

1. Introduction/Background

Crystallisation pathways of REE (Rare Earth Element) carbonates in aqueous solutions depend on:

- The REE in question (carbonates with lighter REE crystallise faster)^{1, 2}
- The ligands present and their concentration^{3, 4}
- Temperature and heating regime^{5, 6}

Similarly to Ca carbonates⁷, REE carbonates in an aqueous solution are thought to crystallise via the dehydration of an x-ray amorphous precursor^{1, 2}. Precipitated mineral phases and crystallisation rates vary depending, in part, on the REE used. REE-rich minerals naturally contain with multiple REEs, yet much of the work on REE aqueous geochemistry focuses on the behaviour of discrete REEs.

2. Project Rationale

What is the effect of mixed REE on the crystallisation pathways of REE carbonates?

We study how mixed REE and their varying ratios affect crystallisation times, precipitate morphologies and final composition.

Understanding this serves to mimic more realistic conditions found in natural geological settings propitious to REE mineralization as well as being useful for applications in materials science.

Summary / Conclusions

- The presence of other REEs in the solution alters the initial crystallisation pathways of REE carbonates
- Growth begins with flocculation of nanoparticles followed by crystal growth via Ostwald ripening
- The resulting product is a unique, single phase, mixed-REE carbonate crystal

UV-Vis: Evolution of REE carbonate crystallisation

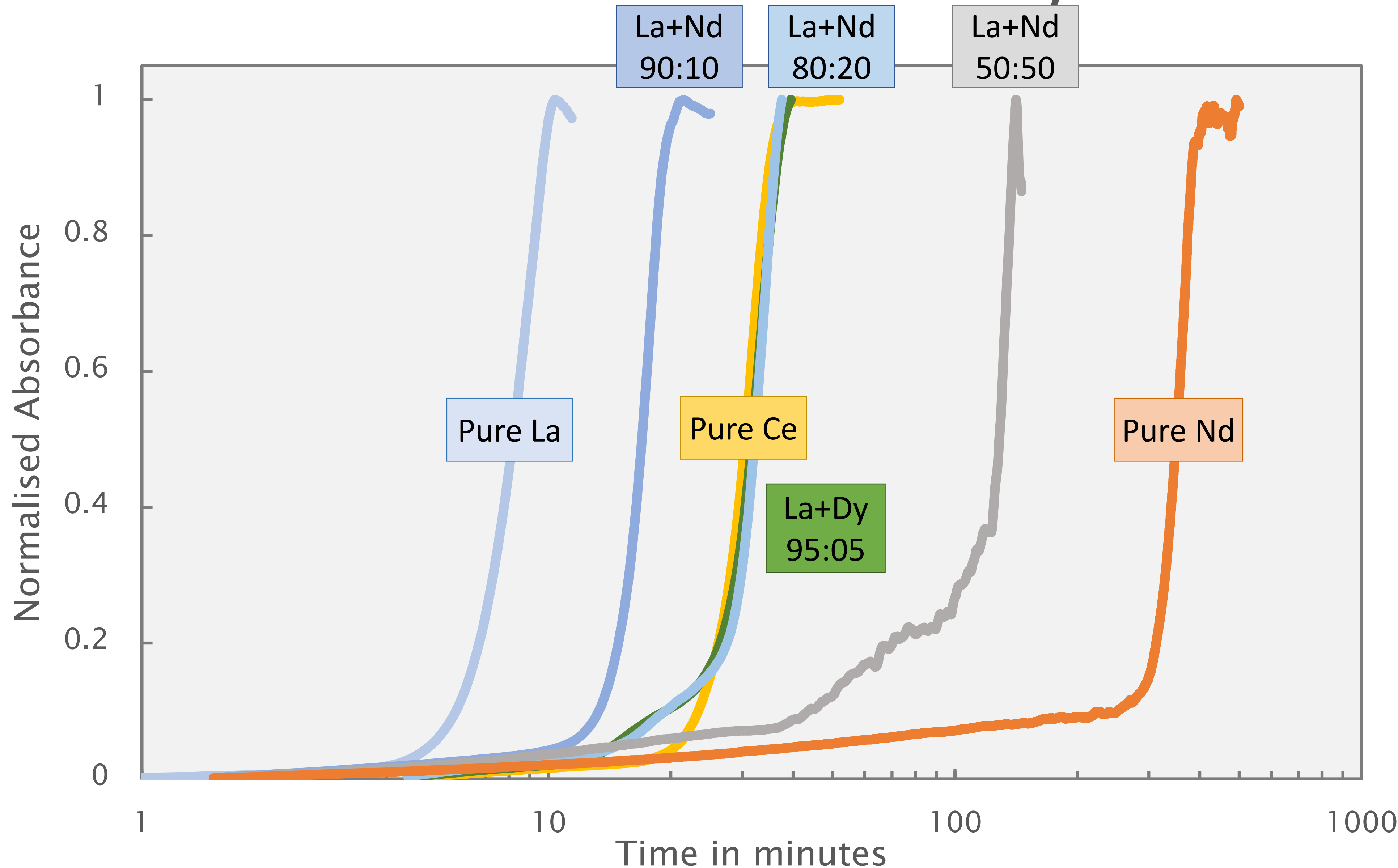


Figure 1. Time-resolved UV-Vis measurements of REE carbonate crystallisation containing various REE ratios. The time between the different ratios and the end-members correlates to the average ionic potential of the mixture. e.g. the hidden La+Dy, Ce and 80:20 La+Nd curves occur simultaneously as all these mixtures have a similar averaged ionic potential (2.498 ± 0.005).

The mixtures also show a single peak, and not a separate peak for each end-member, suggesting a single phase product. The mixed REE precipitate as a single phase and SEM images confirm this

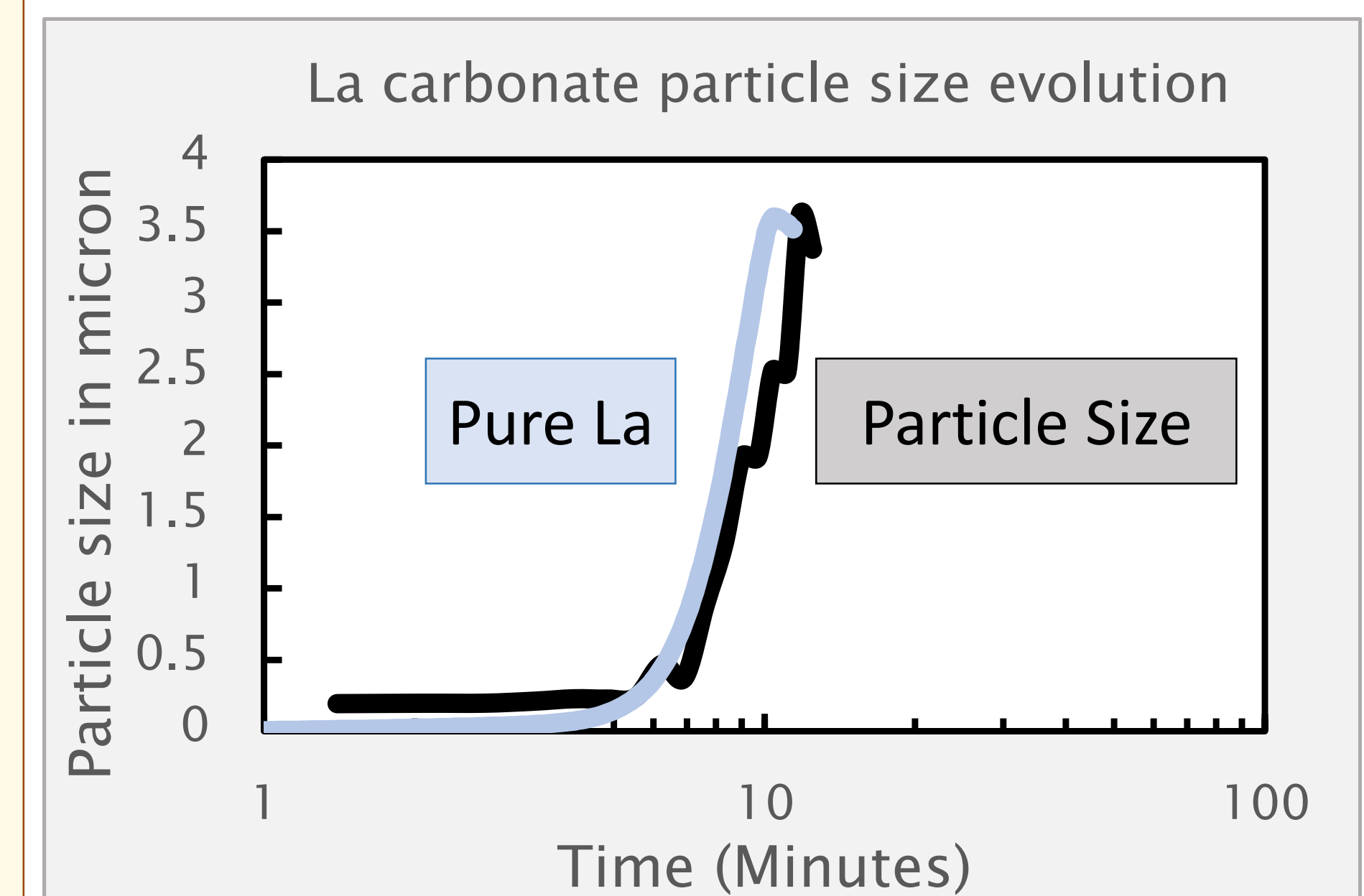
3. Methods

Time-resolved UV-Vis data (Fig. 1) as a proxy for particle growth is obtained using the same method as previous work^{1,2}. 0.01M of $\text{REE}(\text{NO}_3)_3$ (REE=La, Nd, Ce, Dy) of varying ratios is mixed with 0.01M of Na_2CO_3 at 30°C under constant stirring, whilst always maintaining a 1:1 $\text{REE}(\text{NO}_3)_3$ to Na_2CO_3 ratio.

4. Initial Precipitates

SEM images taken at the low-absorbance phase in Fig. 1 shows that all REE mixtures begin the crystallisation process via the formation of spherical nanoparticles (Fig. 2c). The particles are between 20–30nm in diameter, do not vary in size depending on REE mixture, do not grow larger with time and are x-ray amorphous.

Particle size analysis confirms that at the inflection point of the UV-Vis curves, particle size begins to increase. Coupled to SEM images showing particles clustering over time, this suggests a growth process where the nanoparticles agglomerate.



The undefined and rugged edges of Fig. 2d compared to Fig. 2a and the partial growth of the crystal's rosette facets suggest a growth mechanism is via Ostwald ripening.

5. Final Crystals

SEM images taken at the peak of the UV-Vis curves do not exhibit crystalline habits and still contain a vast amount of nanoparticles. Samples appear fully crystalline beyond a period of time (2 to 8 hours) depending on their REE mixture. The higher the proportion of heavier REE in the initial solution mixture, the longer it takes.

Crystals exhibit different habits depending on composition (Fig. 2a, 2b). Mixed samples only show one type of crystal habit: laths or cruciform laths, regardless of the mixture. The single habit suggests that the mix result produces a homogenous, mixed REE crystal and not 2 distinct populations. Pure end-members tend to exhibit distinct habits such as the rosettes for La (Fig. 2a).

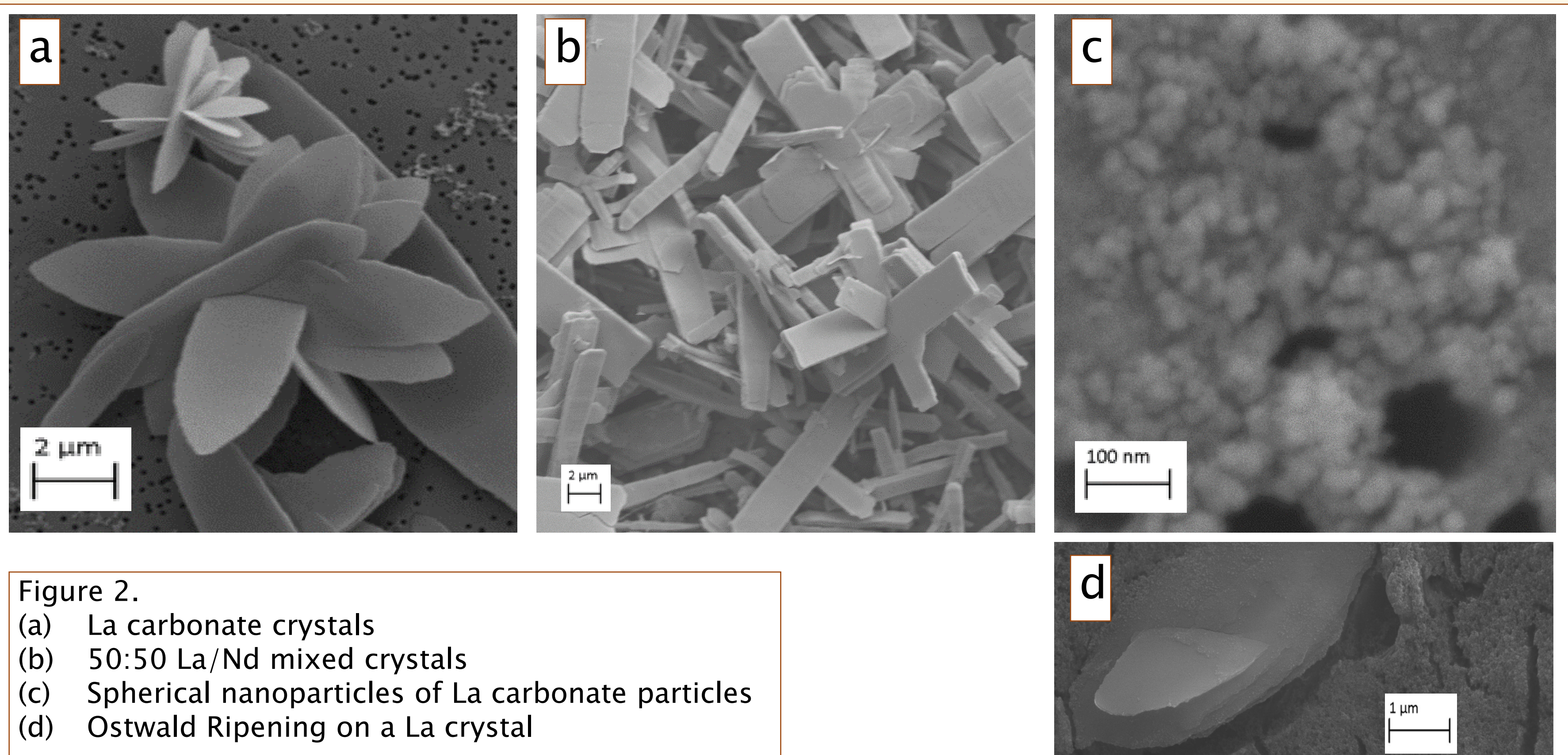


Figure 2.
(a) La carbonate crystals
(b) 50:50 La/Nd mixed crystals
(c) Spherical nanoparticles of La carbonate particles
(d) Ostwald Ripening on a La crystal

References

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