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Heat enhancement of the photoyield from CsI, NaI and CuI photocathodes

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Abstract

We revise the quantum yield of NaI and CuI photocathodes. We have shown that the photoyield from NaI and CuI can be considerably enhanced by a post-evaporation heat treatment, similarly to that observed before for the CsI photocathode. We discuss possible reasons for the heat enhancement.

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Solid photoconvertors coupled to gaseous electron multipliers [1, 2, 3] have important potential applications in the field of photon imaging. Most important applications are in RICH detectors [4] and in the readout of gaseous [5] and solid [6] scintillators.

Of all solid UV photocathodes stable in gas media, CsI is known to have the highest quantum yield (QY) [7]. Other possible candidates, like alkali halides or CuI, were reported to have much lower QY [8, 9, 10]. It has been recently found [11] and further confirmed [12, 13] that the heating of the CsI photocathode for few hours at 50-90 °C at high vacuum following its preparation, is a key element for reaching and stabilizing this high QY value. It was also found that CsI photocathodes, heat-enhanced immediately after evaporation, are much less sensitive to exposure to humidity [14]. The success of this procedure was recently confirmed on large area pad electrodes for RICH [15]. However it should be noted that the mechanism of the heat enhancement is still unclear and is subjected to systematic studies.

In this letter we revise the photoyield from NaI and CuI photocathodes. We have found that the post evaporation heat treatment of these photocathodes results in a dramatic increase of the quantum yield, similar to that observed for CsI [13, 14]. We show that the QY of NaI and CuI can reach much higher values compared to that previously reported.

The experimental setup consists of a high vacuum (1×10^{-7} Torr) evaporation chamber coupled to a vacuum monochromator. After preparation, the photocathode is characterized in the same vacuum chamber without contact to air. Photocathodes were evaporated from Ta or Mo boats on polished stainless steel substrates. Heating of the substrate in the temperature range 50-90 °C was performed *in situ*, in vacuum, with the help of a water heat-exchanger. In this case the sample had no contact to air. Whenever the sample had to be heated up to temperatures higher than 100 °C, it was transferred through ambient air to another small vacuum chamber, where it was heated by a halogen lamp from its back side. Afterwards it was retransferred back to the main vessel for characterization. More detailed description of the setup and of the procedure can be found elsewhere [16, 17].

Fig.1 shows the results of the heating procedure applied to CsI, NaI and CuI photocathodes. Fig.1a shows the QY spectra of a 4000 Å thick CsI film evaporated on a stainless steel substrate with a 500 Å thick Al layer. The QY was measured immediately after preparation, after 15 hours of heating at 50 °C and after further heating at 165 °C. In the latter case the photocathode was kept at the maximum temperature of 165 °C for half an hour and then gradually cooled down to 70 °C during 3 hours. The results of the heat treatment of CsI at 50 °C have been currently reproduced on tens of samples. One generally observes a saturation of the QY after heating for 3-4 hours if the evaporation chamber is clean enough, and after 15-20 hours if several evaporation cycles had been done before. Further heat treatment of the sample at 165 °C does not degrade and even slightly improves the QY. It is particularly important to note that the heat enhancement effect is irreversible: once the QY is stabilized at elevated temperatures, it does not change any more even after cooling down to room temperatures.

Shown on Fig.1b,c are the QY spectra of 500 Å thick NaI and 900 Å thick CuI films, evaporated directly on stainless steel substrates and further heated at 70 °C. No

thickness dependence of the QY has been found for fresh NaI films, in the range of 100-500 Å. For the heat-treated films, the saturation of the QY occurs after 5 hours for NaI and after 15 hours for CuI. For both materials strong effects of heat treatment, larger than for CsI, are observed. In particular, it enhances the photoyield by several orders of magnitude at longer wavelengths and shifts the photoemission threshold by about 1 eV. For comparison, the QY spectra of NaI and CuI measured by other authors [8, 10] are depicted in the figures. Our fresh NaI data reproduce well that of Taft and Philipp [8]. The CuI data of Charpak et al. [10] show higher QY than our fresh QY, presumably due to the different photocathode preparation technique used by them, of deposition from a solution.

Fig.2 summarizes our heat-enhanced QY spectra of CsI, NaI and CuI photocathodes. At shorter wavelengths the QY of NaI is higher than that of CuI, reaching 20%, while at longer wavelengths the CuI has a larger QY, of about 1% at 200 nm. Below 200 nm the CsI conserves its superior photoemission yield.

An important conclusion from the results obtained is that the electron affinity values for NaI and CuI quoted in the literature [9] and derived by a comparison of the energy gap and the photoemission threshold, should be revised. As follows from our data, the electron affinity values of NaI and CuI should be equal to 0.3 and 2.5 eV correspondingly, compared to the previously accepted values of 1.5 and 3 eV [9].

Another result is that CsI, NaI and CuI have a very similar behaviour under the heat treatment. This narrows the number of possible explanations of the heat-enhancement effect. For example, the hypothesis that the cesiation of the photocathode surface is responsible for the QY increase, should be apparently excluded.

It is also unlikely that a transition between different lattice modifications plays a role. Indeed, at room temperature CsI can exist in two distinguished lattice types [18]: CsI(I) of a NaCl-type and CsI(II) of a CsCl-type (the latter is of a more common occurrence). However, though CuI has few forms at high pressures and temperatures, at normal conditions it exists in a single phase only: CuI(III), of a cubic ZnS-type [18]. Also, NaI exists in a single lattice form of a NaCl-type [18].

Another explanation for the effect could be the elimination of residual water molecules during the heating procedure. This explanation seems to fail as well, due to the fact that CsI, NaI and CuI have very different capability to react with water: their solubility in water varies from CuI to NaI by 5 orders of magnitude [19]. Another objection is that we found that the initial QY value does not depend on the vacuum level inside the evaporation chamber.

One feature which is common to the three materials and could provide a hint to a possible explanation, is that all three are iodides. Several arguments speak for the major role of the iodine in the heat enhancement effect. Iodides and bromides are more easy to decompose, as compared to other halides: a good example is the visible light-induced decomposition of AgBr in photoemulsion. If to suppose that an iodide partly decomposes during evaporation, the higher vapour pressure of the iodine as compared to that of Cs, Na, Cu, etc. could enrich its content in the deposited film. This apparently could degrade

the photoelectron transport properties due to a violation of the stoichiometry. The fact supporting this assumption is that there exist stable compounds like for example CsI_3 and CsI_5 [19, 18]. Once the sample is heated, these CsI_n species can start decaying into CsI and I_2 due to their much lower stability as compared to CsI itself, and the I_2 can be liberated out of the bulk. Moreover, it is interesting to note that the melting point of CsI_5 , 73 °C [19], at which CsI_5 species become mobile, falls just within the temperature range of the heat enhancement effect. Local variations of the stoichiometry in CsI have been previously observed in [20].

Summarizing the results, we can state that a trend has been revealed: a heat treatment of iodides drastically enhances their photoyield. One would expect that other halides like for example KI , RbI , AgI , CsBr , AgBr would follow the same trend. The revision of their quantum yield is under coarse at our laboratory.

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Figure captions

Fig.1 Post-evaporation heat enhancement of the photoyield of CsI, NaI and CuI photocathodes.

- a) Quantum yield spectra of CsI measured for the same photocathode: (1) fresh, (2) heated for 15 hours at 50 °C , (3) further heated for 3 hours at 165-70 °C .
- b) Quantum yield spectra of NaI at different heating times after preparation. Data of Taft and Philipp [8] are shown as well.
- c) Quantum yield spectra of CuI at different heating times after preparation. Data of Charpak et al. [10] are shown as well.

Fig.2 A comparison of the quantum yield spectra of heat-enhanced CsI, NaI and CuI photocathodes.

Fig.1

Fig.2