Supporting Information

A closer look at defects and luminescence of nanocrystalline fluorides synthesized via ionic liquids: the case of Ce^{3+}-doped BaF_2

Rahul Kumar Sharma,[a] Yogendra Nath Chouryal,[a] Anatoly I. Slesarev,[b] Konstantin V. Ivanovskikh,*[b] Ivan I. Leonidov,[c,d] Sandeep Nigam[e] and Pushpal Ghosh* [a]

[a]School of Chemical Sciences and Technology, Department of Chemistry, Dr. H. S. Gour University (A Central University), Sagar-470003, Madhya Pradesh, India. Email-pushpalghosh27@gmail.com.

[b]Institute of Physics and Technology, Ural Federal University, 620002, Ekatarinburg, Russia,

[c]School of Engineering, Ural Federal University, 620002, Ekaterinburg, Russia

[d]Institute of High-Temperature Electrochemistry, UB RAS, 620137, Ekaterinburg , Russia

[e]Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India

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Chemicals: Barium Acetate $Ba(CH_3COO)_2$ (Himedia), Cerium Nitrate $(Ce(NO_3)_3.6H_2O)$ (Alfa Aesar), Dichloromethane (CH_2Cl_2), Deionised (DI) water from CDH (Central Drug House), 1-methylimidazole ($C_4H_6N_2$) (Alfa Aesar), n-Butyl Bromide (C_4H_9Br), Sodium Tetrafluoroboarate ($NaBF_4$), Acetone (C_3H_6O), Charcoal from Loba Chemie, Acetonitrile, Ethanol (C_2H_5OH) from Merck.

Synthesis of [C_4mim][Br] ionic liquid: Modifying a literature procedure, 12.37 ml of n-butyl bromide (0.166 mol, Himedia) and 10 ml of N-methyl imidazole (0.126 mol, Alfa Aesar) are stirred under argon (Ar) gas atmosphere at room temperature (RT) for 72 hours in a 250 ml round bottom flask in order to get complete reaction. As a result, solid white crystals were obtained. Ethyl acetate was added to the raw product and crushed it to fine crystals. After that the resultant crude product was washed twice with ethyl acetate and again re-crystallized with acetonitrile. The obtained product was dried in vacuum at 25°C for 24 hours to get white solid product.[1]

Synthesis of [C_4mim][BF_4] **ionic liquid**: The room temperature ionic liquid (RTIL) [C_4mim][BF_4] was prepared by adding $NaBF_4$ (21 gm) and 1-butyl-3-methylimidazolium bromide [C_4mim][Br] (42 gm) in acetone (100 ml) and allowed for stirring at RT for 3-4 days.[2-3] The obtained product was filtered and then kept for stirring for further 16 hours with 1 gm activated charcoal. The activated charcoal was filtered and acetone was finally removed

by rotary evaporator in vacuum. The obtained product was further mixed with about 60 ml of dichloromethane (at least 3-4 times) to make it free of impurities. A little amount of silver nitrate solution was added to the washed ionic liquid to confirm the chloride ions. The pale yellowish liquid was isolated and further dried in a vacuum for 12 hours.

Williamson and Hall method

Thelattice strain can be calculated by using Williamson and Hall method:[4]

$$\frac{\beta cos\theta}{\lambda} = \frac{1}{D} + \eta\frac{sin\theta}{\lambda} \qquad (1)$$

When βcosθ/λ vs sinθ/λ is plotted, lattice strain (η) can be quantitatively determined from the slope of the graph and crystallite size from the intercept.

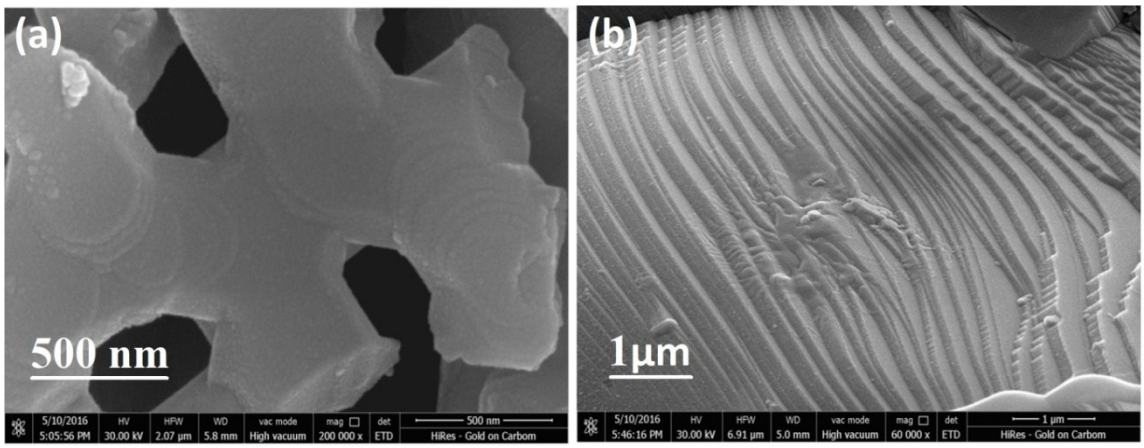

Figure S1. FESEM images of BaF_2:Ce^{3+}(0.1%)nanoparticles calcined at600°C (a) and 800°C (b).

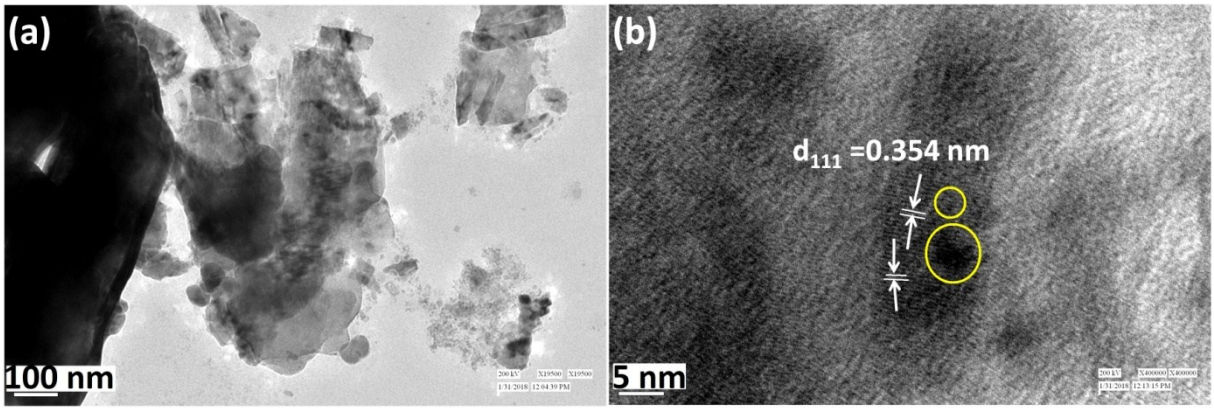

Figure S2. TEM and HRTEM images of BaF_2:Ce^{3+}(0.1%) nanoparticles calcined at 800°C.

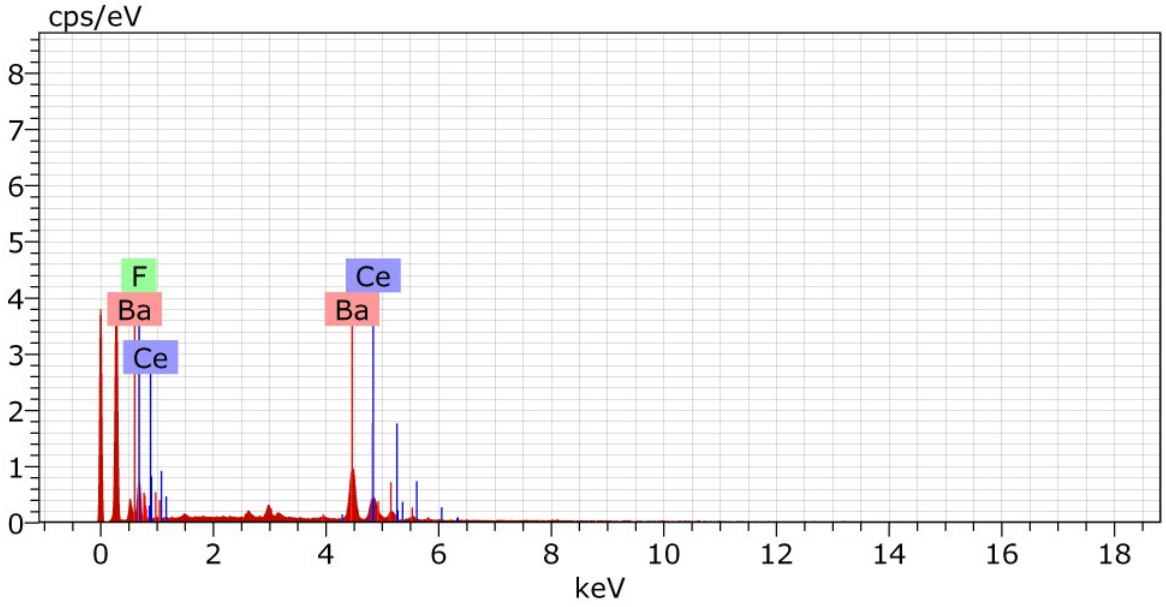

Figure S3. EDX spectrum of as-prepared BaF_2:Ce^{3+} (0.1%) nanoparticles (P1).

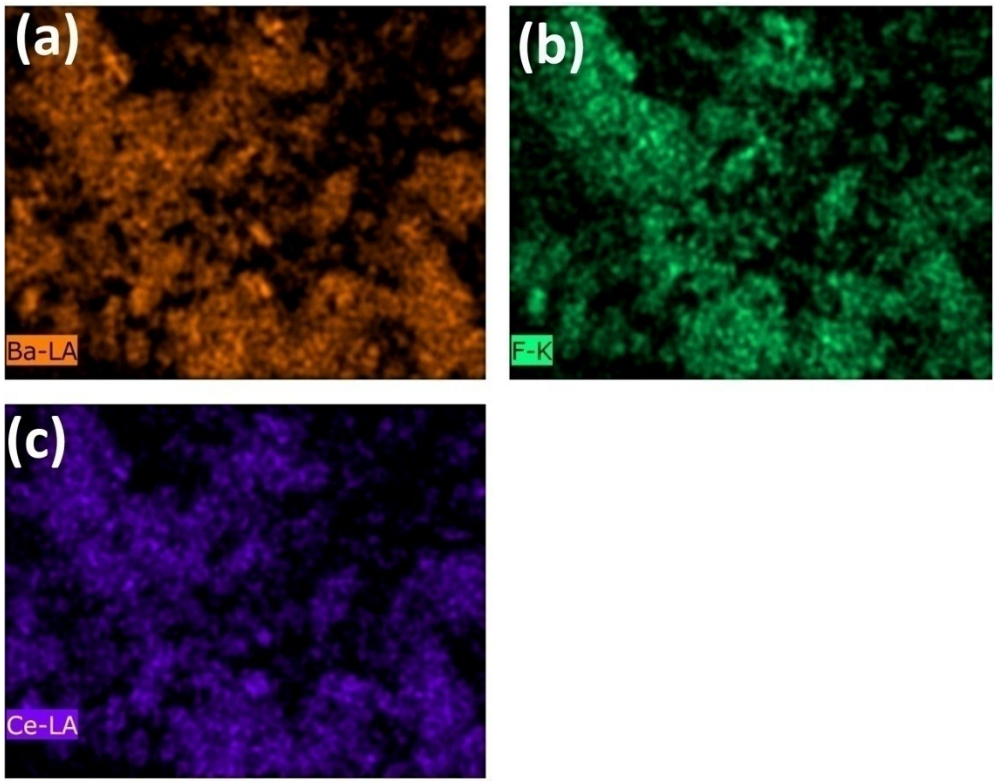

Figure S4. Elemental mapping (a-c) of as-prepared BaF_2:Ce^{3+} (0.1%) nanoparticles (P1).

Reference:

1. R. K. Sharma,Y. N. Chouryal,S. Chaudhari,J. Saravanakumar, S. R. Deyand P. Ghosh, *ACS Appl. Mater. Interfaces*, 2017, **9**, 11651−11661.

2. S. Anghel, S. Golbert, A. Meijerink , A.-V. Mudring, *J. Lumin*., 2017,**189**, 2–8.
3. C. Lorbeer, F. Behrends, J. Cybinska, H. Eckert and A.-V. Mudring, *J. Mater. Chem. C*, 2014, **2**, 9439–9450.
4. R. K. Sharma, S. Nigam, Y. N. Chouryal, S. Nema, S. P. Bera, Y. Bhargava and P. Ghosh, *ACS Appl. Nano Mater.*, 2019, **2**, 927-936.