

Methodological features of determining the composition of α -NiSO₄·6H₂O single crystals activated by low concentration Co²⁺ ions: laboratory diffractometer and synchrotronLevko A. Arbanas^{a,b}, Irina A. Kaurova^a, Galina M. Kuz'micheva^a, Victor N. Khrustalev^b, Vladimir A. Lazarenko^{a,c}^aMIREA - Russian Technological University, Vernadsky pr., 78, Moscow, 119454, Russian Federation^bPeoples' Friendship University of Russia named after Patrice Lumumba, 6 Miklukho-Maklaya st., Moscow 117198, Russia^cNational Research Center «Kurchatov Institute», 1 Akademika Kurchatova pl., Moscow 123182, Russia

INTRODUCTION & AIM

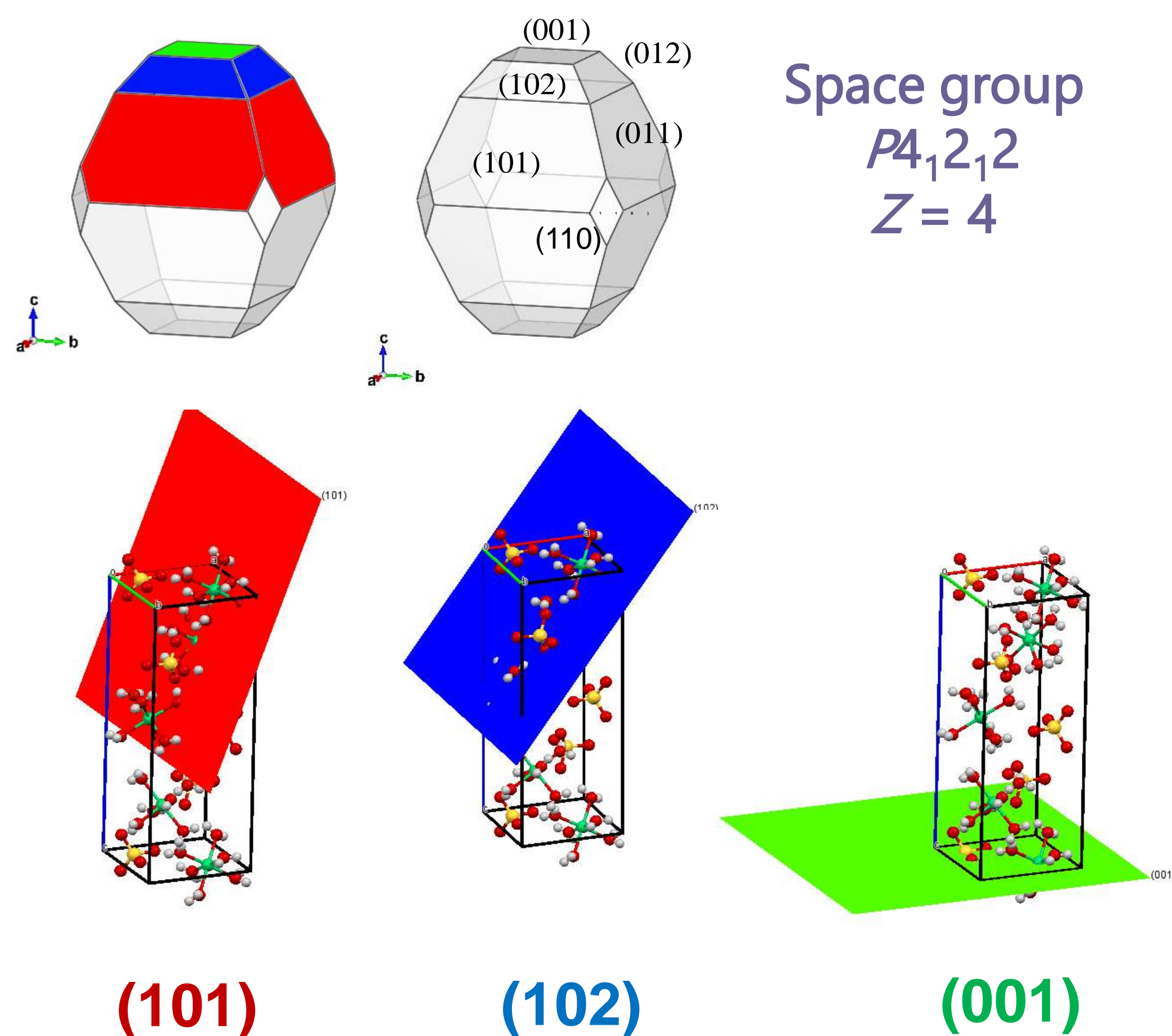
Crystal activation is one of the effective methods that allow influencing functional properties by the nature of dopant ions and their concentration. The region of low dopant concentrations, which is practically not represented in the literature, is of particular methodological, scientific and applied interest.

The aim of the work is to establish the distribution of Co²⁺ ions in the growth sectors of large-sized (~80×80×50 mm) α -Ni²⁺SO₄·6H₂O crystals, used as solar blind UV filters, grown from an aqueous solution with 0.36, 0.68, and 1.0 wt. % Co (α -[Ni,Co]SH).

CRYSTAL GROWTH / GROWTH SECTORS

Temperature reduction method from aqueous solutions:

- NiSO₄ × 7H₂O + H₂O + CoSO₄ × 7H₂O (0.36, 0.68, 1 wt% Co)
- $t = 40\text{--}51^\circ\text{C}$; $v_{\text{stirring}} = 60 \text{ rev/min}$; $\tau = 240\text{--}360 \text{ h}$

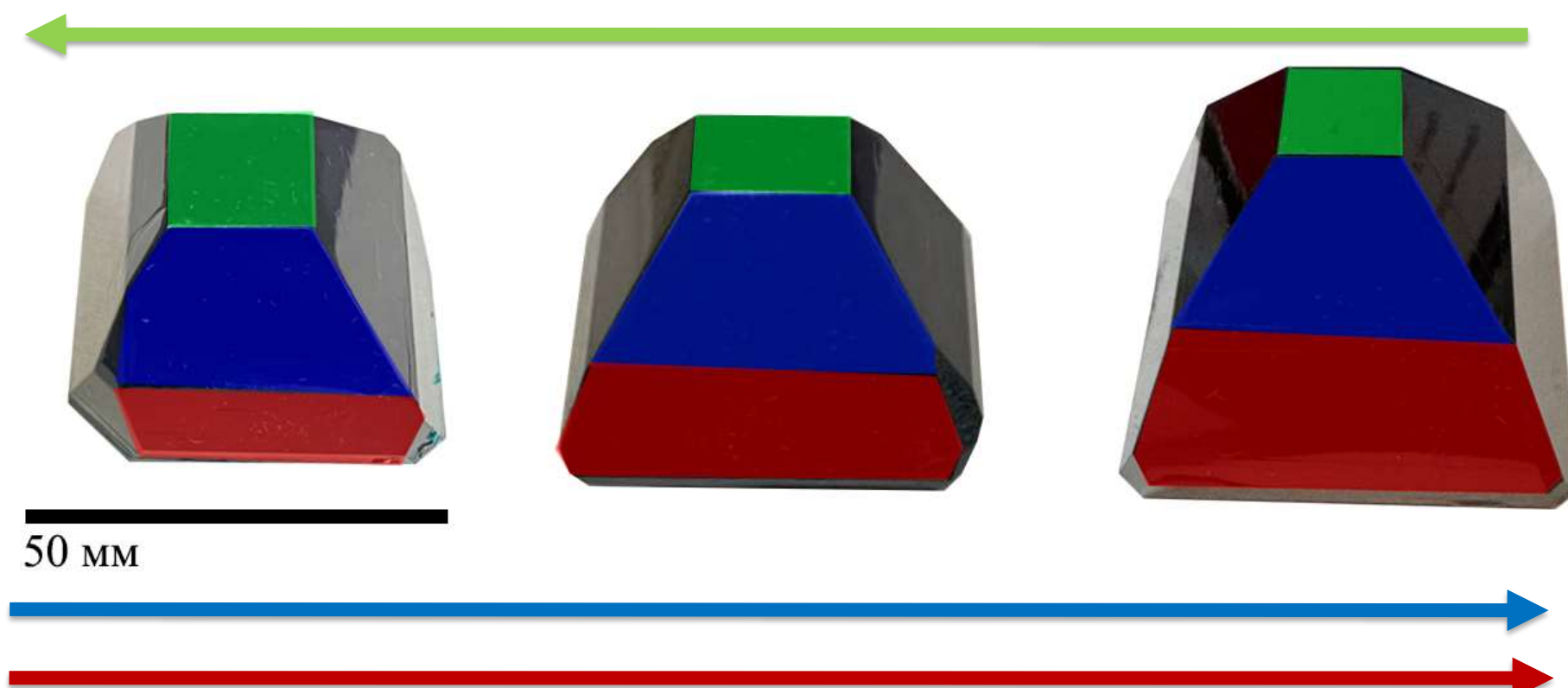


Co, wt%:

0.36

0.68

1.0



X-RAY DIFFRACTION: MACROPARTS

(~0.25×0.25×0.20 mm; Bruker D8 QUEST PHOTON-III)

(101)

(102)

(001)

0.36 wt% Co

 $[\text{Ni}_{0.910(3)}\text{Co}_{0.090}]\text{SH} < [\text{Ni}_{0.939(3)}\text{Co}_{0.061}]\text{SH} > [\text{Ni}_{0.893(3)}\text{Co}_{0.107}]\text{SH}$

0.68 wt% Co

 $[\text{Ni}_{0.871(3)}\text{Co}_{0.129}]\text{SH} < [\text{Ni}_{0.882(3)}\text{Co}_{0.118}]\text{SH} < [\text{Ni}_{0.902(3)}\text{Co}_{0.098}]\text{SH}$

1.0 wt% Co

 $[\text{Ni}_{0.868(3)}\text{Co}_{0.132}]\text{SH} > [\text{Ni}_{0.846(4)}\text{Co}_{0.154}]\text{SH} < [\text{Ni}_{0.936(3)}\text{Co}_{0.064}]\text{SH}$

X-RAY DIFFRACTION: MICROPARTS

(~0.02×0.02×0.02 mm; “Belok/XSA” KISI-Kurchatov)

(101)

(102)

(001)

1.0 wt% Co

 $[\text{Ni}_{0.985(4)}\text{Co}_{0.015}]\text{SH} \approx [\text{Ni}_{0.984(4)}\text{Co}_{0.016}]\text{SH} < [\text{Ni}_{0.989(4)}\text{Co}_{0.011}]\text{SH}$

CONCLUSION

- A decrease in the Co content in the α -[Ni,Co]SH crystals with an increase in its concentration in solution for the (001) sector and *vice versa* for the (101) and (102) sectors is due to *physicochemical reasons*:

According to the analysis of residual electron density, in the (101), (102), (001) growth sectors of α -[Ni,Co]SH with 0.36 and 0.68 wt% Co, the presence of interstitial Co and/or Ni ions in addition to the substitution of Co²⁺ for Ni²⁺ ions is possible. In the Ni crystallographic site in the (101) and (102) growth sectors of α -[Ni,Co]SH with 0.36, 0.68, and 1.0 wt% Co and in the (001) growth sector of α -[Ni,Co]SH with 0.36 and 0.68 wt% Co, the simultaneous presence of Ni, Co and vacancies (\square) is possible.

- Different distribution of Co across growth sectors with increasing its content in solution/crystal is due to *growth reasons*:

Different distribution coefficients of dopant ions among the growth sectors.

- Different compositions calculated using diffractometer and synchrotron data is due to *methodological reasons*: Different crystal regions under investigation; different samples dimensions for analysis; different reflection arrays; different software.

All the above mentioned must be taken into account when interpreting and comparing experimental results to determine the actual compositions of crystals.

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