

Structural quality of CH₃NH₃PbI₃ perovskites for photovoltaic applications analyzed by electron microscopy techniques

Authors: Natalia Fernández-Delgado (1), Miriam Herrera-Collado (1), Francisco Delgado-González (1), Emilio Juárez-Pérez (2), Iván Mora-Sero (2), Isaac Suárez (3), Juan Martínez-Pastor (3), Sergio Molina (1)

1. Materials Science, University of Cádiz, Cádiz, SPAIN

2. Institute of Advanced Materials, Universitat Jaume I, Castelló, SPAIN

3. Institute of Materials Science, University of Valencia, Valencia, SPAIN

DOI: 10.1002/9783527808465.EMC2016.6019

Corresponding email: nataliaferdel@outlook.es

Keywords: perovskites, optoelectronic materials, HAADF-STEM

Hybrid Halide Perovskites (HPVK) are novel materials that have attracted attention in the last few years as promising materials in the photovoltaic field,[1, 2] as efficiencies higher than 20% have been reported[3]. The HPVK can have different compositions, which allows the control of lattice parameters[4] and bandgap values in the visible to near infrared region[5]. In particular, CH₃NH₃PbI₃ presents optimal electronic and optical properties such as direct optical band gap of 1.55 eV or long electron/hole diffusion length (100 nm)[6].

In this communication, we have analysed the structural quality of two CH₃NH₃PbI₃ samples by electron microscopy techniques. The samples have been grown using spin coating solution processing method. The details of the process can be found in[7]. The structure of the samples consists of a substrate of SiO₂ (2µm), a TiO₂ layer (40 nm), an active layer of HPVK and a poly-methyl methacrylate (PMMA) capping layer (1µm) in order to protect the sample from oxidation. The two samples studied (S500 and S100) have different HPVK thicknesses, 500 and 100 nm respectively, obtained by changing the speed in the spin-coating process [7]. The first analyses have been carried out by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), which is sensitive to the atomic number of the atoms in the material. Fig. 1 a shows a HAADF-STEM image of the first sample, where the different layers of the structure can be observed. These layers have been studied by energy dispersive X-ray analysis (EDX) as exhibited in Fig. 1 b, and the layers sequence (SiO₂, TiO₂ and HPVK) has been confirmed. Thus, spectrum 3 in Fig. 1 b shows the presence of Pb and I, indicating that this layer corresponds to the HPVK, despite it shows a reduced size due to the ion bombardment during the sample preparation process for TEM. Electron diffraction patterns have been taken from the HPVK layer and, surprisingly, some areas have shown to be polycrystalline but others are amorphous. Previous analysis of the functional properties of these samples suggests that they are crystalline. Sample preparation to obtain the electron transparent specimen may cause a detrimental effect in the HPVK layer, producing the amorphization of a material. Because of this, the procedure of sample preparation is being optimized in order to analyse in detail the structural properties of this material.

Acknowledgements:

This work was supported by the Spanish MINECO (projects TEC2014-53727-C2-1-R, -2-R and CONSOLIDER INGENIO 2010 CSD2009-00013) and Junta de Andalucía (PAI research group TEP-946). The research leading to these results has received co-funding from the European Union.

References:

- [1] H.J. Snaith, *The Journal of Physical Chemistry Letters*, 4 (2013) 3623-3630.
- [2] H.-S. Kim, J.-W. Lee, N. Yantara, P.P. Boix, S.A. Kulkarni, S. Mhaisalkar, M. Grätzel, N.-G. Park, *Nano Letters*, 13 (2013) 2412-2417.
- [3] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, *Progress in Photovoltaics: Research and Applications*, 23 (2015) 1-9.
- [4] A. Sadhanala, S. Ahmad, B. Zhao, N. Giesbrecht, P.M. Pearce, F. Deschler, R.L.Z. Hoyer, K.C. Gödel, T. Bein, P. Docampo, S.E. Dutton, M.F.L. De Volder, R.H. Friend, *Nano Letters*, 15 (2015) 6095-6101.
- [5] Y.H. Kim, H. Cho, J.H. Heo, T.S. Kim, N. Myoung, C.L. Lee, S.H. Im, T.W. Lee, *Advanced Materials*, 27 (2015) 1248-1254.
- [6] G. Xing, N. Mathews, S. Sun, S.S. Lim, Y.M. Lam, M. Grätzel, S. Mhaisalkar, T.C. Sum, *Science*, 342 (2013) 344-347.
- [7] I. Suárez, E.J. Juárez-Pérez, J. Bisquert, I. Mora-Seró, J.P. Martínez-Pastor, *Advanced Materials*, 27 (2015) 6157-6162.

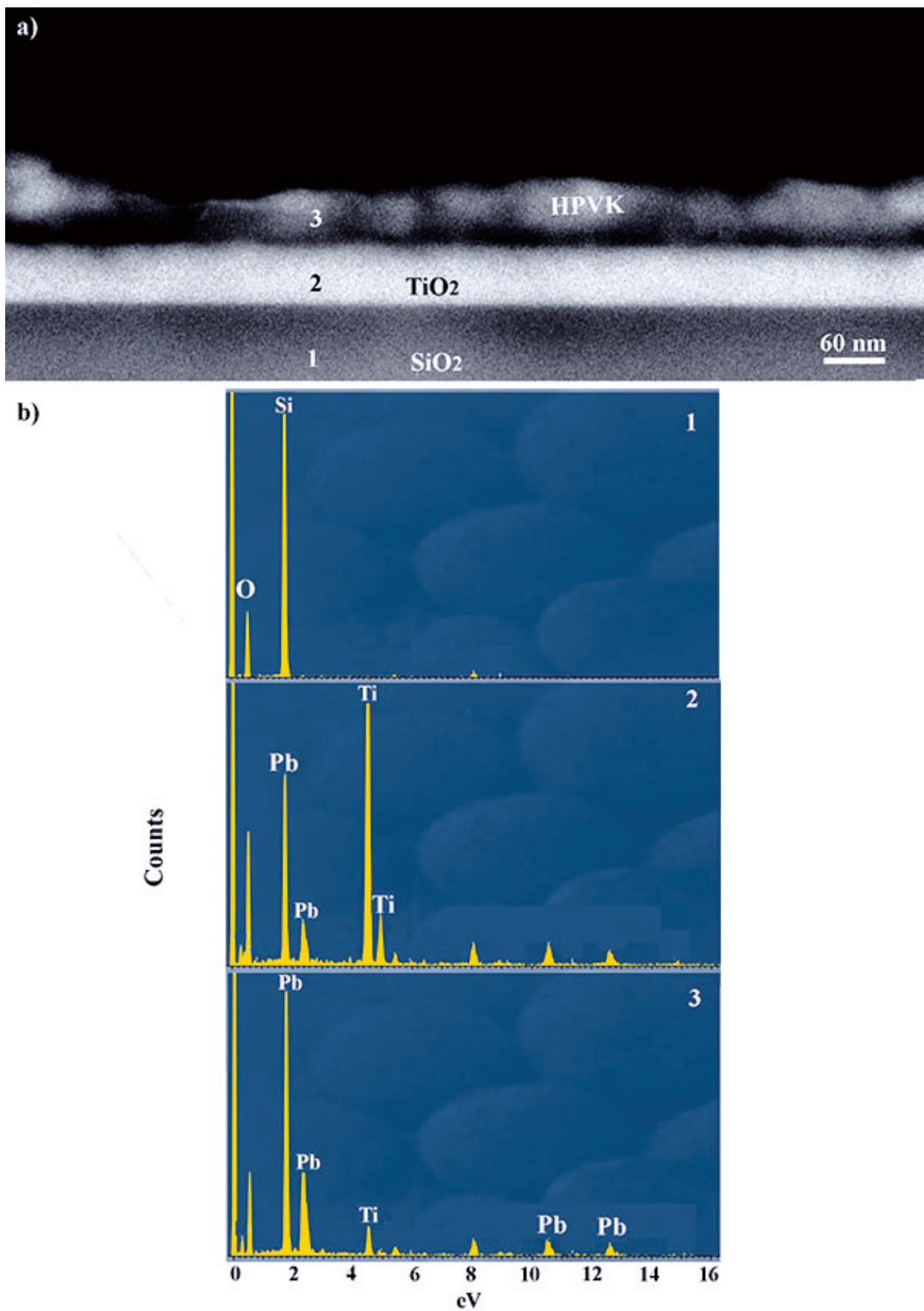


Fig. 1 a) HAADF-STEM image of the structure with the CH₃NH₃PbI₃ perovskite layer of S500; b) EDX spectra taken from the zones marked as 1, 2 and 3 in the HAADF-STEM image in a).