.
5. Mechanical activation of the silver carboxylates is accompanied by phase transition and stabilization of the first high temperature phase.

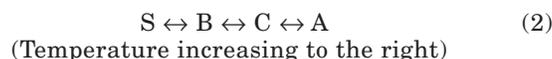
In addition, the optical and electron microscopic investigations provide additional conclusions on these transitions:

6. The first phase transition is characteristic of a Martensitic transition. The layers of the new phase have orientations corresponding to the initial phase. In the first phase transition process, the crystal habit of the initial crystals is maintained.
7. Upon heating to temperatures above the first phase transition, the electron microscopy investigation of the changing silver stearate morphology revealed the presence of order in the basal plane that is related to the formation of a twin structure. The size of the twin structure correlates to the reflections in the SAXS spectra that appear in the 110–120°C range.

In order to understand the structural changes occurring in the phase transformations of silver carboxylates, it is necessary to devote further attention to their structures. As noted earlier, all of the silver carboxylates have layered structures with a long interplanar distance  $d_{001}$  that is the result of the presence of a long hydrocarbon

chain. It is known that materials having this structure show properties of smectic liquid crystals. Therefore, the earlier observation on the mesomorphic transition in the structure of the similar silver carboxylates (the sodium and potassium salts of liquid crystals) can be correlated to the phase transformation of these soaps in various liquid crystalline phases.<sup>17–19</sup>

There is currently substantial experimental and theoretical literature regarding the structure, phase transitions, and physical properties of smectic liquid crystals.<sup>20,21</sup> Regardless of the specific smectic phases, the general characteristics of the layered structures depend on the composition of the hydrocarbon layer. The smectic phases are subdivided into smectic A, smectic C, and smectic B. In smectic A, the layer thickness approximates the length of the molecule and, inside each layer, the centers of gravity are not affected by the subsequent ordered layers, each layer is a two dimensional liquid. In the smectic C phase, despite the fact that the structure is a two-dimensional liquid, there is an optical binary axis that is determined by the correlation of the tilt of the long axis of the molecule relative to the basal plane. If each layer appears as a two-dimensional liquid in the smectic A and C phases, then the smectic B shows a periodicity and rigidity of the two-dimensional crystal. Here, the X-ray reflection corresponds to a regularity under each layer; so, the smectic B phase is the most ordered of the three basic smectic phases. It is known that if such material can exist in all three phases, the transition sequence is:

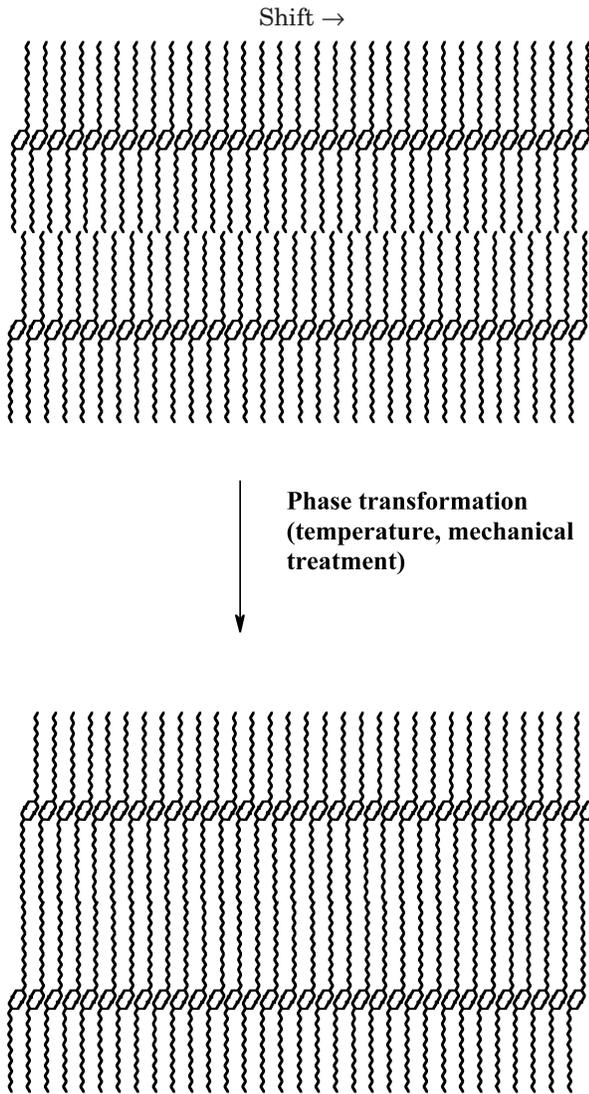


where S is the solid crystalline phase.

According to the above proposals<sup>20</sup> the difference between the smectic B phase and the solid crystalline state is still not known. The symmetry of the distribution of the long-chain hydrocarbon portion of the molecule forming the smectic B crystal is distinguished by at least two sub-groups, which can be called  $B_A$  (the molecules are perpendicular to the basal plane) and  $B_C$  (the molecules are tilted toward the basal plane). It should be noted that, except for the basic smectic A, B, and C phases discussed above, there are still another series of smectic phases that are characterized by differences of types of structural order of the molecules in the layers, for example, the hexagonal for smectic H or smectic E.<sup>21</sup>

One of the fundamental physical properties of the smectic liquid crystals is the possibility of layers slipping relative to each other. Furthermore, under certain conditions (for smectic A and C), the ideal plane can deform in a more complicated ordering with twisted layers. In addition, the experimental data obtained from the investigation of the smectic liquid crystal B with the long aliphatic portion<sup>22</sup> showed that the chain is located in a disordered “melted” state. At the same time, the aromatic rings of that material are strongly ordered. Another demonstration of the disordered state of the aliphatic portion of the molecule is evident from the enthalpy of the phase transition, which was quite close to the enthalpy for melting of paraffins with long chains equal to the long chain smectics.

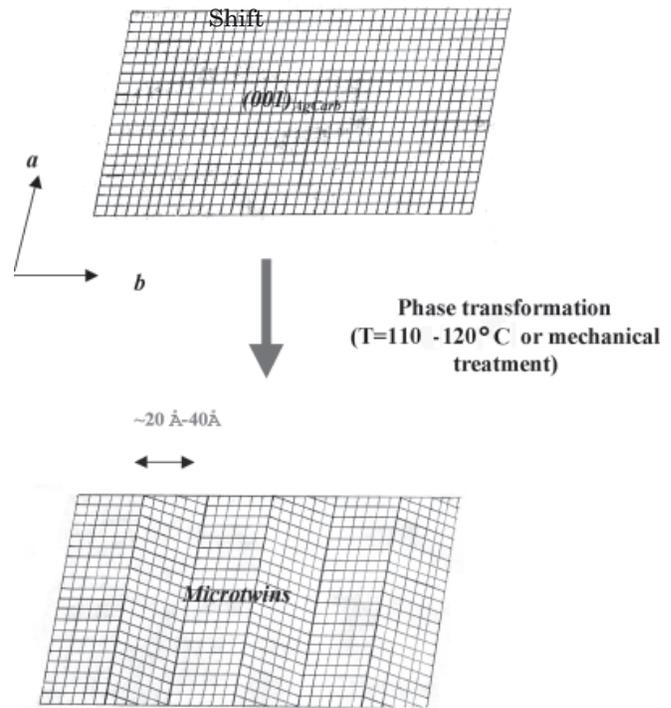
Taking into account the data in the discussion above on the changing structure of the smectic phases and the experimental data on the phase transformations in silver carboxylates given in this work, the following model can be proposed for the changes in the structures of the



**Figure 12.** Schematic of silver carboxylate layer shift during the first phase transition.

silver carboxylates during the heating process of the first transition.

The shift in the reflections from the (001) plane during the first phase transition is due to the fact that the formation of the high temperature phase is more symmetric than the initial triclinic crystal phase of the silver carboxylate. Increasing the symmetry of the crystal structure of the silver carboxylate is due to the shift of the bilayer in the SC structure. This layer shift in the silver carboxylate structure is accomplished in the organic layer and is controlled by the shift of long hydrocarbon chains relative to each other (Fig. 12), which is the consequence of the smaller van der Waal's interaction between hydrocarbon chain ends, relative to the strong Ag–O interdimer bonding interaction between the  $-\text{COOAgAgOOC}-$  groups forming the “silver” layer. This type of layer displacement can lead to the appearance of new symmetry elements in the crystal structure, for example, axial or planar symmetry, that is also the cause of the disappearance of the  $d_{001}$  layer reflections. By analogy with the discussion above, the phase transitions in the smectic liquid crystal can be proposed to account



**Figure 13.** Schematic of microtwin formation during the first phase transition.

for the transition from the crystalline state into the ordered smectic B phase.

The observed formation of an oriented phase, occurring as the result of the first phase transition, has all the characteristics of a Martensitic transformation, and indicates that the new high temperature phase has a higher degree of the symmetry, relative to the initial crystalline state. The Martensitic character of the first phase transition is further confirmed by the formation of multiple twin planes and the propagation of the Martensitic transition. Therefore, the twinning parameters of the high temperature phase, 25 Å for silver laurate and 37 Å for silver stearate, correlate with the long aliphatic chain of the silver carboxylate. The formation of an ordered secondary structure could lead to the appearance in the SAXS spectra of new diffraction reflections having an interlayer distance somewhat less than for the interlayer  $d_{001}$  spacing of the silver carboxylate crystal, Fig. 13. It should be noted that the formation of an ordered domain (twin) structure was observed earlier<sup>23</sup> during the preparation of Langmuir–Blodgett films for cadmium stearate, the bridging carboxylate structure that is similar to the structure of silver stearate.

The high degree of molecular order in the structure of the high temperature phase, which forms during the first phase transition process, is confirmed by the preservation of the single crystal habit after the phase transformation and the presence of the binary refraction of the crystals at temperatures above 120°C. The conservation of the silver carboxylate unit cell crystal structure after the phase transition can be attributed to the relative orientation between the forming phase and the starting crystalline phase.

The changing interlayer spacing in the high temperature phase of forming on heating, i.e., of the diffraction angles to larger values, is unmistakable evidence of the decreasing distance between the silver layers in the sil-

ver carboxylate structure. Such a decreasing distance between layers is related to the process of disorder in the long hydrocarbon chain in the "melting" organic substructure of the silver carboxylate structure.

For the most precise determination of the structures of the high temperature phases of silver carboxylate, it is necessary to carry out additional *in situ* X-ray investigations over the widest range of diffraction angles, where it will be possible to fix the changes not only for the interlayer distances but also to obtain information on the changes in the layer structure itself.

We found that intensive mechanical activation of the silver carboxylate leads to the phase transition and stabilized high temperature phases of the silver carboxylates, just as does the thermal process. There are several possible causes for the phase change during mechanochemical processing. It is known that intensive mechanochemical processing is accompanied by increasing temperature in the zone of the mechanochemical effect.<sup>24</sup> According to some estimations, the temperature can reach several hundred degrees.<sup>24</sup> Therefore, heating samples above the phase transition temperature during mechanical treatment can be one route to the formation of the high temperature phase. On the other hand, mechanical activation of solid materials, as a rule, is accompanied by the formation of various types of defects, such as point defects, dislocations, and shifting of crystallographic planes with the formation of twin boundaries. As we show here, the first phase transition can be considered as a Martensitic transition, one unique characteristic of which is the formation of precisely these types of defects. In this case, the formation of defects in mechanical processing can initiate the phase transformation of the silver carboxylate into the high temperature modification.

It should be noted that within the scope of the current investigation there remains the question of the phase transitions in the silver carboxylate that result at temperatures above 150°C. Continuing the investigation of the structural and morphology characteristics of the silver carboxylates in this temperature range is of great scientific interest, as it would allow new information on the phase transitions between various liquid crystalline states to be obtained.

## Conclusions

Small-angle X-ray scattering, electron and optical microscopy, and thermal analytical investigation have been used to characterize the first important thermal transition observed in silver laurate, myristate, palmi-

tate, and stearate. This investigation has revealed that these fatty acid silver carboxylates undergo an irreversible Martensitic phase change in the 110–120°C temperature range. This phase change is characterized by the formation of a more symmetrical phase, compared to the initial crystalline silver carboxylate. An ordered orientation is observed that separates Martensitic layers in the matrix of the initial crystalline silver carboxylate. A micro-twin structure on the basal plane of the crystal is also formed along with this first phase transition. Increasing the temperature above 120°C leads to a decrease in the distance between silver layers in the high temperature phase structure, which is a result of the disordering of the carbon chains of the molecule. ▲

## References

1. P. J. Cowdery-Corvan and D. R. Whitcomb, Photothermographic and Thermographic Imaging Materials, *Handbook of Imaging Materials*, A. Diamond, D. Weiss, Eds., Marcel Dekker, New York, NY, 2002.
2. D. H. Klosterboer, Neblette's Eighth Edition: *Imaging Processes and Materials*, J. M. Sturge, V. Walworth and A. Shepp, Eds., Van Nostrand-Reinhold, New York, 1989, Chap. 9, pp. 279–291.
3. M. Ikeda, *Photogr. Sci. Eng.* **24**, 277 (1980).
4. M. Chadha, M. E. Dunnigan, M. R. V. Sahyun, and T. Ishida, *J. Appl. Phys.* **84**, 887 (1998).
5. V. Vand, A. Aitken and R. K. Campbell, *Acta Crystallogr.* **2**, 398 (1949).
6. F. W. Matthews, G. G. Warren and J. H. Michell, *Anal. Chem.* **22**, 514 (1950).
7. B. P. Tolochko, S. V. Chernov, S. G. Nikitenko, and D. R. Whitcomb, *Nucl. Instrum. Methods Phys. Res. Sect. A* **405**, 428 (1998).
8. V. M. Andreev, L. P. Burleva, B. B. Bokhonov, and Yu. I. Mikhailov, *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk.* **2**, 58 (1983).
9. V. M. Andreev, Investigation of the thermal and photochemical decomposition reactions of silver carboxylates and their application to photographic materials, Ph.D. Dissertation, Novosibirsk, Russia, 1984.
10. I. Geuens, I. Vanwelkenhuysen and R. Gijbels, *Int. Symp. Silver Halide Imaging*, IS&T, Springfield, VA, 2000, p. 230.
11. I. Geuens, I. Hoogmartens and G. Defieue, EP Patent 1158355 (2001).
12. Yu. E. Usanov and T. B. Kolesova, *J. Imaging Sci. Technol.* **40**, 104 (1996).
13. K. Simonesku and K. Oprea, *Mechanochemistry of High Molecular Weight Compounds*, Mir, Moscow, 1970.
14. A. M. Dubinskaya, *Usp. Khim.* **68**, 708 (1999).
15. M. Ikeda and Y. Iwata, *Photogr. Sci. Eng.* **24**, 273 (1980).
16. A. Kelly and G. M. Drowes, *Crystallography and Crystal Defects*, Longman, London, 1970.
17. R. D. Vold, *J. Amer. Chem. Soc.* **63**, 2915 (1941).
18. R. D. Vold, *J. Amer. Chem. Soc.* **63**, 160 (1941).
19. P. Pacor and H. L. Spier, *J. Am. Oil Chem. Soc.* **45**, 338 (1968).
20. P. G. de Gennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1974.
21. A. S. Sosnin, *Introduction to the Physics of Liquid Crystals*, Nauka, Moscow, 1983.
22. M. Dvolaitzky, F. Poldy and C. Taupin, *Phys. Lett.* **45A**, 454 (1973).
23. G. I. Ivakin, P. I. Ivakin, A. V. Mokeev, and D. V. Laydunko, *Kristallografiya* **43**, 354 (1998).
24. C. C. Koch, *Mater. Sci. Forum* **88–90**, 243 (1992).