

**RAMAN STUDY OF SYNTHETIC  $\text{BaCO}_3$  -  $\text{SrCO}_3$  SOLID SOLUTIONS.** N. Sánchez-Pastor<sup>1</sup>, A. M. Gigler<sup>2</sup>, and L. Fernández-Díaz<sup>1</sup>. <sup>1</sup>Departamento de Cristalografía y Mineralogía. Universidad Complutense de Madrid. 28040, Madrid (Spain), <sup>2</sup>CeNS and Department for Earth and Environmental Sciences, Ludwig-Maximilians-Universität. 80333, Munich (Germany).

The characteristics of the  $\text{Sr}_x\text{Ba}_{1-x}\text{CO}_3$  solid solution have been subject to controversy because of the important implications that the Sr/Ba ratio of naturally occurring members of this series have for the geochemistry of carbonates. The fact that intermediate compositions of the  $\text{Sr}_x\text{Ba}_{1-x}\text{CO}_3$  solid solution are scarce in nature, together with the remarkable difference between the ionic radii of 10.88% between  $\text{Sr}^{2+}$  (1.31 Å) and  $\text{Ba}^{2+}$  (1.47 Å), support the picture that there is a miscibility gap at low temperatures [1]. Nevertheless, experimental studies of its thermodynamic characteristics concluded that this solid solution is ideal and, consequently, complete [2].

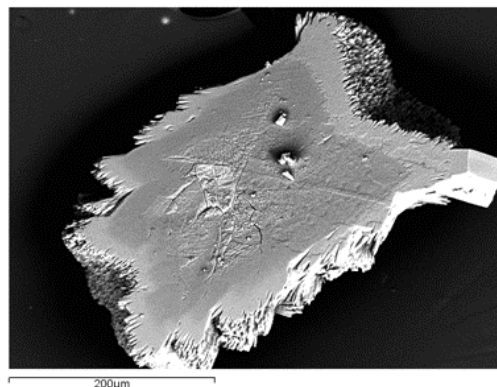
Previous works showed that a variety of zoned  $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$  crystals can be experimentally produced by counter-diffusion within a column of porous silica gel at room temperature [3]. Similar crystal growth gel experiments conducted using mixed  $\text{SO}_4^{2-}/\text{CO}_3^{2-}$  solutions as the anionic reactant, allowed us to observe not only the formation of zoned  $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$  crystals but also their subsequent replacement by the  $\text{Ba}_x\text{Sr}_{1-x}\text{CO}_3$  solid solution. The experimental arrangement consist of a U-tube where a column of silica hydrogel occupies the horizontal branch, while the vertical branches A and B correspond to the reservoirs of the parent solutions. Here, A and B were filled with  $\text{BaCl}_2$  (0.9 M) +  $\text{SrCl}_2$  (0.1 M) and  $\text{Na}_2\text{CO}_3$  (0.5 M) +  $\text{Na}_2\text{SO}_4$  (0.3 M), respectively [4]. One month after starting counter-diffusion, crystals of the  $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$  solid solution were formed within the gel. These crystals show progressive as well as sector zonings, with an increase in the Ba/Sr ratio from core to rim. Moreover, an oscillatory zoning is often superimposed. These characteristics have been observed by both electron microprobe and Raman analysis.

The  $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$  crystals recovered from the gel after one year showed identical size and external morphology, as well as the same type of chemical zonation patterns. However, microprobe analyses indicated that these crystals contain no S, but are completely replaced by the  $\text{Ba}_x\text{Sr}_{1-x}\text{CO}_3$  solid solution: these crystals are now  $\text{Ba}_x\text{Sr}_{1-x}\text{CO}_3$  pseudomorphs after the original  $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$  crystals (Fig. 1). In order to further characterize the replaced crystals, a Raman spectroscopy study has been carried out.

In spite of the importance of the witherite-strontianite solid solution, very few authors report spectroscopic measurements on the intermediate compositions [5, 6]. In the present work, synthetic samples

obtained by co-precipitation were studied. The wide thermodynamic, kinetic, and vibrational spectroscopic database of the end members of the solid solution constitutes an excellent starting point for this investigation.

All spectra of the end members and the intermediate compositions of the solid solution showed the fundamental internal modes and the lattice modes. The  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  internal modes arise from the symmetric stretching, the out-of-plane bending, the asymmetric stretching and the in-plane bending mode of the carbonate ion group, respectively. The variation of wavenumbers of internal and lattice modes as a function of the chemical composition was studied. The results show that progressive substitution of strontium ions by barium ions produces bandshifts towards higher wavenumbers. This is due to the fact that a molecular vibration with a stronger bonding energy has a higher vibration frequency. As the Ba cation has a larger radius (1.6 Å) than that of the Sr cation (1.44 Å), the shorter bonding length and consequently the stronger bonding strength of Sr-O compared to that of Ba-O can explain bandshifts toward higher wavenumbers [7].



**Figure 1.** SEM image of  $\text{Ba}_x\text{Sr}_{1-x}\text{CO}_3$  pseudomorphs after C/S-replacement in the original  $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$  crystals

#### References:

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