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**Abstract**
Recently we have observed that porous CsI prepared by thermal evaporation
spontaneously loses its polarization faculty with the elapse of time. In this
paper the phenomenon of spontaneous polarization faculty loss (SPFL) of
porous CsBr is investigated and compared with that for porous CsI under
the same experimental conditions. It is assumed that the SPFL phenomenon
can be explained by structural modification of these porous materials after
evaporation as well as by the decrease of their forbidden zone—analogously
to crystallization of Ge amorphous thin films prepared by vapour deposition
and carbon nanotubes, respectively.

It has been known for a long time that some dielectrics such as KCl, CsI and MgO that have
a porous structure are characterized by high-gain inertial electron multiplication in an electric
field of positive charges accumulated on their surface (Molter effect) [1–8]. It was found in
1972 that in these dielectrics, under the influence of an external electric field, a controllable
effective drift and multiplication (CEDM) of electrons takes place [9–11]. However, as a
result of the polarization of porous active dielectric materials, the CEDM process becomes
noticeably suppressed and unstable [12–17]. Nevertheless, recent detailed investigations have
shown that these effects take place for a time after preparation of porous CsI, and then CEDM
spontaneously exhibits a high stability and good space localization, i.e. porous CsI does not
display any signs of polarization [18–20]. In other words, this material loses its polarization
faculty spontaneously. It was also shown that when the porous CsI was kept after preparation
at a temperature of $18\,^{\circ}$C, the spontaneous polarization faculty loss (SPFL) phenomenon took
place within a time $t_p$ of a few hours, whereas at $T = 31\,^{\circ}$C, $t_p$ was at most 1 h [20].
It is very important that after attaining the above mentioned changes, porous CsI does not
acquire a polarization faculty regardless of whether or not it is under voltage and/or ionizing
radiation and independently of temperature. Thus, immediately after manufacture of porous
CsI, accumulation of charges starts inside this material in the process of CEDM, but then these
polarization charges spontaneously vanish with time and do not accumulate again.
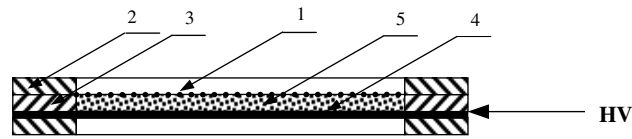
**Figure 1.** Schematic view of the cluster detector: 1, anode wire; 2, fibreglass laminate frame; 3, frame that determines the cluster detector's gap; 4, Al cathode; 5, porous layer.

Later, Chianell *et al* [21] investigated CEDM and its structure in porous CsI. They revealed that the structure of porous CsI took the form of whiskers 10–50 nm in diameter. The results of [21] have opened some opportunities to explain the SPFL phenomenon in porous CsI in terms of nanophysics. In this connection, among the most interesting properties of carbon nanotubes is a relationship between their geometrical structures and electric characteristics [22, 23]. For example, the conductivity of carbon nanotubes could be of both metallic and semiconductor type and the width of the forbidden zone of semiconductor nanotubes depends on their geometrical parameters [24]. Also, carbon nanotubes are highly effective electron emitters [25, 26].

It is well known that secondary electron emission (SEE) occurs at or close to the surface of materials, and, as a result, is very sensitive to the surface properties of emitters. Because the surface-to-volume ratio of nanoparticles is very large, a significant fraction of atoms or ions lie on or close to the surface. Therefore, for nanostructure materials, boundary and surface effects play a major role in SEE. Consequently, investigations of CEDM in nanostructure materials are valuable from both scientific and practical viewpoints.

From the preceding, it is most probable that the SPFL phenomenon taking place in porous CsI (prepared by thermal evaporation) occurs due to its structural modification after evaporation. Note that crystallization of Ge amorphous thin films prepared by vapour deposition was achieved earlier, both upon the deposition on appropriately heated substrates and after the deposition by annealing at elevated temperatures [27]. Taking into account also the possibility of decreasing the forbidden zone of porous CsI analogously to the case of carbon nanotubes, we believe that it is possible to explain the SPFL phenomenon.

As a method for the investigation of the SPFL phenomenon, the CEDM of electron clusters was used. The cluster detector used is presented schematically in figure 1. It consists of an anode (1) made of a gold plated wire (25 $\mu$m in diameter) stretched over an insulator frame (2), a 0.5 mm thick insulator spacer (3) which determines the gap between the anode and the cathode, a cathode (4) made of 60 $\mu$m Al, and a porous active material (5) that fills the gap between the anode and the cathode. An electric field is applied between the anode and the cathode. 5 MeV $\alpha$-particles enter into the porous medium from the anode wire side, pass through the porous dielectric and create ionizing electron clusters in the porous medium. The cluster electrons are accelerated in the pores by the applied electric field. The accelerated electrons produce new secondary electrons in the pore walls. This process takes place for all generations of secondary electrons, and if the average number of secondary electrons emitted after the wall impact of each electron is more than one, an avalanche multiplication of electrons arises. So, electron clusters move to the anode wire and accumulate on it. We had no possibility of measuring the fraction of secondary electrons participating in the drift process.

The porous layers are prepared by thermal deposition of CsI or CsBr placed in a tantalum boat in a low pressure Ar atmosphere [20]. First, the boat was chemically cleaned. The relative density of the CsI and CsBr layers just after deposition was $\rho_{rel} \approx 0.4\%$. This density was obtained for an Ar pressure $p = 3$ Torr at a distance $H = 6.5$ cm between the boat and

substrate and a deposition rate of 56 $\mu$m min$^{-1}$. The accuracy in determining $\rho$ was 12%. The thickness $L$ of the porous layer immediately after the deposition was 0.8 mm $\pm$ 50 $\mu$m, and the non-uniformity of $L$ over the whole area did not exceed the measurement accuracy of 50 $\mu$m. As the gap between the anode and cathode is 0.5 mm, after assembling the device the porous layers were compacted by a factor of 1.5–2.

In our experiments commercially available CsI and CsBr were used with unknown impurity contents. Also, we did not measure the dimensions of the pores or the thickness of the inter-pore walls. To provide high technological purity, all parts of the device were given a preliminary chemical clean, repeatedly washed in distilled water and dried at room temperature.

When in contact with air the emission properties of porous layers deteriorate with time. To exclude such changes, after filling with porous material the cluster detector was assembled in a box filled with Ar, and then quickly moved to the experimental device and installed in its vacuum chamber. The vacuum chamber, first filled with argon, was then brought rapidly to a vacuum of $\approx 7 \times 10^{-3}$ Torr, and the measurements were started.

The number of clusters in which the number of electrons $N_e$ is higher than the threshold of registration $N_o$, was counted. The beam of $\alpha$-particles was not collimated. To determine the transverse dimension of the clusters, the anode wires were divided into two groups. The first group included even-numbered and the second group odd-numbered anode wires. Anode wires in each group were connected with each other, and the number of separately amplified signals from each group was counted. Both $N(s)$, the number of clusters detected by one wire of the anode wire groups, and $N(c)$, the number of clusters detected simultaneously by two adjacent wires of both anode wire groups, were counted. The total number of detected clusters is $N(s + c) = N(s) + N(c)$. It is clear that when the transverse dimension of the electron cluster is much smaller than the distance between the wires, $b$, most clusters are registered by a single anode wire (by one group), i.e. $N(c) \ll N(s + c)$, and the parameter $S_s = N(c)/N(s + c) \ll 1$. When the transverse dimension of an electron cluster is more than $b$, most of the clusters simultaneously registered by two adjacent anode wires (by both groups) are counted, $N(c) \approx N(s + c)$, and $S_s \approx 1$. In our method, $N_o = 10^4$ and $b = 250$ m. The measurements were repeated many time for both the same detector and other similar ones, and the obtained results were the same within 10–15% accuracy.

In recent work [20], the SPFL phenomenon for porous CsI kept after preparation at temperatures of $T = 18, 20, 24$ and $31\,^\circ$C was studied. In all experiments carried out at $T = 18, 20, 31\,^\circ$C, CsI was 99.99% pure, and in the experiments carried out at $T = 24\,^\circ$C, CsI was 99.999% pure. In this paper, the SPFL properties for porous CsBr and CsI kept after preparation at $T = 24\,^\circ$C and for porous CsI kept at $T = 15\,^\circ$C, are presented. All these materials were 99.99% pure.

Figure 2 presents the dependences of the total number of registered clusters $N_{cl}$ $(N_e \geqslant k)$, white circles, and the number of clusters with $z \geqslant \delta$, $N_{cl}$ $(z \geqslant \delta)$, black circles, with an applied voltage $V$, obtained in 1 h after deposition of porous CsBr. The experiment lasted 18 min. It is seen that both $N_{cl}$ $(N \geqslant k)$ and $N_{cl}$ $(z \geqslant \delta)$ increase with the increase of $V$. The increase of $N_{cl}$ $(N \geqslant k)$ is due to the fact that the secondary electron emission factor is directly related to the electric field [28], and the increase of $N_{cl}$ $(z \geqslant \delta)$ shows that the cross dimension of the electron shower $z$ is also increased.

In order to understand how the observed effects depend on time, the stability of CEDM was studied immediately after finishing the preceding measurements (see figure 3: $N_{cl}$ $(N \geqslant k)$, white circles; $N_{cl}$ $(z \geqslant \delta)$, black circles). These measurements have shown that from the beginning, CEDM is stable ($N_{cl}$ $(N \geqslant k)$ is constant), and the spatial localization of secondary electrons is poor ($S_s$ is about 0.6), but afterwards the latter improves somewhat and $S_s$ becomes 0.25. The measurements carried out the next day demonstrate that stability of $N_{cl}$ $(N \geqslant k)$ is
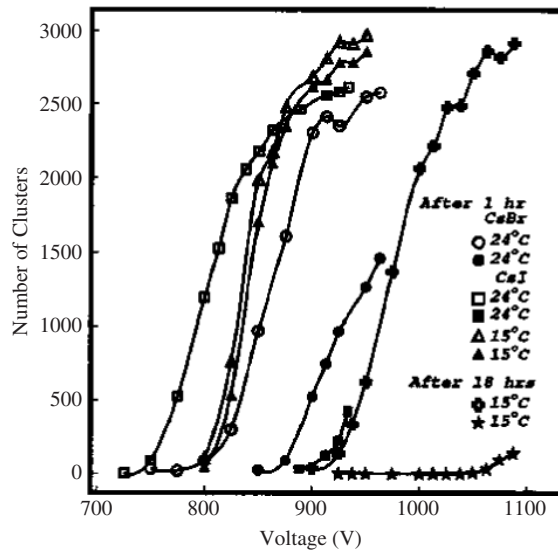
**Figure 2.** Dependences of the number of registered clusters $N_{cl}$ ($N \geqslant k$), unshaded symbols, and the number of clusters with $z \geqslant \delta$, $N_{cl}$ ($z \geqslant \delta$), shaded symbols, versus the applied voltage $V$ for porous CsBr, kept at $T = 24\,°C$ for 1 h after preparation. $N_{cl}$ ($N \geqslant k$), crosses, and $N_{cl}$ ($z \geqslant \delta$), stars, were obtained for porous CsI kept at $T = 15\,°C$ for $t_p = 1$ h and $t_p = 18$ h after preparation.
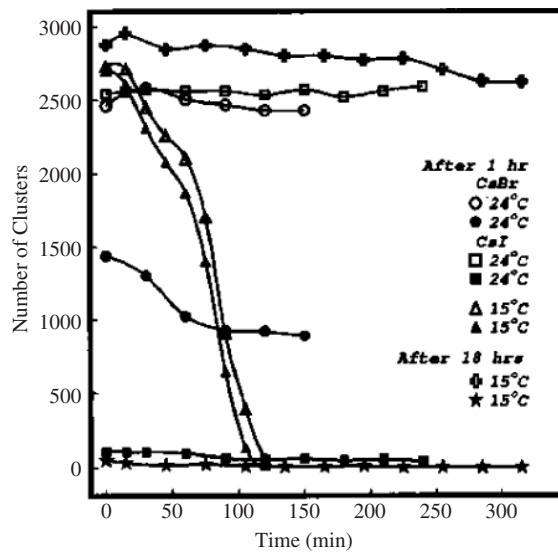


**Figure 3.** Time stability of the number of registered clusters of $N_{cl}$ ($N \geqslant k$), unshaded symbols, and number of clusters with $z \geqslant \delta$, $N_{cl}$ ($z \geqslant \delta$), shaded symbols, at various temperatures for porous CsBr and CsI kept at $T = 24\,°C$ for 1 h after preparation. $N_{cl}$ ($N \geqslant k$), crosses, and $N_{cl}$ ($z \geqslant \delta$), stars, were obtained for porous CsI kept at $T = 15\,°C$ for $t_p = 1$ h and $t_p = 18$ h after preparation.

maintained at the same level as in the beginning, but the improvement in spatial localization of CEDM is continued with $S_s$ reaching 0.2 (in 16 h). This means that the improvement in CEDM spatial localization is continued without applied voltage.

The $V$ dependence and time stability measurements carried out repeatedly on a daily basis over a period of 11 days with 18 h interruptions have shown that the CEDM process is always quite stable, but its spatial localization only becomes stable after 2 days. In the context of the SPFL phenomenon, all obtained results indicate that the porous CsBr kept at a temperature of $T = 24\,°\text{C}$ for 1 h immediately after preparation still had some polarization faculty, which reduces in a given time.

To compare more accurately the SPFL properties of porous CsBr and CsI under the same conditions, we studied CEDM in porous CsI of the same purity (99.99%) and at the same temperature $T = 24\,°\text{C}$. The $V$ dependences of $N_{cl}$ ($N \geqslant k$), white squares, and $N_{cl}$ ($z \geqslant \delta$), black squares, are also presented in figure 2. Experimental results have shown that at $T = 24\,°\text{C}$, CEDM in porous CsI takes place mainly in the same manner as in porous CsBr, but as distinct from porous CsBr, the spatial localization of CEDM in porous CsI is already quite stable from the very beginning (see figure 3: $N_{cl}$ ($N \geqslant k$), white squares; $N_{cl}$ ($z \geqslant \delta$), black squares). Thus, by an hour after preparation, the density of polarization charges in porous CsI is substantially less than that in porous CsBr. Hence, taking into account the results of [20], we state that by an hour after preparation of porous CsI at $T = 24\,°\text{C}$, as in the case of $T = 31\,°\text{C}$, this material loses practically all of its polarization faculty, while under the same conditions, porous CsBr loses all of its polarization faculty in about 24 h.

CEDM investigations in porous CsI kept for 1 h after preparation at $T = 15\,°\text{C}$ have shown that, as in the case of $T = 18\,°\text{C}$ [20], in the beginning CEDM is unstable and has poor space localization, but in a few hours it becomes quite stable and spatially localized (see figures 2 and 3: $N_{cl}$ ($N \geqslant k$), unshaded triangles, and $N_{cl}$ ($z \geqslant \delta$), shaded triangles, for 1 h, and $N_{cl}$ ($N \geqslant k$), crosses, and $N_{cl}$ ($z \geqslant \delta$), stars, for 18 h). Thus, we can conclude that in porous CsI kept after preparation for 1 h at $T = 15\,°\text{C}$, polarization charges accumulate as a result of CEDM under the effect of electric field and ionizing radiation, but then in the course of time these charges spontaneously vanish and thereafter do not accumulate again.

Note that the available experimental data are insufficient for a final quantitative interpretation of this SPFL phenomenon, and further experimental and theoretical studies should allow the use of dielectrics in those fields of science and engineering where they have not been traditionally applied.

## Discussion

Secondary electron emission have great technological and scientific applications, and the search for new highly effective secondary electron emission materials is a very important area. In this respect, nanostructured materials can have a great potential. At present it is known that carbon nanotubes have a high auto electron emission coefficient [26, 27], and nanostructured porous CsI is characterized by extremely high secondary electron emission [10, 11]. These new characteristics of nanosized objects are related to the fact that when the object size approaches the free-path length, de Broglie wavelength or other parameters characterizing electrons in an electron gas, the properties of these objects become dependent on their sizes, and quantum effects appear. These quantum effects change the generation and transfer mechanisms of the charges. The tunnelling effect and decrease of the carbon nanotube forbidden zone [24] are examples of this. Due to these effects, the conductivity of nanostructured materials is increased and the polarization properties of such media are changed too. Possibly, the SPFL phenomenon observed by our team is also related to these quantum effects. We think that further more detailed experimental and theoretical studies of the SPFL phenomenon should allow the use of dielectrics in those fields of science and engineering where they have not been traditionally applied.

## Conclusions

The presented results show that porous CsBr loses its polarization faculty analogously to porous CsI. The authors believe that this phenomenon can be explained within the framework of nanophysics. It is obvious that for more complete understanding of SPFL it is necessary to study other porous dielectrics too.

## Acknowledgments

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