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Comment on: "Nucleation and Growth of BaF_xCl_{2-x} Nanorods"

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In a recent paper, Xie et al[1] reported on the nucleation and growth of BaF_xCl_{2-x} nanorods. In this comment, we wish to draw attention to pertinent experimental results that shed more light on the observed morphology and structure of the nanorods discussed in reference [1]. In an independent paper, Zhang et al[2] present the synthesis and characterization of Ba_2ClF_3 microrods.

The composition Ba_2F_3Cl given in references [1,2] should be corrected. In the Ba/F/Cl system, three compounds have been characterized from single-crystal data: BaFCl,[3] $Ba_{12}F_{19}Cl_5$,[4] and $Ba_7F_{12}Cl_2$.[5] The matlockite-type compound BaFCl can be obtained under different synthesis conditions, and $Ba_{12}F_{19}Cl_5$ forms in a flux only at high temperature. At high fluorine concentrations and at relatively low temperatures, the compound $Ba_7F_{12}Cl_2$ can be obtained in the form of hexagonal needles: melt synthesis with an NaCl/LiCl flux gives an ordered and a disordered modification[5] with space group *P*-6 and $P6_3/m$, respectively. Between 160 °C and 250 °C under hydrothermal conditions, and by gel growth at room temperature, an ordered structure[6] and a superstructure[7] can be obtained, respectively.

Synthesis conditions given in references [1,2] are consistent with the conditions for the formation of $Ba_7F_{12}Cl_2$. The powder pattern given in reference [1] was indexed by using unconfirmed powder diffraction data[8] and should be indexed with the structural data given for ordered $Ba_7F_{12}Cl_2$[5] (Figure 1); an experimental FWHM of 0.03° and a presumed crystal size of about 60 nm according to the fast growth conditions was included in the pattern simulation (PowderCell).[9] The rod-like shaped nano-units given in reference [1] are in agreement with the hexagonal needle shape (Figure 2) obtained during crystal growth and might explain the *a*/*c* ratio of the nanocrystalline material formed on precipitation.

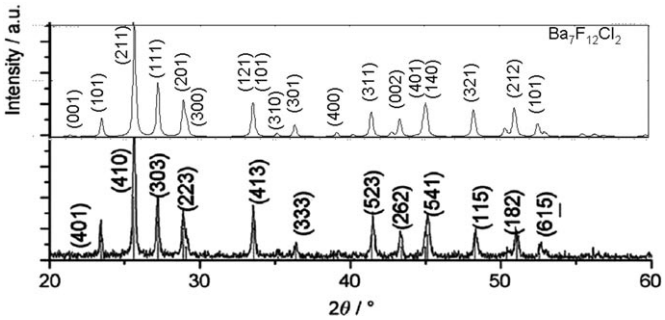

Figure 1. Calculated powder pattern based on the single-crystal structure of $Ba_7F_{12}Cl_2$[5] (upper trace) and reported experimental pattern from reference [1] indexed by using the data from reference [8] (lower trace).

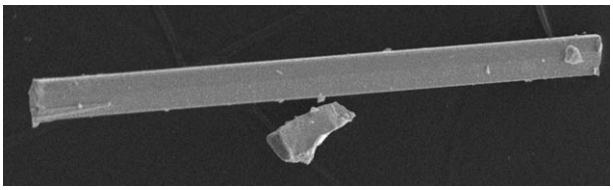

Figure 2. Image of a single crystal and a small fragment of $Ba_7F_{12}Cl_2$, The length of the crystal needle is 400 μm. (REM Quanta 200 Mk2).

A powder sample, kindly provided by Prof. Yadong Li, was measured additionally by X-ray diffraction using a STOE Stadi P diffractometer with capillary equipment and $Cu_{K\alpha 1}$ radiation. Rietveld refinements (Topas 4.2)[10] for this sample yielded the following phase composition: $Ba_7F_{12}Cl_2$ ($a = 10.6281(3)$ Å, $c = 4.17940(14)$ Å) 66 wt %, BaFCl 20 wt %, NaF 12 wt %, BaF_2 2 wt %. The average crystallite sizes in nm (with e.s.d. values of the last digits in parentheses) based on the Scherrer method were: $Ba_7F_{12}Cl_2$ 166(4), BaFCl 9.6(5), NaF 97(8) and BaF_2 30(2).

As a further comparison of the samples using another experimental technique, we have obtained Raman spectra. Figure 3 compares the Raman spectra of the sample provided by Professor Li and an assembly of single crystals of

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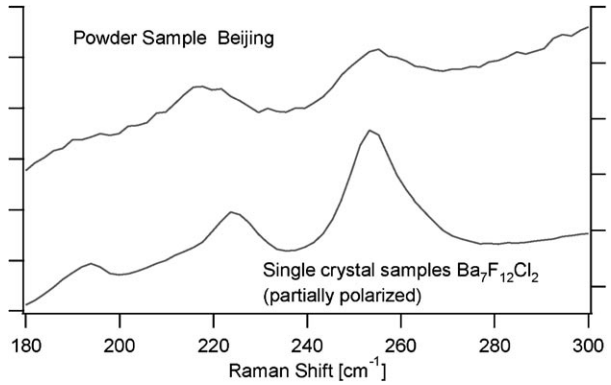

Figure 3. Room-temperature Raman spectra of the sample from Professor Li[1] and of crystals of $Ba_7F_{12}Cl_2$ synthesized from high-temperature flux.[5] Raman spectra were obtained at room temperature by using a Kaiser Holospec Monochromator equipped with a CCD camera. Spectra were excited at 488 nm with 50 mW power.

$Ba_7F_{12}Cl_2$ prepared in our laboratory. The spectra are quite similar; the small shift of the band around 220 cm^{-1} is related to polarization effects, as our crystals are slightly oriented.

A common feature of the crystal structures of BaFCl, $Ba_{12}F_{19}Cl_5$, and $Ba_7F_{12}Cl_2$ is that the Ba atoms have a coordination number of 9. In the crystal, however, the arrangement is quite different. In $Ba_{12}F_{19}Cl_5$ and $Ba_7F_{12}Cl_2$ as well as in the corresponding lead compounds $Pb_7F_{12}Cl_2$[11] and $Pb_7F_{12}Br_2$,[12] the propeller shape arrangement of the halides in the structure as well as the short lattice constant *c* favors a needle shape crystal habitus for all synthesis methods.

Barium halides are interesting hosts for optical applications. $Ba_7F_{12}Cl_2$ is a host for the rare-earth element Eu^{II}[13] and acts as an intense white phosphor.[14] The channel-type structure allows the replacement of Ba^{2+} and Cl^- with other ions and interstitial sites can be occupied.[15] Detailed order/disorder studies on single crystals of substituted $Ba_7F_{12}Cl_2$ are still in progress. Nanocrystalline barium fluoride chloride samples might reveal further interesting optical properties.

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