Agarose gel as an alternative crystallization medium for synthetic mineral phases. The case of sampleite ($NaCaCu_5(PO_4)_4Cl \cdot 5H_2O$).

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INTRODUCTION

The growth of single crystals in gel matrix by controlled diffusion is a useful tool for mineralogical and chemical research since the first observations by Liesegang in 1896 (Liesegang, 1896). Crystallization in gel allows for minimizing precipitation, controlling crystal habits and size, and it is useful to obtain phases that are difficult to crystallize or whose well-developed crystals possesses singular properties applicable to the development of new technologies (Partel & Venkateswara, 1982). An example is the case of copper minerals of the lavendulan group and structurally similar compounds. These are polynuclear copper coordination compounds and have interest in materials science (Lambert et al., 1978; Zhu et al., 2012; Haldar et al., 2017; Antonov, 2020). Due to its scarcity, the synthetic analogues of these phases are problematic regarding its applications, or even their proper mineralogical descriptions. Thus, the synthetic analogues are relevant for its bulk synthesis. In this work, we propose an easy and inexpensive methodology for crystal growth, using agarose gel for the synthesis of the lavendulan group mineral sampleite (($NaCaCu_5(PO_4)_4Cl \cdot 5H_2O$).

METHODS

Ultrapure-grade agarose gel (NZYTech) in water (0.5 %) was used as medium for crystal growth. The gel was prepared by boiling a mixture of agarose and water, pouring it into a U-shaped test tube, and allowing it to solidify at room temperature.

A solution containing 0.4 M sodium phosphate and 0.1 M anhydrous sodium sulfate was added to one end of the test tube, while a solution containing 9 mmol of copper acetate and 2 mmol of calcium chloride in 20 mL of water was added to the other end. The tube was sealed, and the reactants were allowed to diffuse through the gel for two months. Afterward, the agarose gel was melted by heating it in a household microwave oven and the crystals were recovered by filtration through a Büchner funnel (Fig 1).

The crystals were analyzed using Raman spectroscopy, Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy (SEM-EDS), and X-ray diffraction (XRD). For Raman analysis, a B&WTek Cleanlaze microscope with a GlacierX CCD of 2048 pixels cooled by a Peltier cell was used, with excitation at 532 nm. SEM-EDS was performed at the Unidad de Técnicas Geológicas at Universidad Complutense de Madrid (UCM) using a JEOL JSM-820 electron microscope equipped with an EDS system for chemical composition determination during SEM observations. DRX analysis was carried out using a BRUKER D8 Advance with a copper tube as an X-ray source and a SOL-X detector. The data was preprocessed using DIFFRACplus software.

RESULTS AND DISCUSSION

About 120 mg of crystals were recovered after experiment. Its analysis by Raman and SEM-EDS spectroscopy identified it as sampleite. (empirical formula obtained with EDS) (Fig.2). The phase identity was confirmed by XRD.

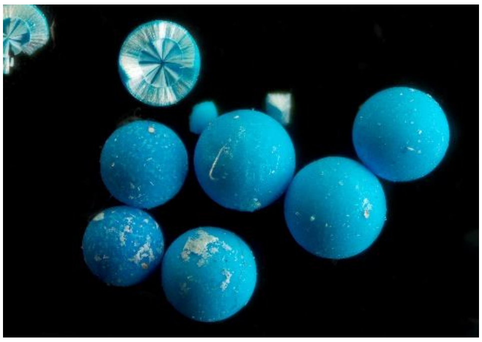

***Fig 1**. Sampleite spherules obtained in agarose-gel crystallization. Field of view: 4mm.*

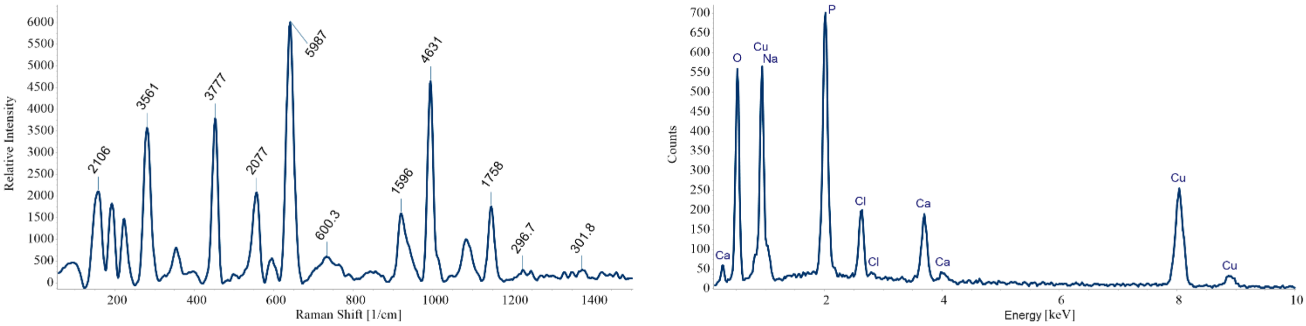

***Fig 2**. Raman spectrum of grown sampleite (left) and EDS spectrum (right)*

The sampleite appears as light blue spherules, ranging in size from 0.15 to 0.25 mm, and forming botryoidal growths. The spherules are composed of radial aggregates and rosettes of very thin lath-like and micaceous plates, which is consistent with its natural occurrence. The spherules crystallize in the gel, forming Liesegang rings, a pattern of periodic growth. No other phosphate phases were identified in the experiment. Sampleite was formed in a pH range between 3 and 7, with the larger and more abundant crystals formed at pH 4-5.

The crystallization of sampleite in agarose gel is inexpensive and straightforward. The recovery of crystals from the gel is easier than with classic silica gel, and it allows for the production of purer phases, although it does take longer. In addition to allowing for the efficient production of pure mineral phases, crystal growth in agarose gel is an ideal medium for studying growth conditions such as pH and reactant concentration, which can be easily modulated, allowing for the modeling of mineral growth.

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