Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Spin-Forbidden Near-Infrared Luminescence from a F_3^+ Color Center Generated in Mechanochemically Prepared Nanocrystalline $BaLiF_3$ upon Annealing

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S1. SEM Images of $BaLiF_3$ before and after annealing

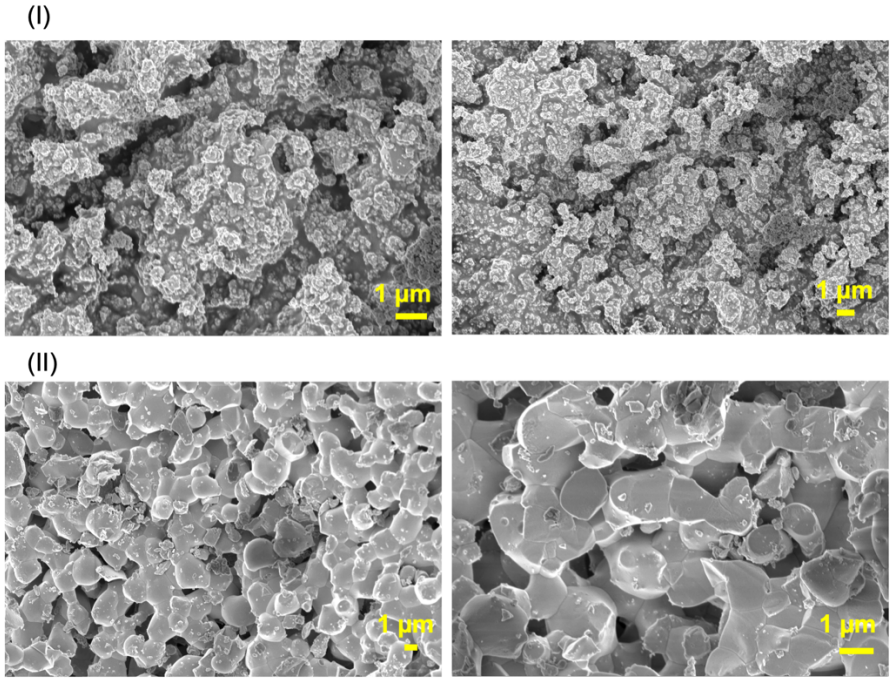

Fig. S1 SEM micrographs of (I) as-prepared $BaLiF_3$ and (II) $BaLiF_3$ annealed at 800 °C.

SEM micrographs of as-prepared (panel I) and 800 °C annealed (panel II) $BaLiF_3$ samples are presented in **Fig. S1**. It shows the annealing process increases the crystallite and particle size.

S2. SEM Based EDS 2D Map

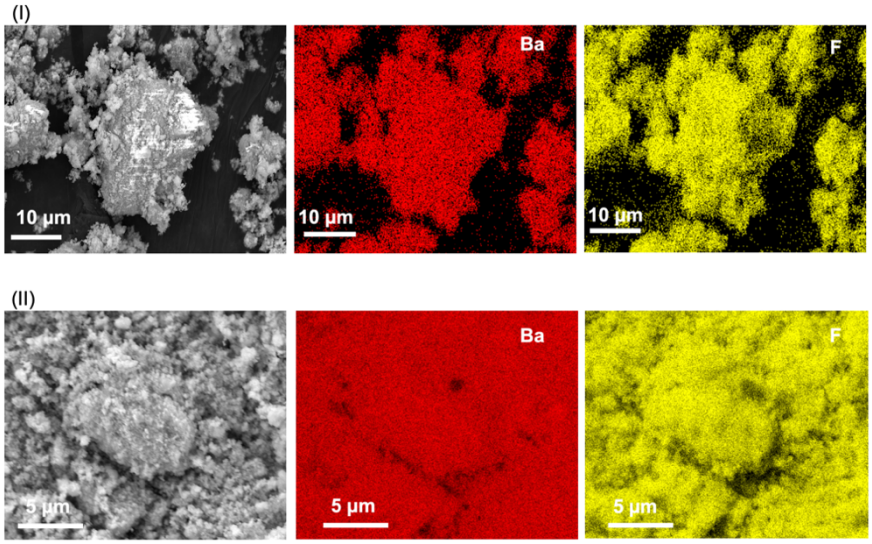

Fig. S2 SEM based EDS 2D map of (I) as-prepared $BaLiF_3$ and (II) $BaLiF_3$ annealed at 800 °C.

2D SEM-EDS elemental maps of as-prepared and annealed $BaLiF_3$ are illustrated in **Fig. S2**. It shows uniform distribution of Ba and F (Li is too light to be detected by SEM-EDS).

S3. Zeeman experiment performed on the Spex 1402 0.75 m monochromator

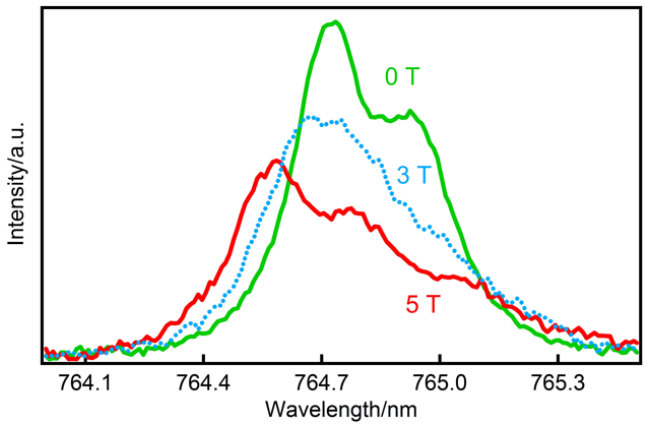

Fig. S3. Magnetic field induced splitting of the zero-phonon line observed in $BaLiF_3$ upon annealing at 764.8 nm. 1.8 K spectra measured at 0 T and in an external magnetic field of 3 T and 5 T, respectively. Spectra were collected on a Spex 1402 0.75 M monochromator. A 470 nm blue LED was used as the excitation source. Sample was annealed at 600 °C.

Low temperature (1.8 K) photoluminescence spectra of the zero-phonon line at 764.8 nm in $BaLiF_3$ annealed at 600 °C was measured in zero-field and in an external magnetic field of 3 T and 5 T as shown in **Fig. S3**. The 5 T spectrum contains three transitions at 764.59 nm, 764.77 nm and 765.03 nm.

S4. Dopant concentration

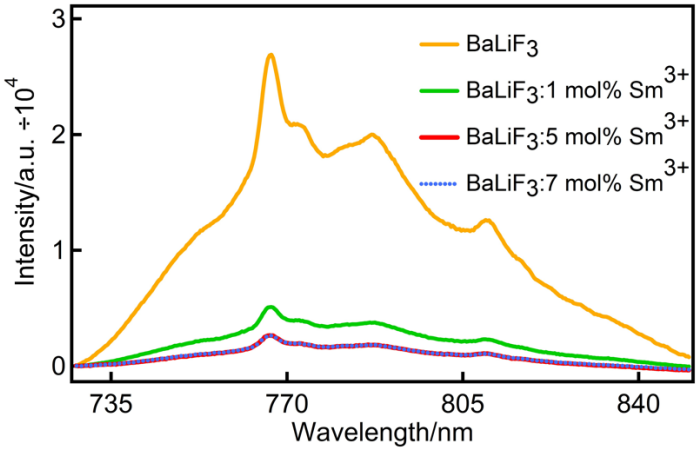

Fig. S4. Luminescence spectra of pure $BaLiF_3$ after annealing compared to $BaLiF_3$ doped with Sm^{3+} (1 mol%, 5 mol% and 7 mol%). Samples were annealed at 600 °C for 2 h. A 462 nm laser diode was used as the excitation source.

In **Fig. S4**, the room temperature photoluminescence spectrum of pure $BaLiF_3$ was compared with different concentration of Sm^{3+} doped $BaLiF_3$ samples after annealing. It shows that an increasing Sm^{3+} dopant concentration prevents the formation of the colour centre.