SOME CONSIDERATIONS ABOUT IMPACT OF LEAD-FREE LEGISLATION ON ELECTRONIC INDUSTRY

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Significant difficulties have recently appeared in the choice of development strategy for various areas of solid-state electronics industry connected with coming into force on July 1, 2006 of DIRECTIVE 2002/95/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUCIL of January 27, 2003. Many rather powerful and law obedient companies refuse to develop electronic devices on the basis of semiconductors with compositions containing the chemical elements listed in this Decision and have heavy losses, because in other parts of the world other companies perceive this law differently. Using the experience in investigation of heavy metals based semiconductor compounds during about 40 years, the author expresses his opinion about separate aspects of this law concerning mainly lead-based compound application in solid-state electronics production. The task of this article is to draw attention of experts in this domain, to use common efforts for developing scientifically proved approaches in application of the given law concerning the problems of each concrete case.

The European legislation requires manufactures to reduce the disposal waste of electronic products by reuse, recycling, and other forms of recovery. For enhancement of these possibilities, elimination of certain hazardous materials from the electrical and electronic equipment was proposed under the supplementary directive (Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 "On the restriction of the use of certain hazardous substances in electrical and electronic equipment") [1]. According to Article 4(1): "Member States shall ensure that, from July 1, 2006, new electrical and electronic equipment put on the market must not contain lead, mercury, cadmium, hexavalent chromium…". According to Annex of Article 4(1), page L37/23 "Applications of lead, mercury, cadmium, and hexavalent chromium, which are exempted from the requirements of Article 4(1)" we can see (p. 5 – p. 7) that concerning lead in this list it is considered basically a lead as an alloying element in steel (up to 0,35 %), aluminum (up to 0,40 %), copper alloy (up to 4%) by weight and different lead-based solders are also considered. Thus, according to P. N7, for some uncertain reasons, high melting temperature solder alloys containing more than 85% lead are of priority in comparison with solder alloys containing less than 85% lead.

It is well known that lead-based solders, as well as many other solders, represent eutectic alloys. By definition, the eutectic alloy is a mechanical homogenized mixture of two or more phases. Indeed, working with traditional eutectic Pb-Sn alloy or with other lead-based solders, atoms of lead can easily penetrate into to human organism if the safety requirements are not respected. From such eutectic alloys lead atoms can become free rather easily and can interact with other elements forming harmful compounds. In this connection, much new solders are already offered for replacing traditional lead-based solders. From this point of view, the Legislation's approach relatively lead-based solders is scientifically proved. However, it is not correct to transfer automatically the restrictions stipulated by Directive 2002/95/EC concerning lead-based solders (eutectic alloys) to components of solid-state electronics based on lead compounds. During last years it became especially fashionable to make political career on ecology problems. Within this context, it is pertinent to remind that we eat salt every day (NaCl) and, in essence, we eat the atoms of Na and Cl, which are connected in molecules by strong ionic bonds. However, we even do not think about individual properties of Cl and Na atoms because we deal with another substance. NaCl is an absolutely other substance with completely different properties.

In the most part of solid-state electronic devices lead as an individual chemical element is not applied. In the most part of solid-state electronic devices, including infrared technique and thermoelectricity, the lead-based compounds PbTe, PbSe, PbS and their alloys are used. Lead is fastened by strong chemical bonds so strongly in these compounds, that even at temperatures exceeding the melting temperature these compounds weakly dissociate. This concept can also be distributed, to a certain extent, to other semiconductor compounds such as GaAs, CdTe, CdSe, etc. widely used in electronic industry. So, the restrictions related to lead application stipulated in decision 2002/95 ES cannot be automatically imposed to lead chalcogenide compound applications.

From the ecological point of view, the restrictions concerning the application of hazardous chemical elements should be taken into account in what form the given element is present in this electronic equipment: pure state, eutectic alloy, solid solution alloy or in the structure of a compound. So, the restrictions related to lead application stipulated in decision 2002/95 ES are not scientifically proved to be imposed as restrictions for lead chalcogenide compounds. The authors of the given law should consider this objective truth because, naturally, these Legislations could impact different industry sectors and product categories.

Significant difficulties in the choice of developing strategy have already appeared in various domains of solid-state electronics industry connected with this law. Many investigation centers and companies refuse to develop electronic devices on semiconductors with chemical elements listed in this Decision and suffer grate losses because other companies perceive this law differently. Lack of proved scientific approach in such questions generates double standards and speculations around this problem.

Restrictions related to lead application stipulated in Decision 2002/95 ES cannot be imposed to lead chalcogenide compounds for the reasons of having exclusively a fundamental character. Decision 2002/95/EC contains legal norms, which provide such cases. In point N11 on p. L37/20 is specified: “Exemptions from the substitution requirement should be permitted if substitution is not possible from the scientific and technical point of view or…”.

Indeed, a full refusal of some components of solid-state electronics, which contain heavy elements including hazardous ones, is not real due to several fundamental reasons.

It is impossible to obtain bulk narrow band semiconductor necessary in infrared technique on light elements. Therefore, we will have to work with alloys of PbTe-SnTe and CdTe-HgTe systems for a long time. Unfortunately, existing problems of IR-technique by doping Si, Ge, and other semiconductors cannot be solved.

It is well known that high efficiency of thermoelectric conversion $Z = S^2\sigma/(K_L + K_e)$ can be achieved by using materials with a high Seebeck coefficient S, high electrical conductivity σ, and low thermal conductivity $K = K_L + K_e$ (K_L is the lattice thermal conductivity; K_e is the thermal conductivity due to charge carriers) Traditionally, there are two basic ways of increasing thermoelectric material efficiency. One of the ways is to increase Z by minimizing K_L. For these tasks, first of all, heavy constituent atoms are required. The other way is to increase the power factor $S^2\sigma$ without increasing the total thermal conductivity K. The values of S, σ, and K_e determining the figure of merit Z are strongly interconnected with each other, because all of them are the function of temperature T and carrier concentration n. Due to different nature of the dependences S=f(n, T) and σ=f(n, T) for obtaining of a larger power factor

$S^2\sigma$ a compromise is necessary between values of thermopower S and electrical conductivity σ. High value of Seebeck coefficient, in its turn, requires the multivalley nature of energetic spectrum of charge carriers. For the latter it is necessary to have a great value of spin-orbital interaction parameter Δ. Large value of Δ-parameter can be realized only in phases formed on the basis of heavy atoms.

For more than 50 years lead chalcogenides have been among the best thermoelectric materials [2] for working temperatures in the range 500-900 K and have been widely applied in power generation from heat sources. High value of thermoelectric figure of merit in lead chalcogenides is conditioned by their unique favorable set of important parameters and characteristics:

– multi-valley nature of energetic spectrum of charge carriers;
– low value of lattice thermal conductivity caused by heavy atoms which form these phases;
– high mobility of carriers at high doped level caused by low scattering efficiency on electrical centers because of high static electrical permittivity;
– positive sign of thermal coefficient of band gap; due to it the contribution of intrinsic conductivity, sharply declining figure of merit Z, appears at a higher temperature.

As these parameters are unique it is necessary to enlarge the number of such materials; this has been a dream of researchers for more than 50 years. Late results in this area surpassed all our expectations. Some alloys of $AgSbTe_2$ - PbTe system at appropriate doped level exhibit [3] a record-breaking high value of thermoelectric efficiency (ZT~2,2 at 800 K) that outperform all reported bulk thermoelectrics. It is necessary to note that for more than 50 years this value has not exceeded unity.

The legislation norms limiting the presence of lead in solid state electronic products are caused mainly by requirements of environmental safety of reuse, recycling, and other forms of recovery processes of electronic lead-based products waste. Adopting such laws, experts should take into account the technical opportunities of such recovery processes and their ecological after-effects. In this connection, restrictions stipulated by law 2002/95/EC should not concern application of lead chalcogenide compounds PbTe, PbSe, and PbS in manufacture of thermoelectric power generators. First, thermoelectric modules are the simplest electronic devices; therefore, reusing of a thermoelectric material in this case is not a problem. Second, today thermoelectric modules are the most reliable and durable devices due to highly doped semiconductors applied for their production

Prevalence of respective elements in the earth's crust is another problem to think at developing similar laws and it is especially important for thermoelectric device manufacture. It is important to mention that in thermoelectric modules the amount of a used thermoelectric material it is comparable to the weight of the device itself. Consequently, it becomes a sharp problem to replace such expensive and not widely spread components as Bi, Se, and, especially, Te by cheaper ones. In conformity with results of the analysis carried out in [4], the stocks of lead and antimony and their manufacture are significant. According to [5, 6], alloys on the basis of galena (PbS), stibnite ($CuSbS_2$), and other similar minerals, which are abundant in the earth's crust can appear promising as thermoelectric materials.

So, there are all scientifically proved motivations and legal rights (item N11 of Decision 2002/95/EC) to investigate and develop manufacture of new electronic components based on lead chalcogenide compounds PbTe, PbSe, and PbS. Taking into account that lead is considerably inferior to the rest of the elements marked in Decision 2002/95 ES in respect of toxicity, this is especially justified.

References

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