

Refinement of the crystal structure of copiapite-group synthetic compounds using synchrotron radiation

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Introduction

Compounds equivalent to the end-members of the copiapite-group were synthesized with the purpose of refining their crystal structures. The general formula of the copiapite-group minerals is $(A^{(II)})_{1-3x}A^{(III)}_{2x}Fe^{(III)}_4(SO_4)_6(OH)_2 \cdot 20H_2O$,

where the positions A are completely filled by divalent cations (Ca, Cu, Fe, Mg, Zn) for $x = 0$, or 2/3 by trivalent cations (Al, Fe) for $x = 1/3$. Only intermediate natural species and the Fe(III) synthetic end-member were known. The synthetic Mg, Zn, Al and Fe(III) end-members and also the naturally and synthetic unknown Mn, Ni and Co end-members were now obtained.

In spite of their relative frequency, the copiapite-group minerals are not very well-known as to optical and crystallographic properties and conditions of stability. The main objectives of this research included the development of studies on synthesis of products equivalent and analogous to copiapite-group minerals, with the purpose of obtaining, by means of crystalline improvement, crystals in enough dimensions for optical and crystal structure studies, and also X-ray diffraction data of good quality for indexation and calculation of cell parameters. The possibility of determination of crystal structures starting from monocrystals seems now more remote, due to the reluctance of growth of crystals with appropriate dimensions.

All the published conventional X-ray diffraction data for copiapite-group minerals are imperfect, with inversion of the diffraction intensity of the two first and more important reflections. Structural data are available for only two intermediate terms. It was verified that the use of the Göbel mirror facilitates the observation of the real intensities for the peaks obtained in low 2θ angles.

Objectives

This research has as main objective the refinement of the crystal structure of synthetic terms of the copiapite-group, using X-ray diffraction data with the Göbel mirror and with synchrotron radiation. This will allow comparing the methods.

Materials and amount of samples to be studied

The copiapite-group is composed by seven mineral species.

calciocopiapite $CaFe_4(OH)_2(SO_4)_6 \cdot 20H_2O$,
cuprocopiapite $CuFe_4(OH)_2(SO_4)_6 \cdot 20H_2O$,
copiapite $FeFe_4(OH)_2(SO_4)_6 \cdot 20H_2O$,
magnesiocopiapite $MgFe_4(OH)_2(SO_4)_6 \cdot 20H_2O$,
zincocopiapite $ZnFe_4(OH)_2(SO_4)_6 \cdot 20H_2O$,
aluminocopiapite $Al_{2/3}Fe_4(OH)_2(SO_4)_6 \cdot 20H_2O$,
ferricopiapite $Fe_{2/3}Fe_4(OH)_2(SO_4)_6 \cdot 20H_2O$.

They are secondary minerals of very common occurrence, mainly in coal mines and sulfide veins. The optical and crystallographic properties, and conditions of stability of ferricopiapite were studied by Recoura (1907), Scharizer (1913), Posnjak & Merwin (1922) and Walter-Lévy & Quéméneur (1963) through its synthetic analogue. The other members of the copiapite-group, just known in natural occurrences, correspond to compounds of composition intermediary among the mentioned ideal compositions.

Among the papers about the copiapite-group, the more important are those that contain, at the same time, chemical and X-ray diffraction data:

magnesiocopiapite: Kravtsov (1971) and Bayliss & Atencio (1985);
aluminocopiapite: Jolly & Foster (1967);
copiapite: Schmetzer & Medenbach (1983);
ferricopiapite: Margulis et al. (1973), Ramusino & Giuseppetti (1973), Kubisz (1964) and Kravtsov (1971);
cuprocopiapite: Escobar & Gifford (1961).

The minerals calciocopiapite and zincocopiapite were just registered once, respectively by Kashkai & Aliev (1960) and by Tu et al. (1964).

Among the revision papers, Berry (1947) tried to establish the correlation between optical properties and chemical composition of copiapite-group minerals, and Bayliss & Atencio (1985) studied the variation of the unit-cell parameters for the known minerals.

The only crystal structure studies are for magnesiocopiapite (Süsse 1972) and ferricopiapite (Famfani et al. 1973).

Atencio (1986) obtained some preliminary results in the synthesis of copiapite group minerals, producing naturally and artificially unknowns, as "manganocopiapite", "nickelcopiapite" and "cobaltocopiapite".