

Original Research Paper

Cold Crystallization Behavior of a $Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25}$ Metal Glassy Alloy

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Abstract: Liquid crystals, a substance that flows like a liquid but has some degree of ordering in the arrangement of its molecules. "Depending on temperature or the presence of an electric potential difference, molecules in a liquid crystal can either be randomly, partially or completely aligned." Isothermal cycles of the metalized metallic alloy $Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25}$ (cold crystallization obtained by heating the glassy glass samples) were investigated in this study in the metastable state of the overheated liquid metal at elevated temperatures above the glass transition. Complex crystallizing behaviors with multiple and selective exothermic peaks crystallization of higher mobility atoms from an alloy induced by isothermal annealing have been observed to result in an experimentally observed increase in temperature required to induce glass metal relaxation (vitreous transition). Dynamic DSC analysis indicated that only two atomic species present in the metastable liquid are involved in the recrystallization process below 450-470°C. Isothermal isolation in the temperature range between 400° and 450°C was chosen for subsequent investigation of the thermal kinetics occurring in the supercooled chilled liquid. The activation energies associated with the two crystallization processes are, respectively, -181 kJ/mol and -262 kJ/mol.

Keywords: Liquid Metals, Cold Crystallization, Isothermal Cycles, Metallic Alloy, Glass Transition, Isothermal Isolation

Introduction

Liquid crystals, a substance that flows like a liquid but has some degree of ordering in the arrangement of its molecules.

"Depending on temperature or the presence of an electric potential difference, molecules in a liquid crystal can either be randomly, partially or completely aligned."

Liquid Crystals (LCs) are a matter in a state of aggregation that has properties between those of conventional liquids and those of solid crystals. For example, a liquid crystal can flow like a liquid, but the molecules can be oriented in a certain direction, like in a crystal. There are several different types of liquid crystal phases, which can be distinguished by different optical properties (such as birefringence). When viewed under a microscope, using a polarized light source, the different

phases of the liquid crystal will appear to have distinct textures (d). The contrasting areas of textures correspond to those in which liquid crystal molecules are oriented in different directions. Within a domain, molecules are well-ordered. Materials that may have liquid crystal states may not always be in a liquid crystal phase (just as water can turn into ice or steam).

Liquid crystals can be divided into thermotropic (d), lyotropic (d) and metallotropic phases. Liquid thermotropic and lyotropic crystals are mostly formed from organic molecules, although some minerals are also known. Liquid thermotropic crystals have a phase transition in the liquid crystal phase when changing the temperature. Lyotropic displays phase transitions depending on temperature and concentration of liquid crystal molecules in a solvent (usually water). Metallotropic compounds are composed of organic and

inorganic molecules; their transition to the liquid crystal phase depends not only on temperature and concentration but also on the compositional ratio between inorganic and organic molecules.

Examples of liquid crystals can be found both in the natural world and in technological applications. Most contemporary electronic displays (d) use liquid crystals. Lyotropic phases are abundant in living systems, but can also be found in the mineral world. For example, many proteins and cell membranes are liquid crystals. Other well-known examples of liquid crystals are soap solutions and various detergents, as well as tobacco mosaic virus (d) and some clays.

In 1888, Austrian botanist physiologist Friedrich Reinitzer, who worked at Karl-Ferdinand-Universität, examined the physicochemical properties of various cholesterol derivatives (d), which are now part of the class of materials known as cholesteric liquid crystals. Previously, other researchers observed distinct color effects when cholesterol derivatives cooled down close to the freezing point but did not associate them with a new phenomenon. Reinitzer understood that color changes in cholesterol benzoate (d) are not the most unusual feature (Crystal Liquid, From Wikipedia).

He found that cholesteryl benzoate does not melt in the same way as other compounds but has two melting points. At 145.5°C melts in a cloudy liquid and at 178.5°C melts again and the cloudy liquid becomes clear. The phenomenon is reversible. Seeking the help of a physicist, on March 14, 1888, he wrote to Otto Lehmann (d), at that time Privatdozent (d) in Aachen. They exchanged letters and evidence. Lehmann examined the intermediate turbid liquid and saw crystallites (d). Reinitzer's Viennese colleague, von Zepharovich, also indicated that the intermediate liquid is crystalline. Letter exchange with Lehmann ended on April 24, many questions remained unanswered. Reinitzer presented his results, crediting Lehmann and von Zepharovich, at a meeting of the Chemistry Society in Vienna on May 3, 1888.

Until that time, Reinitzer had also discovered and described three other important features of cholesteric liquid crystals (Otto Lehmann's invented name in 1904): The existence of two melting points, the reflection of circularly polarized light (d) and the ability to rotate the direction of the light polarization.

After accidental discovery, Reinitzer did not pursue the study of liquid crystals. The research was continued by Lehmann, who realized that he had met a new phenomenon and was in the position of investigating: In postdoctoral years, he had acquired expertise in crystallography and microscopy. Lehmann began a systematic study, first on cholesteryl benzoate and then on related compounds that had the double melt phenomenon. He managed to make observations in

polarized light and his microscope was equipped with a hot stage (a sample heater equipped with a heater) to allow him observations at high temperatures. The intermittent cloudy phase definitely supported the flow, but other features, such as the signature under the microscope, convinced Lehmann that it had to do with a solid. By the end of August 1889, he published his results in *Zeitschrift für Physikalische Chemie* (d).

Lehmann's work was continued and expanded significantly by German chemist Daniel Vorländer (d), who, from the beginning of the twentieth century until his retirement in 1935, synthesized most of the known liquid crystals. However, liquid crystals were not popular among scientists and the material remained a scientific curiosity for about 80 years.

After World War II, liquid crystal synthesis was resumed at European research laboratories. George William Gray (d), an important scientist in the field of liquid crystals, began investigating these materials in England in the late 1940s. His group synthesized many new materials presenting the liquid-crystalline state and developed a better understanding of how to design molecules presenting this state. His book *Molecular Structure and Liquid Crystal Properties* has become handmade in this subject. One of the first American chemists to study liquid crystals was Glenn H. Brown, since 1953, at the University of Cincinnati and later at Kent Universitatea State University (d). In 1965, he organized the first international Liquid Crystal Conference in Kent, Ohio, attended by over 100 top researchers of liquid crystals. This conference marked the beginning of a worldwide effort to carry out research in this area, which soon led to the development of practical applications for these unique materials.

Liquid crystals have become the subject of research in the development of flat electronic displays since 1962 at RCA Laboratories. When the chemist-physicist Richard Williams applied an electric field to a thin layer of nematic liquid crystal at 125°C, he noticed the formation of a regular pattern that he called a "domain" (now called the "Williams Field"). This led his colleague George H. Heilmeyer (d) to research to develop a liquid crystal display panel to replace the vacuum cathode tubes used in TVs. But the para-azoxy anisole (d) used by Williams and Heilmeyer had a state of nematic liquid crystal only at over 116°C, which made it impossible to use it in a commercial display system. There was a need for a material that could work at room temperature.

In 1966, Joel E. Goldmacher and Joseph A. Castellano, chemical investigators in the RCA Heilmeyer group, found that blends made exclusively of nematic compounds that differ only in the number of carbon atoms in the terminal end of the chains could produce liquid crystals nematic at room temperature. With a ternary mixture of Schiff (d) base compounds resulted in

a material having a 22 to 105° nematic matrix. Operation at room temperature allowed the production of the first practical liquid crystal display device. The team then began to prepare numerous mixtures of nematic compounds, many of which had much lower melting points. This technique of mixing the nematic compounds to obtain a wide range of operating temperatures (d) has ultimately become industry standard and is used up to date to adapt the materials to meet certain applications.

In 1969, Hans Kelker was able to synthesize a substance that has a nematic phase at room temperature, MBBA (d), one of the most popular liquid crystal research topics. The next step towards commercializing liquid crystal displays was the synthesis of low-melting stable chemicals (cyanobiphenyls) by George Gray (d). His work with Ken Harrison and UK MOD (RRE Malvern (d)) in 1973 led to the design of new materials and the rapid adoption of small-area LCDs in electronic products (Crystal Liquid, From Wikipedia).

These molecules are in the form of a rod, some created in the laboratory and some appear spontaneously in nature. Since then, two new types of LC molecules have been discovered, both artificial: In the form of a disc (created by the group of S. Chandrasekhar in India, 1977) and in the form of a bowl (invented by Lui Lam in China, 1982 and synthesized in Europe three years later).

In 1991, when liquid crystal displays were already well established, Pierre-Gilles de Gennes, who worked at the University of Paris-Sud (d), received the Nobel Prize for Physics "to discover that the methods developed to study phenomena in simple systems can be generalized to more complex forms of matter, especially liquid crystals and polymers."

There are known a large number of chemical compounds having one or more liquid crystal phases. Despite the significant differences in chemical composition, these molecules have some common characteristics in physical and chemical properties. There are three types of thermotropic liquid crystals: Disco, calamity and bowl-shaped ones. Discotics are plate-shaped molecules formed from a core of adjacent aromatic rings; bowl-shaped ones have a three-dimensional shape. This allows a two-dimensional column arrangement, for both disco and bowl. The calamitous molecules (in the form of a rod) have an elongated, anisotropic geometry, which allows preferential alignment (d) along with a spatial direction.

The molecular form should be relatively thin, flat or bowl, especially in rigid molecular frames.

The molecular length must be at least 1.3 nm, consistent with the presence of long alkyl groups on many liquid crystals at room temperature.

The structure should not be branched or angular, except for bowl-shaped molecules.

A low melting point is preferred to avoid the mono-liquid metastable liquid crystalline phases. Low-temperature mesomorphic behavior is usually more technologically useful and alky terminal groups promote this.

An expanded, structurally rigid, highly anisotropic shape appears to be the main criterion for the behavior of liquid crystals and as a result, many liquid-crystalline materials are based on benzene rings.

The various liquid crystal phases (called mesophase (d)) can be characterized by the type of ordering. It is possible to distinguish the positional order (if the molecules are arranged in some orderly structure) and the order of orientation (if the molecules are largely oriented in the same direction). Moreover, the order may be either short-range (only between molecules close to each other) or long-range (greater extension, sometimes at macroscopic dimensions). Most thermotropic liquid crystals will have an isotropic phase (d) at elevated temperatures, that is to say, the heating will ultimately transform them into a conventional liquid phase characterized by random and isotropic molecular ordering (without any large-scale order) and with flow behavior similar to any liquid. Under other conditions (e.g., at a lower temperature), a liquid crystal could have one or more phases, with significant anisotropic orientation and small-scale orientation, while still having the ability to flow.

The arrangement of liquid crystal phases is extended to the molecular scale. This order extends to the size of the entire range, which may be in the order of the micrometers, but usually does not extend on a macroscopic scale as often as in the case of classical solid crystals. However, some techniques, such as the use of boundaries or the application of an electric field, can be used to apply a single ordering range to a macroscopic sample of liquid crystals. Arrangement in a liquid crystal could extend along a single dimension, the material being essentially disordered in the other two directions.

Thermotropic phases are those that occur within a certain temperature range. If the temperature rise is too high, the thermal agitation will destroy the cooperative ordering of the liquid crystal phase by pushing the material into a conventional isotropic liquid phase. At too low a temperature, most materials will form conventional crystals. Many thermotropic liquid crystals have a variety of phases as temperature variation. For example, heating a certain type of liquid crystal molecules (called mesogens (d)) may present different smectic phases, followed by the nematic phase and eventually the isotropic phase as the temperature is increased. An example of a compound exhibiting thermotropic liquid crystal behavior is para-azoxy anisole (d).



Fig. 1: Alignment in the nematic phase

One of the most common phases of liquid crystals is the nematic. The nematic word comes from the Greek thread (in Latin letters, *nema*), which means "thread". This term derives from topological defects (d) observed in nematicides, officially called "disclinations" (d), Fig. 1.

Nemethas also present the so-called "hedgehog" topological defects. In a nematic phase, organic calamity molecules (rod-shaped) do not have a positional order but align themselves to have a large-scale directional order with the approximately parallel longer axes. Thus, the molecules are free to flow and the positions of their mass centers are randomly distributed, as in a liquid, but they still maintain their directional order on a large scale. Most nematicates are uniaxial: They have one axis that is longer and preferred, the other two being equivalent (can be approximated by a cylinder). However, some liquid crystals are biaxially nematic (d) in the sense that, in addition to the longer axis orientation, they are also oriented along a secondary axis. Nemethas have fluidity similar to that of ordinary (isotropic) fluids, but they can be easily aligned with an external electric or magnetic field. Aligned nematicates have the optical properties of uniaxial crystals and this makes them extremely useful in Liquid Crystal Displays (LCD), Fig. 1.

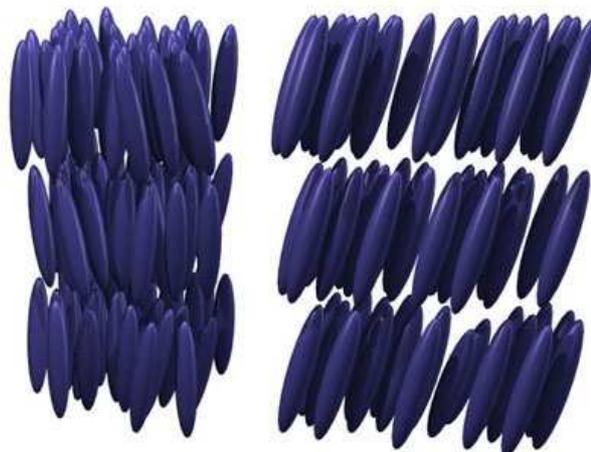


Fig. 2: Alignment in the smectic phase

The smectic phases (Fig. 2), which are found at lower temperatures than the nematic, form well-defined layers that can glide over each other in a manner similar to that in which the soap slides. The word "smectic" comes from the Latin word "smectics", which means "cleaning" or with properties like soap. Smectics are thus positioned positively along a single direction. In smectic phase A, the molecules are oriented along the normal to the layer, while in the smectic phase C they are inclined towards it. These phases are similar to liquids only between layers. There are many different smectic phases, all characterized by different types and degrees of positional and orientation.

Phase shift between Nematic (left) and smectic (right) is observed by cross-polarized filters (Fig. 3). The black color corresponds to the isotropic environment.

The moth chiral phase exhibits chirality (preference for right/left), (Fig. 4). This phase is often called cholesterol phase (d) because cholesterol derivatives have been observed for the first time. Only chiral molecules (i.e., those without internal symmetry planes (d)) can give rise to such a phase.

This phase presents a twist of molecules perpendicular to the directories, with the molecular axis parallel to the director. The finite angle of twisting between the adjacent molecules is caused by their asymmetric agglomeration, resulting in greater chiral order.

In smectic phase C* (the asterisk denotes chiral phase), the molecules have a positional ordering in a layered structure (as in other smectic phases), with the molecules inclined at a certain angle relative to the normal layer. Chirality induces a finite azimuthal twist from one layer to another, which in turn produces a spiral twist of the molecular axis around the normal to the layer.

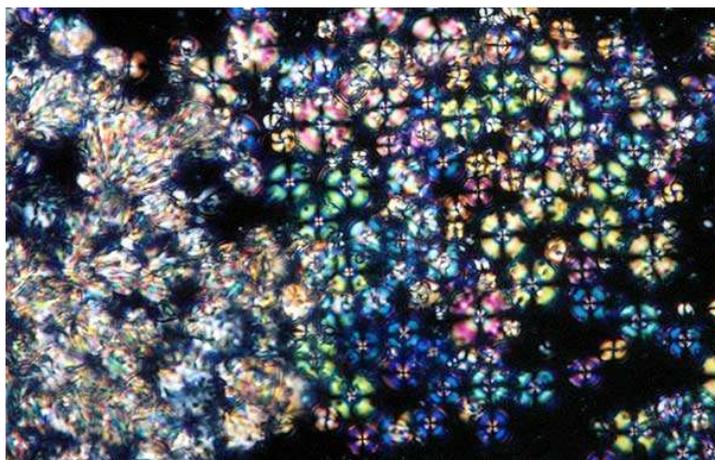


Fig. 3: Phase transition between the nematic (left) and smectic (right) phases observed by cross-polarizing filters. The black color corresponds to the isotropic environment

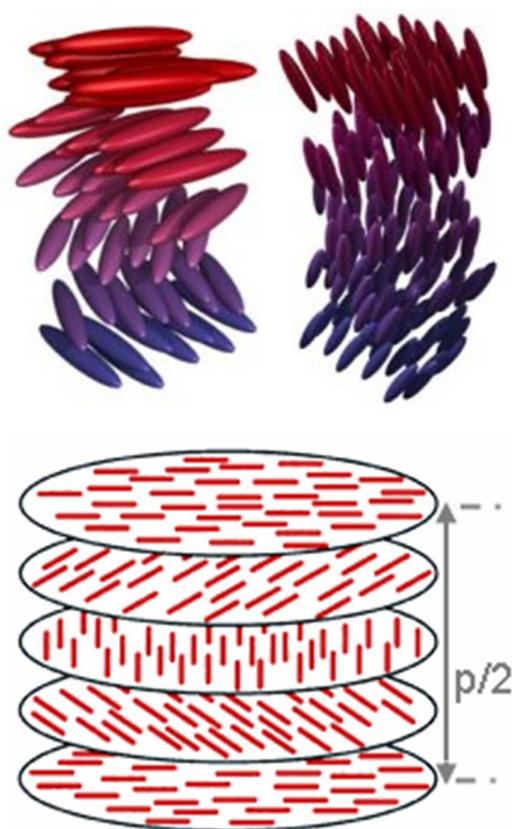


Fig. 4: The cholesteric phase exhibits chirality (preference for right/left). This phase is often called cholesteric phase (d) because cholesterol derivatives have been observed for the first time

The chiral period, p , refers to the distance at which the liquid crystal molecules undergo a total 360° twist (but the structure of the nematic chiral phase is repeated

every half-period since at this stage the 0° and $\pm 180^\circ$ directories are equivalent). The period p usually changes when the temperature changes or when other molecules are added to the host material (an achiral host material will form a chiral phase when doped with a chiral material), allowing the period of a particular material to be adjusted accordingly. In some liquid crystal systems, the period is the same order of magnitude as the visible light wavelength. This makes these systems have unique optical properties, such as Bragg reflections and low threshold laser emissions and these properties are exploited in many optical applications. For Bragg reflection, only the lowest order reflection is allowed if the light is incident along the helical axis, while for higher-order oblique incidences, reflections become permissible. The nematic liquid crystals also have the unique property that reflects circularly polarized light when it is incident along the helical axis and the polarized elliptical (d) if it falls at an oblique angle.

The blue phases are liquid crystal phases occurring in the temperature range between a phase with a chiral phase and a liquid isotropic phase (d). The blue phases have a three-dimensional cubic defect structure with periods of a crystalline structure of several hundred nanometers and thus exhibit selective Bragg (d) reflections in the wavelength range of visible light corresponding to the cubic crystalline structure. He had theoretically predicted in 1981 that these phases may have icosahedral symmetry similar to quasicrystals (d).

Although the blue phases are of interest for the fast light modulators or the tunable (?) Photonic crystals (?), They exist in a very narrow range of temperatures, usually less than a few kelvin degrees. Recently, stabilization of the blue phases over a temperature range greater than 60 K, including at room temperature (260-326 K), has been demonstrated. The blue-stabilized

phases at room temperature allow electro-optical switching with response times of 10-4 sec.

In May 2008, the first Blue-Screen LCD (d) was developed.

The disc-shaped liquid crystal molecules can be oriented in a layer, known as the nematic discotic phase. The discs can be grouped together, forming columns. The columns can be rectangular or hexagonal. Discotic chiral phases, similar to chiral nematic, are also known.

Lytotropic (Li) liquid crystal (d) consists of two or more components that exhibit liquid-crystalline properties at certain concentration ranges (Fig. 5). In the lyotropic (d) phases, the solvent molecules fill the space around the compounds to provide fluidity to the system. In contrast to liquid thermotropic crystals, lyotropic liquids have another degree of freedom, of concentration, which allows them to induce a variety of different phases.

A compound having two immiscible, one hydrophilic and one hydrophobic moiety in the same molecule is called an amphiphilic molecule (d). Many amphiphilic molecules have liquid-crystalline liquid phase sequences depending on the volumetric balance between hydrophilic and hydrophobic moieties. These structures are formed by the micro-phase segregation of two incompatible nanometric nanoparticles. Soap is an everyday example of Lytropic Liquid Crystal.

The content of water molecules or other solvent changes the self-assembled structures. At very low amphiphilic concentrations, the molecules will disperse randomly, without any order. At slightly higher (but still low) concentrations, amphiphilic molecules will spontaneously assemble in the micelles or vesicles (d). This is done in such a way as to "hide" the hydrophobic part of the amphiphilic within the base micelle, exposing a hydrophilic (water-soluble) surface for the aqueous solution. These spherical objects do not ordinate themselves in solution. At higher concentrations, the assemblies will become orderly. A typical phase example is a hexagonal colonial phase, where amphiphiles form long cylinders (again with a hydrophilic surface), which are arranged in approximately hexagonal structures. At even higher concentrations, a lamellar phase can be formed, in which sheets stretched out of amphiphiles are separated by thin layers of water. For some systems, there may also be a cubic phase (isotropic viscous) between the hexagonal and the lamellar one, in which spheres are formed that create a dense cube network. These spheres can be linked to one another, forming a bicontinuous cubic phase.

Objects created by amphiphiles are usually spherical (as in the case of micelles), but they may also be in the form of a disk (whip), rod, or biaxial (with all three distinct axes). These self-assembled anisotropic nanostructures can then be ordered just like liquid thermotropic crystals, forming large-scale versions of all thermotropic phases (such as a rodless phase of rod-shaped micelle).

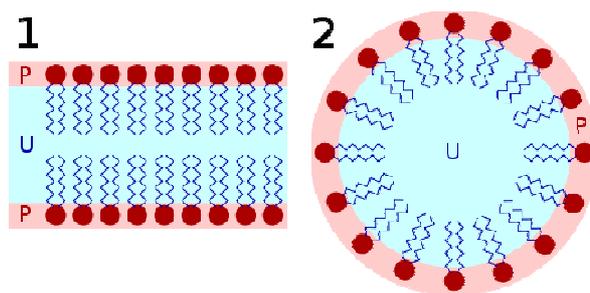


Fig. 5: Crystal Lyotropic Liquid Crystal Structure. The red faces of the surfactant molecules are in contact with the water and the tails are sunk in the oil (blue): the battered (left) and the small (right)

For some systems, at high concentrations, inverse phases can also be seen, ie an inverse hexagonal colon phase (amphiphilic encapsulated water columns) or a reverse micellar phase (a massive liquid crystal sphere with spherical cavities) can be generated.

P generic phase progression, from low amphiphilic concentration to high concentration, is:

- Discontinuous cubic phase (cubic micellar phase \square (d))
- Hexagonal phase \square (d) (hexagonal, middle-phase)
- The lamellar phase (d)
- Cubic phase bicontinuous
- Reverse hexagonal colon phase
- Reverse cubic phase (reverse micellar phase)

Even in the same phase, self-assembled structures are tunable by concentration: For example, in lamellar phases, the spacing between layers increases with the volume of solvent. Since lyotropic crystals are based on a subtle balance of intermolecular interactions, it is much more difficult to analyze structures and their properties than those of liquid thermotropic crystals.

Similar phases and characteristics can be observed in diblock non-viscous copolymers.

The phases of the crystals may be based on low melting inorganic phases, such as $ZnCl_2$, which have a structure formed from linked tetrahedra and easily form glass. Addition of soap-like long chain molecules leads to a series of new phases exhibiting a variety of liquid-crystalline behaviors both as a function of the inorganic-organic composition and the temperature ratio. This class of materials is called metabotropic.

The thermotropic mesophases (d) are detected and characterized by two major methods, the original method being the use of thermal optical microscopy, in which a small sample of material was placed between two cross polarizers; the sample was then heated and cooled. As the isotropic phase would not significantly affect the polarization of light, it would seem very dark, as the crystalline and liquid-crystal phases will polarize the

light in a uniform way, resulting in brightness and color gradients. This method allows the characterization of the particular phase since the different phases are defined by specific order, which must be observed. The second method, the differential calorimetry, allows a more precise determination of phase transitions and transition enthalpy. A small sample is heated in a way that generates a very precise temperature change over time. During phase transitions, the heat flow required to maintain this heating or cooling rate will change. These changes can be observed and assigned different phase transitions, such as the key transitions of liquid crystals.

Lytropic mesophases are analyzed in a similar manner, although these experiments are somewhat more complex since the mesogenic concentration is a key factor. These experiments are performed at different concentrations of mesogen (d) in order to analyze their impact.

The liquid-crystalline lyotropic phases are abundant in living systems, the study of which is called lipid polymorphism (d). Consequently, liquid lyotropic crystals attract particular attention in the field of biomimetic chemistry. In particular, biological membranes (d) and cell membranes are a form of liquid crystals. Their constitutive molecules (e.g., phospholipids) are perpendicular to the surface of the membrane, but the membrane is flexible. These lipids have different forms. The constituent molecules can easily mix with each other, but they do not tend to leave the membrane due to the high level of energy required for this process. The lipid molecules can turn from one side of the membrane to the other. These liquid-crystalline membrane phases can also host important proteins, such as receptors that "float" freely inside, or partially out of the membrane, e.g., CCT.

Many other biological structures have liquid crystal behavior. For example, a concentrated protein solution that is extruded by a spider to generate silk (d) is, in fact, a liquid crystal. Exact ordering of silk molecules is essential for their renowned strength. DNA and many polypeptides can also form liquid crystal phases, this being an important part of the current academic research.

There are examples of liquid crystals in the mineral world, most of which are lyotropic. The first discovered was Vanadium (V) (d) vanadium oxide by Zocher in 1925. Since then, several others have been discovered and studied in detail. The existence of a real nematic phase in the case of the smectic clay family was advanced by Langmuir in 1938, but remained open for a very long time and solved only recently. With the rapid development of nanoscience and the synthesis of anisotropic nanoparticles, the number of such liquid crystal minerals is growing rapidly, for example, with carbon nanotubes and graphene. A lamellar phase, $H_3Sb_3P_2O_{14}$, was found which exhibited hyperlumulation up to ~ 250 nm for interlamellar distance (Crystal Liquid, From Wikipedia).

Anisotropy of liquid crystals is an unobserved property to other liquids. This anisotropy causes the flow of liquid crystals to behave more distinctly than ordinary fluids. For example, injecting a liquid crystal flow between two parallel plates causes a molecule-oriented orientation coupled with the flow, resulting in the emergence of dendritic models. This anisotropy is also manifested in superficial tension between different phases of the liquid crystal. This anisotropy determines the equilibrium form at coexistence temperature and is so strong that forms usually occur. When the temperature is changed, one phase increases, forming different morphologies depending on the temperature changes. Since growth is controlled by heat diffusion, anisotropy in thermal conductivity favors growth in specific directions, which also has an effect on the final form.

The theoretical microscopic treatment of fluid phases can become quite complicated due to the increased density of material in the sense that strong interactions cannot be ignored. In the case of liquid crystals, the anisotropy of all these interactions complicates the analysis even further. There are several simple theories, however, which at least predict the general behavior of phase transitions in liquid crystal systems.

As we have seen above, nematic crystals are composed of molecular cylinders with long axes approximately aligned between neighboring molecules. To describe this anisotropic structure, a vectorial vector, called director, is introduced to represent the preferred direction of a molecule orientation near any point. Because there is no physical polarity (it does not matter the meaning, but only the direction) in the longitudinal direction of the axis, n and $-n$ are completely equivalent.

A simple model that predicts lyotropic phase transitions is the rigid rod model proposed by Lars Onsager. This theory considers the excluded volume in the center of an idealized cylinder while approaching another. Particularly, if the cylinders are parallel to one another, there is very little out of the center of the approaching cylinder (it may be close enough to the other one). If, however, the cylinders are tilted relative to each other, then there is a large volume around the cylinder in which the center of the other cylinder cannot penetrate (because of the rejection between the two idealized objects). Thus, this angular arrangement sees a decrease in the positional entropy of the approaching cylinder (there are fewer states available for it).

The fundamental vision here is that while parallel arrangements of anisotropic objects lead to a decrease in orientation entropy, there is an increase in position entropy. Thus, in some cases, the positional ordering will be favorable from the point of view of entropy. This theory thus predicts that a solution of cylinder-shaped objects will undergo a phase transition at a sufficient concentration in a nematic phase. Although this model is conceptually useful, mathematical

formulation makes several assumptions that limit its applicability to real systems.

Scientists and engineers are able to use liquid crystals in a variety of applications because external disturbances can cause significant changes in the macroscopic properties of liquid crystal systems. Electrical and magnetic fields can be used to induce these changes. The magnitude of the fields, as well as the speed with which the molecules align, are important characteristics for the industry. Special surface treatments can be used in liquid crystal devices to force certain director orientations for directions.

The ability of the director to align along an external field is caused by the electrical nature of the molecules. Permanent electrical dipoles occur when one end of the molecule has a net positive charge while the other end has a negative negative charge. When an external electric field is applied to liquid crystals, dipole molecules tend to orient in the direction of the field.

Even though a molecule does not form a permanent dipole, it can still be influenced by an electric field. In some cases, the field produces a slight rearrangement of electrons and protons in molecules, resulting in an induced electrical dipole. Although it is not as strong as permanent dipoles, it nevertheless shows orientation with the external field. The effects of magnetic fields on liquid crystal molecules are analogous to those given by electric fields. Since magnetic fields are generated by moving electric charges, permanent magnetic dipoles are produced by moving electrons. When a magnetic field is applied, the molecules will tend to align with or against the field.

In the absence of an outer field, the head of a liquid crystal is free to move in any direction. It is possible, however, to force a director to move in a certain direction by introducing an external agent into the system. For example, when a thin polymer layer (usually a polyimide) is spread on a glass substrate and scrubbed in a single direction with a cloth, it is observed that the liquid crystal molecules in contact with the surface align with the direction friction. The currently accepted mechanism for this is believed to be an increase in the epitaxial growth of liquid crystal layers on polymer chains partially aligned near the superimposed layers of the polyimide.

The competition between the orientation produced by surface anchoring and the effects of the electric field are often exploited in liquid crystal devices. If you consider the case where liquid crystal molecules are aligned parallel to the surface and an electric field perpendicular to the cell is applied, then, first, as the electric field increases in intensity, no change of alignment occurs. However, at a certain intensity of the electric field, deformation occurs. Deformation occurs when the principal changes direction from one molecule to another. The occurrence of such changes on a deformed state is called the Fredericks

transition and can also be produced by applying a sufficiently strong magnetic field.

The Fredericks transition is fundamental to the operation of many liquid crystal screens because the orientation of the director (and thus its properties) can be easily controlled by applying a field.

As already described, chiral liquid crystal molecules usually give rise to chiral mesophases. This means that the molecule must have a form of asymmetry, usually a stereogenic center (d). A further requirement is that the system is not racemic: A mixture of right and left-hand molecules will cancel out the chiral effect. Due to the cooperative nature of the liquid crystal ordering, doping with a small amount of chiral in an otherwise achiral mesophase, it is often sufficient to select a domain targeting to make the system as a whole chiral.

Chiral phases typically present a helical twist of molecules. If the period of this twist is in the order of the visible light wavelength, then interesting interfering optical effects may be observed. The chiral twist that occurs in the chiral phases can make the system respond differently to circularly polarized light to the right and to the left. These materials can thus be used as polarization filters (d).

It is possible for chiral molecules to produce substantially achiral mesophases. For example, at a certain concentration and molecular weight ranges, the DNA will form a linear hexahedral achiral phase. An interesting recent observation is the formation of chiral mesophases from achiral liquid crystal molecules.

Particularly, bent-core molecules (sometimes called liquid-banana crystals) have been shown to form liquid crystals with phases that are chiral. In any sample, different domains will have opposite orientation, but in any given area, a strong chiral order will be present. The mechanism of this of this macroscopic chirality is not yet very clear. It seems that the molecules are stacked in layers and are oriented in the layers in an inclined manner. These phase liquid crystal phases may be ferroelectric (d) or anti-ferroelectric, both of which are of interest to applications.

Chirality can be incorporated in one phase by the addition of a chiral dopant (d) which can not form liquid crystals alone. Non-twisted (d) or super-twisted mixtures (d) often contain a small amount of such dopants.

Liquid crystals have found a widespread use in liquid crystal displays, which are based on the optical properties of liquid-crystalline substances in the presence or absence of an electric field. In a typical device, a layer of liquid crystals (typically about 4 microns thick) lies between two polarizing filters that are crossed (90 ° oriented relative to each other). The alignment of the liquid crystals is chosen so that its relaxed phase is twisted. This twisted phase reorients the light that has passed through the first polarizer, allowing it to be transmitted through the second polarizer (and reflected back to the observer if there is a reflector). The device

appears transparent. When an electric field is applied to the liquid crystal layer, the long molecular axis tends to align in parallel with the electric field, thereby gradually deforming the liquid crystal layer in the center. In this state, liquid crystal molecules do not reorient light so that the polarized light of the first polarizer is absorbed by the second polarizer and the device loses its transparency with increased voltage. In this way, the electric field can be used to make a pixel switch between transparent and opaque to order. Color LCD systems use the same technique, with color filters used to generate red, green and blue pixels. Chiral smectic crystals are used in ferroelectric LCDs that are fast binary light binary modulators. Similar principles may be used to make other optical devices based on liquid crystals (Crystal Liquid, From Wikipedia).

In some vitreous substances, when heated, only a physical crystallization mechanism was discovered, but two physical mechanisms were discovered by scientists working at the Institute of Nuclear Physics in Krakow, Poland. The first use of numerical image processing to evaluate the degree of crystallization of liquid crystals has produced surprising results.

Organic substances present in pharmaceuticals should generally be in a glassy form. However, it may happen that under long-term storage conditions the compounds will crystallize and a drug will lose its therapeutic properties. In order to better understand the fundamental processes that arise during this transformation, researchers at the Institute of Nuclear Physics at the Polish Academy of Sciences in Krakow, Poland, conducted a series of studies on a particular type of crystallization that occurs during the heating of a certain type of liquid crystal. The results, recently published in *Crystal's Growth and Design* magazine, revealed an unexpected dual nature of the studied process.

"Crystallization is most often associated with the cooling process, but we know about another quite counter-intuitive phenomenon: Certain compounds under certain conditions are beginning to crystallize with temperature rise, this effect being known as cold crystallization and we have seen almost 20 for years, in liquid crystalline substances that tend to vitrify," explains Prof. Maria Massalska-Arodz (IFJ PAN), (Rozwadowski *et al.*, 2015; PAS, 2016).

Liquid crystals are liquids in which elongated molecules have a sort of order, generally found in ordinary crystals. The simplest nematic liquid crystal can flow, but its relatively large clusters are oriented in space in one direction. At the same time, they are distributed at random distances between them (unlike ordinary crystals, where they are found in crystal nodes).

Scientists from IFJ PAN analyzed changes in the elongated molecule arrangement of one of the liquid crystals (4CFPB), which undergoes mild vitrification in the nematic phase.

"Selection of nematic crystals as an object of study was not accidental. When looking at a polarizing microscope, they present multicolored areas arranged in a characteristic texture. We want to see whether the texture change changes during the nematic heating of a glassy phase about crystallization of the process" says student Tomasz Rozwadowski (IFJ PAN).

Doctors from IFJ PAN have performed a series of experiments on a change that occurs in liquid crystals because they are subject to warming at a constant rate of temperature rise. In a first experiment, it was just a Kelvin grade per minute, while in the last experiment it was 50° per minute.

The degree of crystallization obtained by numerical analysis of polarized microscopic images was compared with data collected at the same time by two conventional methods, calorimetry and dielectric spectroscopy. The results proved consistent, confirming the usefulness of graphical evaluation of texture changes in the crystallization study and allowing scientists to describe the process with high reliability and here the researchers found a surprise.

The data collected by physicists at IFJ PAN has demonstrated the existence of not one, but two mechanisms responsible for crystallizing the studied material. In experiments where the temperature rise rate was greater than 8° Kelvin per minute, crystallization was performed according to classical thermodynamic predictions at a temperature of about 275°.

However, when the sample was heated at a lower rate, there was a diffusion associated with the mobility of the molecules, which was mostly responsible for the crystallization process. This had an influence on the temperature of crystallization: When the process was diffuse, the temperature was significantly lower, because crystallization required, as said, less energy.

"If cold crystallisation was only a thermodynamic phenomenon, it would be enough to keep the temperature below 275° to protect the substance from uncontrolled transformation." Now that we know that the diffusion of the molecule begins to play a decisive role at higher temperatures, the crystal arrangement takes place at lower temperatures so that cold crystallization can take place in a rather wide range of unexpected temperature conditions in front of the teacher Massalska – Arodz, (Rozwadowski *et al.*, 2015; PAS, 2016).

Scientists working at IFJ PAN make important contributions to crystalline science, which fits with the greatest Polish tradition of this art. The electronics industry owes its existence today to the discovery of Jan Czochralski's method of producing monocrystals in 1916, where the crystals are "extracted" from the melted material using a bar that reaches the surface (Rozwadowski *et al.*, 2015; PAS, 2016).

Liquid crystals combine contradictory features such as chaos of liquid molecules and crystal control features. Due

to the innovative application of antimatter, it has been demonstrated at the Institute of Nuclear Physics of the Polish Academy of Sciences in Cracow that the structures made up of certain liquid crystal molecules must, in fact, be different from those previously considered.

Liquid crystals are found in many areas of technology and in the future, their use will probably increase, for example, as organic semiconductors. But to do this, basic research is needed using a variety of experimental techniques to reveal the structure of these compounds and their dynamics. For this purpose, the researchers performed new experiments on the Smectic-E (Sm-E) phase quenched with liquid crystals. Smectics of this type are composed of well-ordered particles separated in layers. Until recently, it was thought that the distance between the individual particle layers was very small. The research done by Krakow physicists helped to verify the correctness of the current models and accurately determined the crystalline structure.

"We used an interesting measurement technique, rarely used in liquid crystals." The method uses the specific features of positrons, which are counterparts of ordinary electronic antimatter, "explains Dr. Ewa Dryzek (IFJ PAN), (Rozwadowski *et al.*, 2015).

Positron as an electron counterpart has a positive charge. When a positron encounters an electron, it can lead to annihilation, where the mass of both particles turns into electromagnetic radiation with a characteristic energy.

"In the world of ordinary matter, antimatter is produced by physical processes only in small quantities." In our

measurements, we used positrons created in the radioactive decay of the isotope sodium 22, "says Dr. Ewa Juszynska-Galazka (IFJ TIGAIE), (Rozwadowski *et al.*, 2015).

Positrons of a radioactive source penetrated into the test material they encountered with electrons. Before the antithesis of a positron and a pair of electrons, an exotic atom called positronium can form. In soft matters, such as liquid crystals or polymers, the positive can be formed in nanopores, which are small differences between molecules. Measuring its lifetime - the time between the emission of a positron from a radioactive source and its annihilation - allows us to determine the size of nanoparticles. The smaller the nanoparticles, the faster the annihilation will take place.

Research from IFJ PAN focused on the positronic irradiation of a compound called 4TCB, which, unlike many other substances, does not crystallize with a decrease in temperature but with growth. The results showed that positrons are formed in this material. However, given the configuration of the existing model of molecules in the Sm-E phase, it was difficult to identify the place where it could be housed (PAS, 2016; Petrescu and Petrescu, 2011; 2014; Petrescu, 2012a; 2012b; 2014; Petrescu, *et al.*, 2016a; 2016b; 2016c; Petrescu and Calautit, 2016a; 2016b), Fig. 6.

Our measurements show that positron nanoparticles are about six angstroms. These results were consistent with one of the variants of the new Sm-E model, which was recently proposed by Prof. Kazuya Saito Group in Japan, "says Dr. Dryzek.

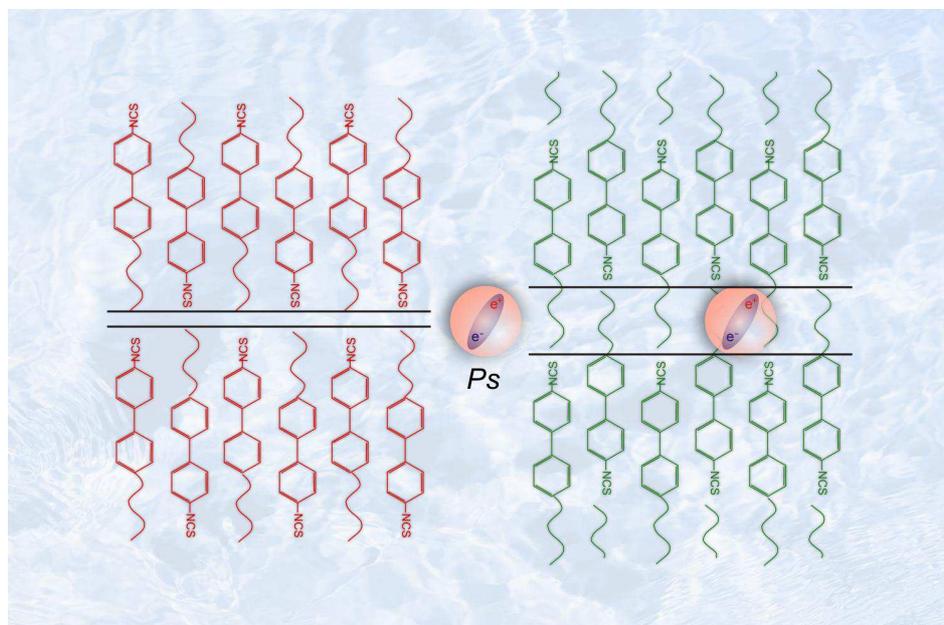


Fig. 6: Liquid-crystal SMEs have a different structure than previously expected, as shown by measurements using antimatter particles conducted at the Institute of Nuclear Physics of the Polish Academy of Sciences in Krakow. On the left is the current model of Sm-E and on the right is the new model, with a distinct gap between the layers, large enough to be able to accommodate positronium. Credit: IFJ PAN

The measurements confirmed that the alkyl chains - the "tail" of the molecules - are in the liquid state and thus have freedom of movement as in an isotropic liquid. It is noteworthy that in liquids, as a result of interacting with surrounding molecules, positron repulses neighboring molecules or their parts to produce an empty space around it. Such an arrangement can be imagined as a positron ball in its center.

The Japanese Sm-E model, proposed based on calorimetric tests and diffraction, assumed that liquid crystal molecules are arranged in two layers - the first consisting of rigid phenyl rings and the other of the alkyl chains.

"At this point, all information has begun to match together. Positronium can produce a bubble in the layer containing alkyl tails because they are in the liquid state. The size of the resulting balloon corresponds to the width of the layer," says Dr. Dryzek.

Positron lifetime temperature measurements have confirmed that, at low temperatures, quench 4TCB creates glass in which the position cannot be formed. The cart movements are frozen and the posterior position cannot produce a balloon.

With a rise in temperature, the glass softens, which can be described as the formation of liquid-like domains. In these areas, the position begins to form.

Pozurron Anesthetic spectroscopy is used to test metallic, semiconductor and polymeric materials.

The IFJ PAN results show that when properly applied, this method can be a source of interesting and detailed information about the liquid crystal structure (PAS, 2016; Petrescu and Calautit, 2016a; 2016b; Aversa *et al.*, 2015; 2016a; 2016b; 2016c; 2016d; 2016e; 2016f; 2016g; 2016h, 2017a; 2017b; 2017c; 2018).

Although research on metal glasses began in the early 1960s (Klement *et al.*, 1960; Schroers, 2010), which led to the development of several metal glasses with a pronounced ability to form glass (Busch, 2000; Trachenko, 2008), the processing of these glass forming systems does not simply demonstrate the solution to the challenges, especially when complex components are processed. The casting thicknesses, the maximum thickness of a glass bulb sample (BMG) can be amorphous, may be essential for melting the melt.

The composition of direct casting and melt solidification requires, in fact, an understanding of the crystallization process of the bulk metallic glass which forms an alloy and the cooling rates fast enough to avoid unwanted localized crystallization during mold cavity filling, while maintaining homogeneous vitrification in all parts of the processed part.

Even for the production of simple geometries by direct casting of BMGs, it is necessary to carefully select processing parameters, namely slow mold filling and bulk temperature control, which is (Lewandowski *et al.*, 2005; Morito and Egami, 1984; Schroers *et al.*, 1999).

The technologies of thermoplastic polymers are gradually transferred to BMG processing. The

metallic glass may be reheated from the glass state and formed in the temperature zone in which the glass relaxes in a thin metastable thin fluid before the eventual crystallization begins.

Plastification of an alloy that forms BMG in the supercooled liquid region can be used for thermoplastic formation. Due to recent advances in BMG alloys and thermoplastic casting, some BMG wagons can be considered as high strength alloys that can be processed as plastics.

The main criticism, however, still arises because of an unwanted crystallization and a phase separation that could drastically reduce the mechanical properties of the glass alloy (tenacity and strength).

The crystallizing cards of overlapping metallic melts are in the composition was thoroughly investigated using Time-Temperature-Transformation (TTT) diagrams (Busch, 2000).

These C which is characterized by a peak in the crystallization kinetics located at intermediate temperatures between thermodynamic melting and second glass transition describe how isothermal low-temperature crystallization results from the competition between a driving force of thermodynamic crystallization and slower progressive velocity diffusion controlled by the kinetics of lattice atoms.

The glass alloy that was brought over its glass transition results in a viscous metastable the liquid state in which the constituent atoms increase their mobility as the temperature increases.

This improved mobility allows the mixture of glass that did not crystallize when quenched from melting, rearranged in various configurations and eventually leading to unwanted selective crystallization, when brought from the metastable liquid state into the top layer, (cold crystallization).

The nature of the crystallization mechanism and the effect of the presence of residual nuclei on the crystallization kinetics must be taken into account in order to better understand the physical phenomena that appear in superfluid fluids and how they correlate with processability parameters such as viscosity and final mechanical properties.

Thermodynamic properties can be measured in a differential scanning calorimeter (DSC).

Higher liquid isothermal growth at progressive growth temperatures on the glass transition of the glass, an alloy is proposed in this study.

Materials, Procedures and Methods

Materials – A one-millimeter thick plate of Zr44-Ti11-Cu10-Ni10-Be25 (at.%) alloy (Liquid metal alloy LM001B from LiquidMetals Technologies Inc, Ca USA) was used in the thermo-calorimetric testing. The plate was cast on a commercial Engel injection molding machine operating at 1050-1100C.

Table 1: Isothermal DSC scans were run at the following temperatures

°C	°K
450,00	723,15
440,00	713,15
430,00	703,15
420,00	693,15
410,00	683,15
405,00	678,15
400,00	673,15

Procedures – A Mettler ADSC Differential Scanning Calorimeter was used in the dynamic and isothermal scans.

Dynamic DSC scan was run at heating rates of 1°K/min and 20°K/min on the as-received samples and glass transition and crystallization events were recorded. Thermal scans on the post-annealed samples (after DSC isothermal annealing) were run at 10°K/min

Isothermal DSC scans were run at the following temperatures (Table 1).

Aluminum pans containing 20-50 mg of Liquid metals glassy samples were inserted in the DSC at 200°C temperature and heated up to the annealing temperature at a rate of 50°k/min (no crystallization pecks were evident during the heating procedures). Samples were held for times varying from 30 to 300 min (depending on the annealing temperature) until no further exothermal events were recorded.

The initial fast heating step (3 min) and the signal transient zone have been omitted in the figure time scale.

Heating time has been considered in the calculation of the actual annealing time (Aversa *et al.*, 2015).

Results and Discussion

Dynamic DSC Temperature Scans on as Received Samples

A first DSC temperature scan at 1°K/min is shown in Fig. 7.

A glass transition relaxation is evident as a stage in the thermogram curve and takes place in the temperature range between 375° (Ti) and 390°C (Tf). The Tg glass transition temperature, defined by the similar phenomenon occurring in glassy polymeric materials, is the central point of this range (382.5°C). Above this glass transition, the metal metal cools down the liquid may undergo selective crystallization of larger mobility atoms. In transitions from high energy liquid to lower energy crystals, heat is released and exothermic crystallization peaks are observed. DSC Thermal Scanning of Fig. 2 showed a complex crystallization behavior in which, in fact, multiple crystallization peaks were observed.

The first crystallization, at this very slow heating rate, begins at 405°C, just above the end of the glass transition (Tf). The first observed peak has a complex shape with a major peak at 428°C and a shoulder at 417°C, which can be attributed to the overlapping of two different atomic atom atomization processes.

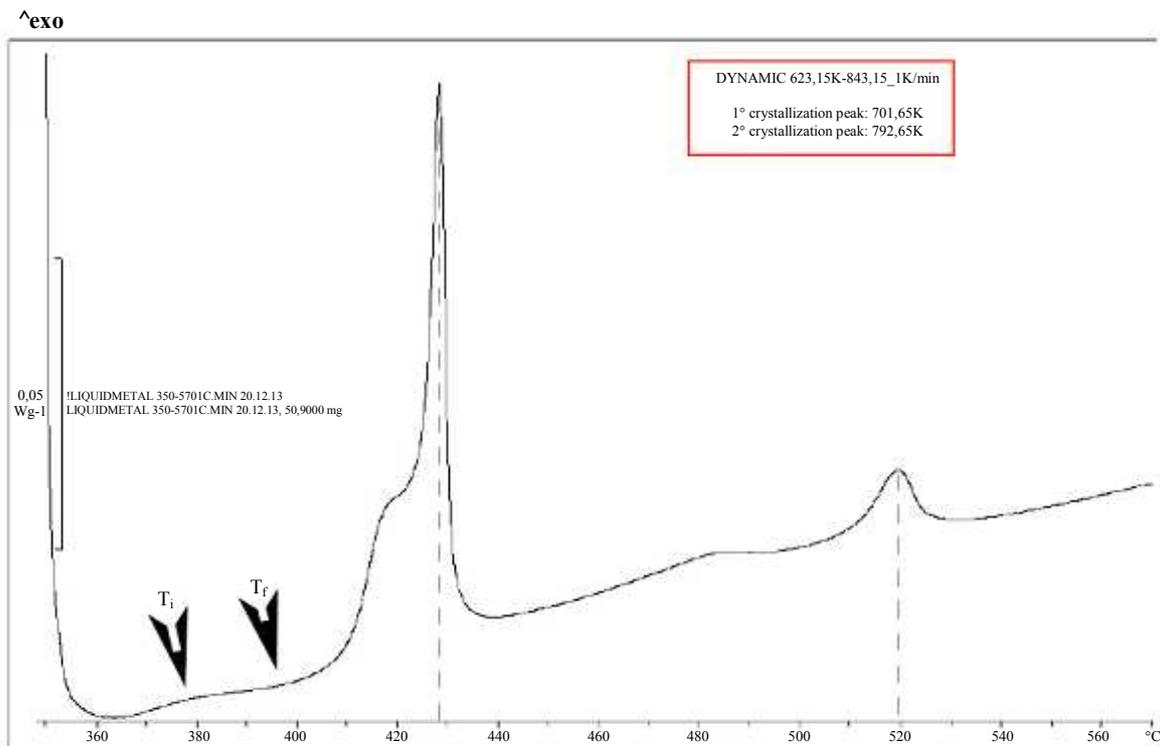


Fig. 7: DSC thermogram of $Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25}$ metal glass alloy: heating rate 1°K/min

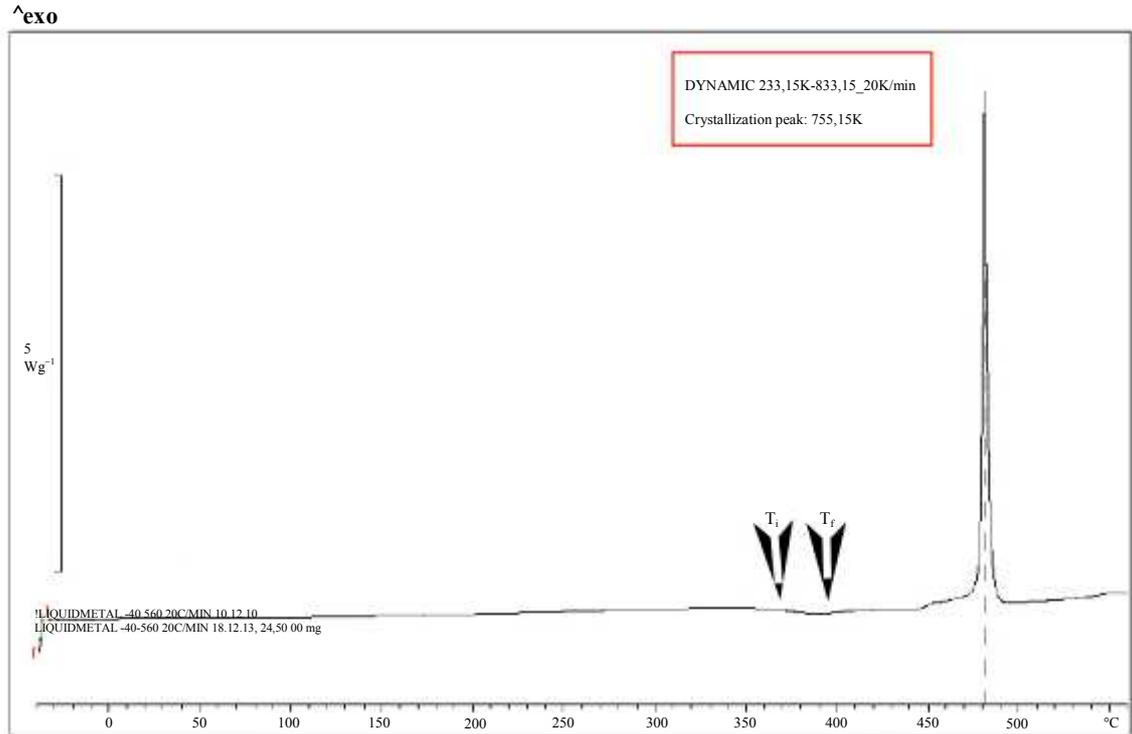


Fig. 8: DSC thermogram of $Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25}$ metal glass Alloy: heating rate 20°K/min

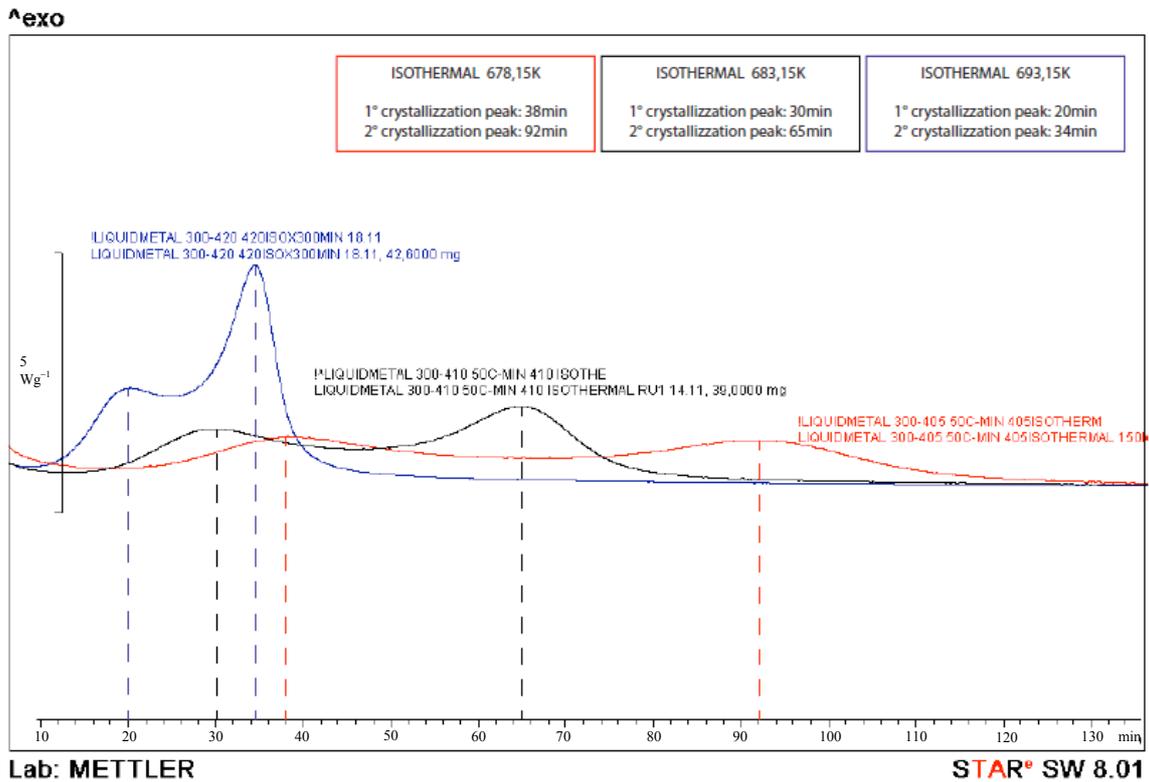


Fig. 9: Isothermal DSC annealing thermograms of $Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25}$ metal glass Alloy at 405°C (678,15°K), 410°C (683,15°K) and 420°C (693°K)

There are still two less intense crystallization peaks at 485°C and 520°C, respectively. Like the above, these events may be associated with the crystalline nucleation of smaller diffusion atoms and metallic mobility atoms. Probably beryllium and copper or nickel are smaller (atomic radii of 105, 145 and 149 respectively) at lower temperatures and zirconium and titanium (atomic radii 206 and 176 pm, respectively) at a higher temperature.

Figure 8 shows the thermogram of a DSC scanned operation just like the received glass alloy, but at a high heating rate of 20 K/min. Glass transformation is performed in the same test temperature range at 1 K/min, while crystallization in the superheated liquid begins at elevated temperatures and exhibits a seemingly less complex behavior. Previous authors (Schroers *et al.*, 1999) have found that a heating rate of about 200 K/s is sufficient to avoid crystallization at the temperature of the equilibrium fluid (melting of the alloy, i.e., 900-1000°C in our case).

Various critical heating rates for crystallization can be explained by the fact that the nuclei formed during heating are exposed to different thermal histories.

Isothermal DSC Annealing on as Received Samples

It is evident from the previous DSC dynamic investigation that only two atomic species present in the metastable liquid are involved in recrystallization process below 450-470°C. For this reason, isothermal annealing in the range of temperatures between 400° and 450°C has been chosen for further investigation on thermal events kinetics occurring in the super-cooled liquid.

Figure 9 compares the thermograms of isothermal DSC scans run at 405°, 410° and 420°C.

As previously assumed only two exothermic crystallization peaks characterize each isothermal annealing curve.

The thermogram reported in Fig. 9 for the isothermal sample of 405°C clearly shows two symmetrical peaks with peak peaks of 27 and 89 min. The peak peak could be taken as a measure of the kinetic moment of crystallization (half-time of crystallization). The positions of the first and second peaks on the annealing thermograms at 410°C are, respectively, at 27 and 62 min, while those for samples maintained at 420°C are respectively 17°C and 31 min. Table 2 summarizes the results of all 7 isothermal annealing tests performed in our study.

As expected from kinetic considerations, the higher the annealing temperature, the shorter the time it takes to complete crystallization. Since it has been reported in literature (Busch, 2000; Geyer and Johnson, 1995), effective diffusion of lower atoms at lower temperatures of overlapping metastases the liquid near the glass transition is higher than would have been expected if it had been follow the viscosity (Busch, 2000).

This means that, at low temperatures, broadcasting is no longer governed by the Vogel-Fulcher-Tammann (VFT) law, but by Arrhenius's law. The kinetic data for

cold crystallization of our metal alloy to form the glass were thus represented in Fig. 10 using the Arrhenius law representation. The first two separate crystallisation processes turn into high temperatures in one event. The kinetics of these two crystallizations is represented in the plot by two straight lines of different slopes.

The activation energies associated with the two crystallization processes are, respectively, -181 kJ/mol and -262 kJ/mol for the first time and for the second generation crystallization.

The first phenomenon of lower activation crystallization could be attributed to the higher mobility of Beryllium Atom, which is significantly lower than that of Nickel or copper (i.e., 105 vs. 147-149 pm).

Total heat of crystallization (first and second peak contribution) is H_c is 45.0 J/g (SD 5.5 J/g).

DSC Temperature Scan after Immersion

The passing of the cold glass transition could be changed by separating and losing small Be and Ni and Cu smaller atoms. A second dynamic DSC thermal scan was performed on isothermal alloy samples. Figure 11 shows thermograms of the hot scanned operation on the cooled alloy at 410°C (Fig. 9).

The glass transition behavior shown in the thermogram of Fig. 11 was significantly modified from that of the essentially amorphous samples essentially as described in Fig. 7 and 8. Selective crystallization of the higher mobility atoms of the annealing-induced alloy leads to an experimental observation of temperature rise induces relaxation of the bottle. More specifically, the transition start (T_i) is observed at 385°C instead of 375°C, while the transition end (T_f) moves from 390°C to 440°C. Relaxation and flow into a liquid have have been described as being worn by local elemental relaxation events during which atoms are removed from their position (LREs). The frequency of these LREs is accelerating with increasing temperature. Once the state of the overlapped liquid is reached by the glass starting material above 440°C, a new crystallization begins and an exotherm is observed on the thermal scan. The experimental high probe temperature actually activates the nucleation and crystallization of less mobility residual atoms (e.g., Zr and Ti) present in the metastable liquid state. The increase in the glass transition temperature range can then be attributed to the lowest diffusivity and hence high viscosity of the residual cooling agent.

Table 2: The results of all 7 isothermal annealing tests performed

°C	1 st $t_{1/2}$	2 nd $t_{1/2}$	H, J/g
450	5,5	5,5	50,3
440	8	10	39,7
430	10	18	37,0
420	17	31	56,1
410	27	62	47,8
405	35	90	45,0
400	47	131	40,0

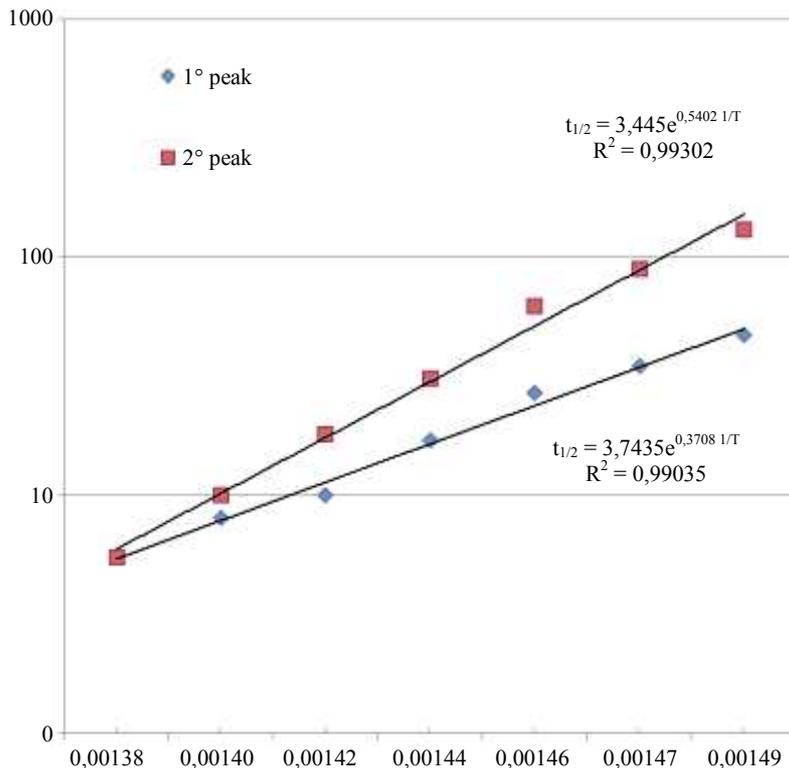


Fig. 10: Arrhenius plot of isothermal DSC half crystallization times of Zr₄₄-Ti₁₁-Cu₁₀-Ni₁₀-Be₂₅ metal glass Alloy in the temperature range 400-450°C

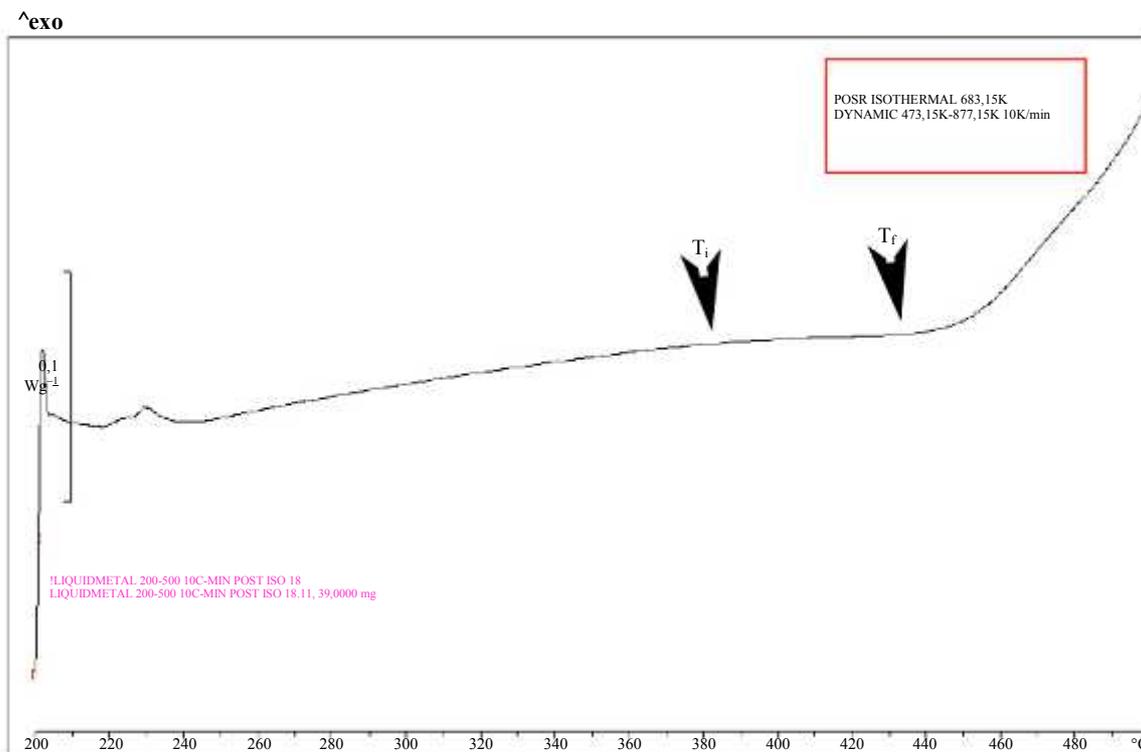


Fig. 11: DSC thermogram of Zr₄₄-Ti₁₁-Cu₁₀-Ni₁₀-Be₂₅ metal glass Alloy after isothermal annealing at 410°C: heating rate 10°K/min

Conclusion

Isothermal cycles of the metalized metallic alloy $Zr_{44}-Ti_{11}-Cu_{10}-Ni_{10}-Be_{25}$ (cold crystallization obtained by heating the glassy glass samples) were investigated in this study in the metastable state of the overheated liquid metal at elevated temperatures above the glass transition. Complex crystallizing behaviors with multiple and selective exothermic peaks crystallization of higher mobility atoms from an alloy induced by isothermal annealing have been observed to result in an experimentally observed increase in temperature required to induce glass metal relaxation (vitreous transition).

Dynamic DSC analysis indicated that only two atomic species present in the metastable liquid are involved in the recrystallization process below 450-470°C. Isothermic isolation in the temperature range between 400° and 450°C was chosen for subsequent investigation of the thermal kinetics occurring in the supercooled chilled liquid. The activation energies associated with the two crystallization processes are, respectively, -181 kJ/mol and -262 kJ/mol.

Due to recent advances in BMG alloys and thermoplastic casting, some BMG wagons can be considered as high strength alloys that can be processed as plastics.

The processing of metallic glasses in bulk by thermoforming requires a deeper understanding of the physical phenomena occurring in the metastable overload condition.

Plastification of an alloy that forms BMG in the supercooled liquid region can then be used for thermoplastic formation.

The metal bottle can be reheated from the state of glass and modeled in the temperature zone in which the bottle relaxes in a metastable before the atoms crystallize.

However, selectively the crystallization of the upper alloy movement and the lower diffusion atoms can induce an unwanted increase in viscosity and not a homogeneous flow in the molten liquid matrix.

The data presented in this paper describe some of the thermal events that can alter the glass transition and the mechanical properties of the thermoformed BMGs.

The glass transition behavior shown in the thermogram of Fig. 11 was significantly modified from that of the essentially amorphous samples essentially as described in Fig. 7 and 8.

Selective crystallization of the higher mobility atoms of the annealing-induced alloy leads to an experimental observation of temperature rise induces relaxation of the bottle.

More specifically, the transition start (Ti) is observed at 385°C instead of 375°C, while the transition end (Tf) moves from 390°C to 440°C. Relaxation and flow into a liquid have been described as being worn by local elemental relaxation events during which atoms are removed from their position (LREs).

The frequency of these LREs is accelerating with increasing temperature. Once the state of the overlapped liquid is reached by the glass starting material above 440°C, a new crystallization begins and an exotherm is observed on the thermal scan.

The experimental high probe temperature actually activates the nucleation and crystallization of less mobility residual atoms (e.g., Zr and Ti) present in the metastable liquid state.

The increase in the glass transition temperature range can then be attributed to the lowest diffusivity and hence high viscosity of the residual cooling agent.

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Author's Contributions

All the authors contributed equally to prepare, develop and carry out this manuscript.

Ethics

This article is original and contains unpublished material. Authors declare that are not ethical issues and no conflict of interest that may arise after the publication of this manuscript.

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