A multi-methodological study of the bastnäsite-synchysite polysomatic series: Tips and tricks of polysome identification and the origin of syntactic intergrowths

ROBERTO CONCONI¹, PATRIZIA FUMAGALLI²†, AND GIANCARLO CAPITANI¹,*

¹Dipartimento di Scienze dell’Ambiente e della Terra, Università degli Studi di Milano-Bicocca, Piazza della Scienza 4, 20126 Milano, Italy
²Dipartimento di Scienze della Terra Ardito Desio, Università degli Studi di Milano, Via Botticelli 23, 20133 Milano, Italy

Abstract

In this paper, we evaluated the potentialities of Raman spectroscopy and electron backscattered diffraction (EBSD) in the microscopic characterization of Ca-REE fluorcarbonates (CRFC) belonging to the bastnäsite-synchysite series to provide a “road map” for further investigations with transmission electron microscopy (TEM). EBSD was effective in establishing the sample orientation, setting up the oriented cuts, and ascertaining the effective syntactic relationship among all the detected CRFC phases; however, it failed to distinguish between different polysomes. On samples with different orientations that were preventively ascertained by EBSD and characterized by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), micro-Raman spectroscopy allows for distinguishing between polysomes based on the differences in intensity and position of the symmetric stretching vibration ($v_1$) of the carbonate group ($CO_3^{2-}$) in the region around 1080–1099 cm$^{-1}$. However, as evidenced by TEM-EDS, what appears as a homogeneous polysome in backscattered electrons (BSE) images may be a disordered intergrowth of compositional faults with a bulk composition being matched with that of a real polysome only by accident. Therefore, we conclude that the Raman signal is sensitive to different Ca/(Ca+REE) ratios but not to any ordered distribution of Ca-poor and Ca-rich lamellae within the analyzed volume, making the unambiguous identification of a polysome tricky. Finally, several ordered polysomes were detected at the TEM scale, including a $B_S$ and a long-range polytype with a 32 nm repeat distance along c. The possible implications of the detected microstructure for ore mineral formation are discussed.

Keywords: Raman spectroscopy, electron backscattered diffraction, transmission electron microscopy, bastnäsite, synchysite, parasite, polysomatism

Introduction

The Ca-REE fluorcarbonates (hereafter CRFC) are important minerals for at least two (apparently) distant reasons, one tied to fundamental research and the other to critical raw materials. Indeed, from a crystallographic point of view, CRFC form a polysomatic series (Veblen 1991) with bastnäsite [REE(CO$_3$)$_2$F] and synchysite [CaREE(CO$_3$)$_2$F] as the end-members (Fig. 1). Accordingly, intermediate terms can be described by bastnäsite ($B$) and synchysite ($S$) modules ($B_S$) and their composition calculated as [REE(CO$_3$)$_2$F]$_x$[CaREE(CO$_3$)$_2$F]$_{1-x}$ (Donnay and Donnay 1953). Intermediate terms of the series are parasite [CaREE$_x$(CO$_3$)$_2$F$_{3-x}$] (or $BS$) and röntgenite [CaREE$_x$(CO$_3$)$_2$F$_{3-x}$] (or $B_S$). Possible additional intermediate polysomes have been described by high-resolution transmission electron microscopy (HRTEM) studies (Van Landuyt and Amelinckx 1975; Wu et al. 1998; Meng et al. 2001a, 2001b, 2002; Ciobanu et al. 2017; Capitani 2019, 2020; Zeug et al. 2021). Moreover, the layer sequence within a polysome may be different: a given layer ($B$ or $S$) may be differently rotated with respect to the ordered sequence, giving rise to polytypism and polytypic disorder as in micas (Banfield et al. 1994). Finally, within a polysome, $B$ and $S$ layers may exchange relative positions, leading to polymorphism (Capitani 2019).

On the other hand, bastnäsite and synchysite are the most important ore minerals for Ce, La, Nd, and Y. The demand for these REEs has spiked in recent years due to their increasing usage in numerous high-technology applications, including electronics and green technologies. For instance, Ce oxide (Ce$_2$O$_3$) is used in catalytic converters; La and Nd are used in the manufacturing of hybrid and electric motors and rotors of wind turbines; Nd compounds are used for the manufacturing of the most powerful permanent magnets in microphones, speakers, and hard disks; and synthetic Y garnet (Y$_3$Al$_2$O$_12$) is used in filters for micro-waves, acoustic transmitters and transducers, LEDs, lasers, and even as gems (e.g., Goonan 2011; Charalampides et al. 2015).

In nature, CRFC rarely occur as single crystals. Commonly, they form microscale syntactic (crystallographically oriented) intergrowths (Donnay and Donnay 1953) of different polysomes/polytypes, often with stacking faults at the nanoscale. Due to this recurrent microstructure, definitive structural analyses by single-crystal X-ray diffraction (SCXRD) have been achieved relatively recently and only for some basic polysomes, namely bastnäsite-(Ce) (Ni et al. 1993), synchysite-(Ce) (Wang et al. 1994), and parasite-(Ce) (Ni et al. 2000). Apart from these fortunate cases, for most of the occurrences with intergrowths at the microscale, reliable structural analysis can only be performed via TEM.

Regarding SEM-EDS analysis, which is a relatively faster characterization technique compared to HRTEM, syntactic intergrowths can be revealed by the average atomic number ($Z$)