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Published in:
Applied Physics Letters

DOI:
[10.1063/5.0033370](https://doi.org/10.1063/5.0033370)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2020

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Groeneveld, B. G. H. M., & Loi, M. A. (2020). Detecting alcohol vapors using two-dimensional copper-based Ruddlesden-Popper perovskites. *Applied Physics Letters*, 117(22), [221903].
<https://doi.org/10.1063/5.0033370>

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Cite as: Appl. Phys. Lett. **117**, 221903 (2020); <https://doi.org/10.1063/5.0033370>

Submitted: 16 October 2020 . Accepted: 16 November 2020 . Published Online: 30 November 2020

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ABSTRACT

The detection of alcohol vapors has many important applications, such as measuring the breath ethanol content to prevent drug-impaired driving. A medical application is the detection of 1-propanol because this compound was found to be a potential marker for lung cancer screening. This work reports an alcohol sensor using the two-dimensional Ruddlesden–Popper perovskite bis(phenethylammonium) tetrachlorocuprate—(PEA)₂CuCl₄, also known as phenethylammonium copper chloride—as the sensing material. The device is based on a change in conductance upon exposure to alcohol vapors. A comparison between pristine (PEA)₂CuCl₄ and (PEA)₂CuCl₄ after a treatment with ultraviolet light shows that the latter has a higher conductance. Devices made with this UV-converted material show a strong response to 1-propanol vapors, starting from a concentration around 2000 parts per million (ppm). Additionally, these devices demonstrate stable behavior in a nitrogen atmosphere. During the stabilization of the 1-propanol flow rate, the concentration fluctuates. These fluctuations were detected by monitoring the current of the device over time, down to steps in 100 ppm around a concentration of 8000 ppm. The conductance of the devices decreases in contact with air. However, this process can be reversed by additional ultraviolet illumination, thereby making the devices reusable.

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One of the strengths of hybrid inorganic–organic metal halide perovskites is their versatility, which is evident from the various types of devices that were made with this class of materials. Besides the predominant application in thin film solar cells,^{1–5} there have been reports on other devices such as photodetectors, lasers, and light emitting diodes.^{6–11} The focus on optoelectronic applications does not do the unique character of metal halide perovskites justice because their tunable composition and excellent electronic properties enable their use in many more fields of research.^{3,5,12}

Examples of these underrepresented, yet technologically relevant devices are gas sensors. Only a small number of these devices were reported in the literature. Maity *et al.* demonstrated an ammonia sensor based on methylammonium lead iodide,¹³ and Li *et al.* used methylammonium lead bromide to detect the same compound.¹⁴ Zhu *et al.* were able to detect p-xylene in the parts per million (ppm) range using (C₄H₉NH₃)₂PbI₄.¹⁵

The capability of methylammonium lead bromide (MAPbBr₃) to detect gases, such as oxygen and water vapor, was demonstrated by our group.¹⁶ It was found that the photoluminescence intensity of a MAPbBr₃ single crystal kept in air is higher than that in vacuum and a nitrogen atmosphere. This was explained by the physisorption of

oxygen onto the crystal surface, where the O₂ molecules passivate surface trap states. The nature of these trap states and the passivation mechanism were recently revealed through calculations based on density functional theory, demonstrating that bromide vacancies can generate localized charge traps on the MAPbBr₃ surface.¹⁷ Restoring the fully delocalized charge density can take place through passivation of the undercoordinated lead atom by hydroxyl (OH[−]) groups.

Another well-known type of chemical compound containing hydroxyl groups is the alcohol. Two types of alcohols that play very important roles in society and healthcare are ethanol and 1-propanol. The detection of these alcohols is crucial: ethanol is a cause of drug-impaired driving and 1-propanol is found in the breath of lung cancer patients and is seen as a potential marker for lung cancer screening.¹⁸ There are a number of papers describing sensors that can detect these two alcohols, but these are often based on complicated mechanisms. Examples are sensors based on oxides, whose conductance changes are based on adsorption of the gas; these devices typically operate at high temperature (130–400 °C).^{19–22} Other sensors have working mechanisms based on arrays of micromechanical cantilevers,²³ changes in the refractive index²⁴ or the emission wavelength,²⁵ or use materials which require a lot of energy for their fabrication such as single-walled

carbon nanotubes.²⁶ The importance of the aforementioned applications justifies the need for a portable alcohol sensor without a complex working mechanism.

Our previous work on MAPbBr₃ gas sensors demonstrated that a perovskite single crystal with two metal contacts can be used to sense oxygen through changes in its conductance, without needing high temperature.¹⁶ We hypothesized that such a simple device architecture might also be promising for the detection of alcohol vapors. We looked into alternative perovskites due to the response of methylammonium lead bromide to oxygen and water, which would not make for reliable sensors under ambient conditions. Since stability in air is often low for three-dimensional lead- and tin-based halide perovskites,^{27,28} we turned our attention to the two-dimensional copper-based Ruddlesden–Popper perovskite bis(phenethylammonium) tetrachlorocuprate (also known as phenethylammonium copper chloride), (PEA)₂CuCl₄. The reason for selecting a copper-based perovskite is to prevent the use of lead and tin, which can be harmful to the environment and human life.²⁹

(PEA)₂CuCl₄ is an air-stable ferromagnetic insulator (at temperatures below 13 K),³⁰ whose surface conductivity can be increased by covering it with an organic electron donor.³¹ Arkenbout *et al.* found that (PEA)₂CuCl₄ has a low conductivity and attributed this to two factors; the first is the ionic character of the bonds between copper and chloride, which leads to localized charge carriers. The second factor is the Jahn–Teller effect occurring in Cu²⁺ compounds, which leads to an antiferrodistortive ordering of the orbitals of the copper ions.³¹ Our recent publication on (PEA)₂CuCl₄ demonstrated that this material exhibits photochromism, i.e., it changes from a yellow to a brown phase upon exposure to ultraviolet (UV) light.³² During this process, the octahedral copper-chloride structure at the surface changes to

isolated square-planar CuCl₄^{2−} ions, destroying the structural order in the inorganic *xy*-plane. In this work, we compare both phases of (PEA)₂CuCl₄, with the goal of using these materials for vapor sensing applications. For both phases, the conductance of the devices is on the order of picosiemens in an inert atmosphere (N₂). Devices with UV-converted (PEA)₂CuCl₄ have a higher conductance on average, which makes them more resilient to measurement errors. We find that exposure to 1-propanol vapor significantly improves the conductance of the material in the brown UV-converted (PEA)₂CuCl₄. Fluctuations in the 1-propanol concentration on the order of 100 parts per million were detected, making UV-converted (PEA)₂CuCl₄ a very promising compound for use in 1-propanol vapor sensors. Despite the stability in air of pristine (PEA)₂CuCl₄, the brown phase is not stable in air, which is evident from a decrease in conductance. However, the conductance can be increased again by illuminating the device with UV light; the regeneration of the devices makes them reusable.

Fabrication of the (PEA)₂CuCl₄ film [see Fig. 1(a) for the crystal structure of the pristine material] was based on the spin coating technique (the details are provided in the [supplementary material](#)), which leads to a strong parallel orientation of the inorganic planes with respect to the substrate.³² This orientation is favorable for conduction in two-dimensional hybrid perovskites when a planar device geometry is used.³³ Devices were fabricated by evaporating 80 nanometer interdigitated gold contacts with a 200 μm channel in-between [see Fig. 1(b) for a device schematic and Fig. S1 for a microscope image of the interdigitated contacts]. By applying a bias across the device, we can measure the current flowing through the surface plane, which we can alter by exposing the device to alcohol vapors [Fig. 1(c)]. From the current–voltage (*I* – *V*) curves, we extracted the conductance of our devices.

FIG. 1. (a) The crystal structure of pristine (PEA)₂CuCl₄, as determined by Caretta *et al.*,³⁴ visualized using Mercury.³⁵ A schematic diagram of the (PEA)₂CuCl₄ alcohol vapor sensor in (b) inert atmosphere and (c) in the presence of 1-propanol vapor.

First, we compared the conductance of pristine and UV-converted $(\text{PEA})_2\text{CuCl}_4$ devices in nitrogen without any alcohol present. We found that the average conductance of a device made with a pristine film is 5.4×10^{-13} S (see Fig. S2 for an overview of the data). The mean conductance of the UV-converted devices is 1.2×10^{-12} S, two times higher than that of the pristine devices (Fig. S3). A possible explanation for this behavior is that the charge carrier blockade caused by the antiferrodistortive orbital ordering—a characteristic of the pristine material³¹—is removed by the structural change from an octahedral copper chloride structure to square-planar CuCl_4^{2-} ions upon UV exposure.³² This would lead to a higher conductance, analogous to the findings of Arkenbout *et al.*³¹ For both the pristine and UV-converted material, our conductance varied from device to device. We attributed this to slight variations in perovskite film morphology due to the spin coating technique used to fabricate the layer, which could also affect the quality of the gold contacts. However, the lower conductance of the pristine material is undesirable since it approaches the detection limit of our experimental setup, making the measurements with these devices more prone to errors. Therefore, we focused our experiments on the UV-converted devices.

As mentioned, the low currents observed in the measurements are sensitive to noise. It is important that a sensor displays stable values under steady-state conditions to ensure reliable operation. We tested the stability of our device by measuring the conductance in nitrogen over time; the results are shown in Fig. 2. This device has an initial conductance of 1.1×10^{-12} S, which is relatively constant over time, showing that the device has a stable baseline.

With the nitrogen measurements in mind, we look at the response of the device to alcohol vapor. We mix anhydrous alcohol with nitrogen using a custom-made setup (see Fig. S4), where we can control the flow rate of both the alcohol and the gas into a mixer device. The resulting mixture is led into the chamber with the sample. By controlling the flow rate of the alcohol, we can expose our device to various concentrations of the alcohol. First, we checked whether our setup without a $(\text{PEA})_2\text{CuCl}_4$ device is affected by the presence of alcohol vapors. We made reference devices consisting of gold electrodes

deposited directly on glass and exposed them to various concentrations of 1-propanol (1-PrOH). The response in terms of conductance vs concentration is shown in Fig. S5, along with an average response of the three reference devices. It is clear that increasing the 1-PrOH concentration leads to a significant improvement in conductance for our reference, and therefore, we corrected the data of our actual $(\text{PEA})_2\text{CuCl}_4$ devices for this effect. This increase in conductivity might be explained by adsorption of 1-propanol at the surface of the glass between the gold electrodes. Voorthuyzen *et al.* found an increase in surface conductivity of silicon dioxide after exposure to humid air.³⁶ They attributed this to physisorption of water vapor.

The response of a UV-converted $(\text{PEA})_2\text{CuCl}_4$ device to various concentrations of 1-PrOH was measured, after which we subtracted the conductance of the reference devices. Here, the response (R) is defined as the ratio of the conductance in 1-PrOH (σ_V) and N_2 (σ_N): $R = \sigma_V/\sigma_N$. Figure 3 shows the response of the best performing device. It is clear that the conductance of the UV-converted $(\text{PEA})_2\text{CuCl}_4$ improves with the increasing 1-propanol concentration. After correction for the glass reference device, we observe a 37-fold increase in conductance at around 10 000 ppm. At lower concentrations, the improvement is also visible (see Fig. S6 for a closer look at this regime). However, due to the low currents, the device is still affected by small fluctuations, which prevents us from discerning a clear response until 2000–3000 ppm, after which the effect becomes very pronounced. The responses from additional devices with UV-treated $(\text{PEA})_2\text{CuCl}_4$ are shown in Fig. S7. Although there is some variation in the response between devices, we see that they are all capable of detecting 1-propanol. Like the variation in σ_N , we attribute this to differences in device quality, and we believe that with proper control over the film formation, we can reach both better sensitivity and reproducibility.

An important aspect of vapor sensors is that the devices should sense a variation in the concentration quickly. Although we could not accurately measure the rise time due to the limitations of the setup, we did investigate the sensitivity of the sensor to variations in the alcohol concentration over a longer time scale. Figure 4 shows the time

FIG. 2. The conductance of a UV-converted $(\text{PEA})_2\text{CuCl}_4$ device in nitrogen over time.

FIG. 3. Response of the best performing UV-converted $(\text{PEA})_2\text{CuCl}_4$ vapor sensor to varying concentrations of 1-PrOH in the nitrogen environment, plotted on a semi-logarithmic scale.

FIG. 4. Fluctuation in the concentration of 1-PrOH in the alcohol/nitrogen mixture over time (top) and the resulting signal in the form of current (at 10 V bias) in a UV-converted $(\text{PEA})_2\text{CuCl}_4$ device (bottom). This fluctuation in the concentration is a result of the stabilization of the flow rates of 1-PrOH and N_2 , and the 1-PrOH concentration is an approximation based on these flow rates.

evolution of both the concentration of 1-PrOH in the alcohol/nitrogen mixture and the current of a device biased at 10 V. The concentration fluctuates around 8000 ppm, a region where we see a relatively strong response, which allows us to measure these fluctuations in the concentration reliably. The resemblance between the two signals is very strong, indicating that our setup accurately measures these fluctuations, even the ones on the order of 100 ppm.

The sensitivity S —at a concentration around 8000 ppm—can be approximated by the difference in current (ΔI) for each fluctuation in the concentration (ΔC): $S = \Delta I / \Delta C$. Looking at the difference between peaks and subsequent valleys in the signals (and excluding the peak around 10 s for the lack of a clear signal), we find that the device has an average sensitivity of 0.14 pA/ppm. Additionally, the response seems to be very fast. This indicates the potential of these devices for vapor detection applications.

After detecting 1-PrOH, we tested whether UV-converted $(\text{PEA})_2\text{CuCl}_4$ is capable of detecting ethanol (EtOH) too. The reference measurement described above was also carried out for EtOH (one device, see Fig. S8), and the response of the actual device was corrected for this, as for 1-PrOH. Three devices were characterized, and surprisingly, the response to EtOH is very different from that to 1-PrOH. If there is any response at all, it is much weaker, as can be seen from the best performing device in Fig. S9. The response fluctuates between 1 and 1.3 over the entire range (0 to about 12 000 ppm), with some outliers in the data points. There might be an underlying trend, but the response is not as clear as for 1-PrOH. Based on the available data, we cannot conclude whether UV-converted $(\text{PEA})_2\text{CuCl}_4$ can detect ethanol vapor. The reason for the difference in response to the two alcohols is still under investigation. However,

our data indicate that UV-converted $(\text{PEA})_2\text{CuCl}_4$ is a promising material for the detection of 1-PrOH.

Finally, we tested the stability of our devices over time and in air. We compared the initial conductance of a device with the conductance 3 months later. Both measurements were carried out in nitrogen, and the device was also kept in nitrogen between the measurements. However, the device was transported through air, and the contacts with the gold electrodes (made with silver paste) had to be reapplied after 3 months. Figure 5 shows that the conductance of the device after 3 months is much lower (8.2×10^{-13} S) than the initial conductance (2×10^{-12} S). This value remains quite constant over the course of 30 min. After that, the sample holder was evacuated and refilled with ambient air. This resulted in a drop of the conductance over 30 minutes to 6.4×10^{-13} S. Considering that UV-converted $(\text{PEA})_2\text{CuCl}_4$ is not stable in air,³² this degradation in conductance is not unexpected. After the air exposure, the sample was illuminated with UV light for 45 minutes in a nitrogen-filled glovebox. This led to an increase in the conductance in nitrogen to 1.54×10^{-12} S. Therefore, the UV treatment recovered the conductance significantly. Until the device was exposed to air again, this value was fairly stable. However, upon air exposure, the conductance drops considerably over the course of 10 minutes. After that, it seems to stabilize around 9.2×10^{-13} S. From this experiment, we conclude that the conductance of our sensor can degrade over time (e.g., in air), a process that is reversible by UV treatment in nitrogen.

We have made a $(\text{PEA})_2\text{CuCl}_4$ -based alcohol vapor sensor, by using the brown UV-converted $(\text{PEA})_2\text{CuCl}_4$ as the sensor material. This UV-converted phase has a higher conductance than pristine $(\text{PEA})_2\text{CuCl}_4$, making it more resilient to fluctuations in current. Our best performing device has a response R of 37 at 10 000 ppm and could detect 1-propanol concentrations in nitrogen down to 2000–3000 ppm. Although quantitative measurements could not be

FIG. 5. Conductance of a UV-converted $(\text{PEA})_2\text{CuCl}_4$ vapor sensor over time. The blue triangle depicts the initial average conductance in nitrogen. The measurements depicted in the blue frame were acquired after 3 months of storage in nitrogen. Here, the black squares depict measurements in nitrogen, and the red circles are air measurements. After the air exposure, the device was brought into a nitrogen-filled glovebox and illuminated with 254 nm light for 45 min. The subsequent measurements in nitrogen and air are shown in the green frame.

made, it is clear that the response of the sensor to fluctuations in the 1-PrOH concentration is fast. Moreover, fluctuations in the concentration on the order of 100 ppm could be detected at high concentrations (around 8000 ppm). The devices are stable in nitrogen, but their conductance decreases in air. Subsequent UV treatment in nitrogen leads to a recovery of the conductance, thereby making the devices reusable. Our results show that UV-converted (PEA)₂CuCl₄ has great potential as material to sense 1-PrOH vapor. Interestingly, with the current data, we cannot conclude whether the device can detect ethanol vapor due to the lack of a strong response in our experiments. Future research is needed to explain the mechanism behind the response to 1-PrOH and to improve the conductance of the devices to make the output more resilient to fluctuations in current and, therefore, more sensitive to lower concentrations. Additionally, more elaborate device architectures might help improve the sensitivity of the devices.

See the [supplementary material](#) for additional data on 1-PrOH and EtOH detection.

The authors are thankful to A. Kamp and T. Zaharia for technical support. This work is part of the research program of the Netherlands Organisation for Scientific Research (NWO). This is a publication of the FOM-focus Group “Next Generation Organic Photovoltaics,” participating in the Dutch Institute for Fundamental Energy Research (DIFFER).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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