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THE AGING OF SOME METAL DOPED As_2S_3 GLASSES

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It is shown that powdered glassy samples of Sn, Ag and Cu doped As_2S_3 exhibit a partial crystallization after twenty years of storage in ambient conditions. The crystalline phases are AsS and sulphur but also some As_4S_3 and traces of As_2O_3 were revealed on X-ray diagrams of tin doped glasses. The separation of AsS was evidenced on the surfaces of diamond-cut As_2S_3 samples. No crystallization was observed in glassy ingots.

The need for new recording media and for optical fibers stimulated the study of As_2S_3 glassy materials which show important photostructural transformations [1]. The influence of the metal introduced in glassy chalcogenides was studied in order to fiind new materials with interesting properties for applications. Many years ago Andreichin et al. [2] have shown that concentrations of silver as much as x=0.06 in the bulk glass $As_2S_3Ag_x$ bring about a decrease of electrical resistivity of approximately forty times as compared to the pure As_2S_3 glass.

The development of many optical and optoelectronic devices [3] raised the question of the stability of the glasses against aging in ambient atmosphere.

For the purpose to gain new insight into the aging phenomenon we performed X-ray investigations on some metal doped As_2S_3 glasses in bulk, powdered and diamond-cut state after very long storage.

The investigated glassy samples of compositions $As_2S_3Sn_x$, $As_2S_3Ag_x$ and $As_2S_3Cu_x$ were prepared in the Institute of Physics, Sofia, starting from As 99.9998% purity, semiconducting purity sulphur, 4n purity tin and spectral purity silver and copper by heating the appropriate mixtures of element sat 900 ^oC and then cooling the melts in 12h [4].

In order to check by X-ray diffraction the glassy state, samples were prepared from glassy chunks using the mortar and pestle method. The powders were pressed in special supports and were measured in a Siemens Kristalloflex IV diffractometer provided with copper target tube.

No crystalline inclusions were revealed in the fresh samples up to a certain limit of metal concentration: 2.5 at% Sn, 12 at% Ag and 4 at% Cu in As_2S_3. The crystalline phases observed in the partially crystalized compositions were SnS_2, Ag_3AsS_3 (xanthoconite), Cu_3AsS_4 (lizonite) and AsS (realgar) [5].

The powdered glassy samples were stored at ambient temperature (the maximum reached in summer was 40 ^oC) for 20 years. After this long storage we have again measured their diffraction patterns.

$As_2S_3Sn_x$ (x=0.026; 0.10)

Two samples of As_2S_3 with 0.5 at% Sn and 2.0 at% Sn were investigated. Both samples show crystalline phases identified on the basis of narrow peaks superposed on large maxima characteristic to glass. The samples rich in Sn show a more advanced crystallization. AsS, As_4S_3 and some As_2O_3 (claudetite) were revealed. Sulphur appears in the monoclinic form, seggregated on the grain surface, as confirmated by optical microscopy.

$As_2S_3Ag_x$ (x=0.038; 0.21; 0.32)

Three samples with 0.75 at% Ag, 4.0 at% Ag and 6.0 at% were investigated. The crystalline phases

are AsS and sulphur. As the silver content increases the separation of the crystalline phases is inhibited.

The investigated sample $As_2S_3Cu_x$ (x = 0.038) contained 0.75 at % Cu. The crystalline phases identified by X-ray diffraction were AsS and sulphur.

The aging process in chalcogenide glasses can be ascribed to the combined action of temperature and ambient atmosphere. The specific behaviour of the compositions with tin is probably due to the formation of SnS_2 structural units.The glassy matrix will be thus depleted in sulphur. As_2S_{3-2x} is less stable and crystallization of dimorphite (As_4S) will be facilitated. At a later stage the combined action of oxygen and water vapour on arsenic will produce claudetite (As_2O_3) (the reaction of arsenic with oxygen is catalysed by the water vapours from the ambient atmosphere [6]).

In Ag doped samples the separation of realgar is more efficient for low silver concentration. For high Ag concentrations both AsS and S phases diminish due presumably to the stabilizing role played by the numerous structural units of Ag_3AsS_3 and Ag_2S against the As_2S_3 decomposition. The Ag_2S structural unit was suggested on the basis of the radial distribution curves of the glassy samples [7] which revealed a considerable amount of atomic pairs situated at 0.275 nm, ascribed to Ag-S distances characteristic to the Ag_2S compund.

An interesting observation is related to the aging effect induced by cutting. A piece of As_2S_3 glass has been cut by a diamond disk and then stored for 20 years. The sample has been studied in the optical microscope. The surface of the sample, abraded during cutting shows a turbid film of red colour spots due to small crystallite realgar (aurora red). The bulk glassy samples and the normal fracture surfaces do not show any trace of crystallization or phase separation.

In conclusion, the aging of metal doped As_2S_3 glass consists mainly in decomposition and crystallization of some phases. The aging is effective in mechanically processes samples and is accelerated in powders.

The combined action of oxigen and humidity gives rise to a complex process of chemical and physical modifications which must be taken into account in the case of long time use in electronic devices.

The alloying by metals can promote or diminish the aging process as a function of type and concentration of the metallic elements.

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