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The influence of an ultra-small amount of heterovalent Y^{3+} activator ions in aqueous solution on the defect formation of different growth sectors of α-$Ni^{2+}SO_4·6H_2O$ crystals

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INTRODUCTION & AIM

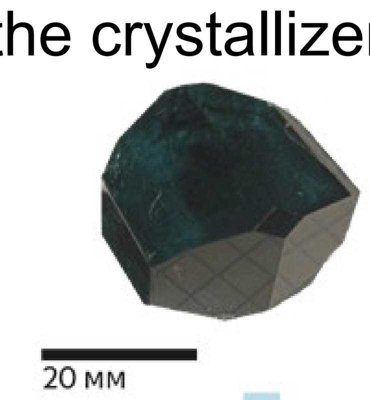
Materials based on α-$NiSO_4·6H_2O$ (NSH) (sp. gr. $P4_12_12$, Z = 4) are used for lithium-ion batteries and UV filters for the solar-blind range. Their performance characteristics can be varied by introducing activator ions *M* [*Kuz'micheva, G. M., Arbanas, L. A., Manomenova et al. Journal of Alloys and Compounds, 965 (2023) 171369*]. The structure behaviour of *M* ions in NSH depends on differences in crystallochemical characteristics of M^{n+} and Ni^{2+} ions, the way of introducing *M* ions into the solution, and the growth sectors of the crystals.

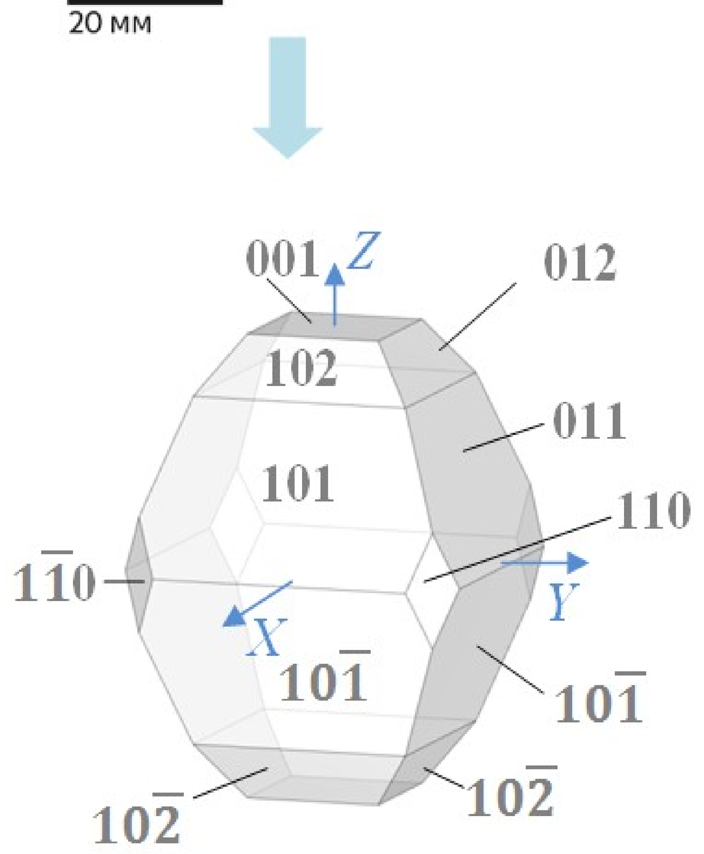
The goal of this work is to establish the distribution of Y^{3+} ions over the largest growth sectors (001), (101) and (102) of α-$Ni^{2+}SO_4·6H_2O:Y^{3+}$ crystals when they are introduced into a solution in extremely small quantities (c = 10 mM).

TEMPERATURE REDUCTION METHOD

NSH:Y-1 (32 g):

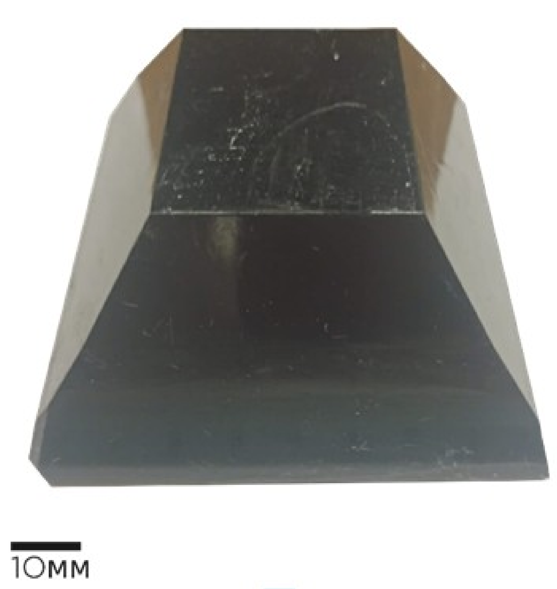
- perpendicular to <001>;
- in 144 h growth was interrupted;
- Edge (010) was in contact with the bottom of the crystallizer.

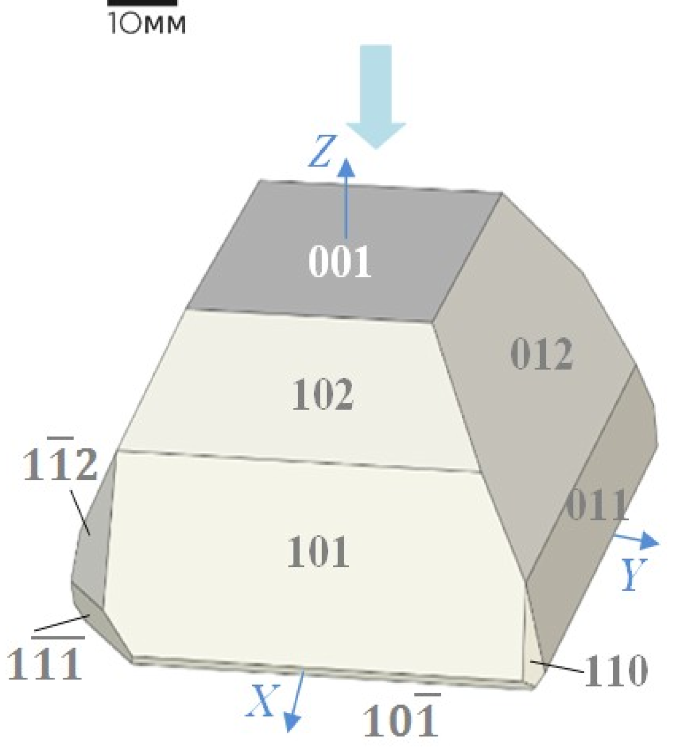




NSH:Y-2 (269 g):

- parallel to <001>;
- growth duration, 336 h;
- Face (001) was in contact with the bottom of the crystallizer

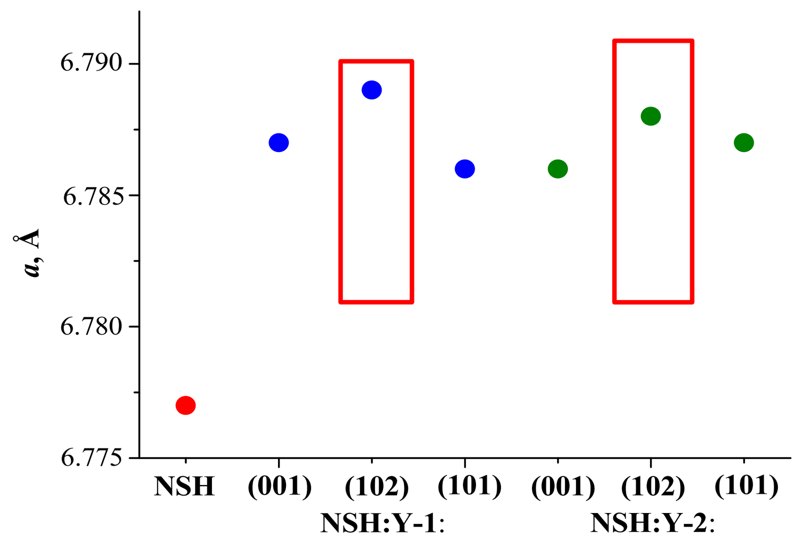


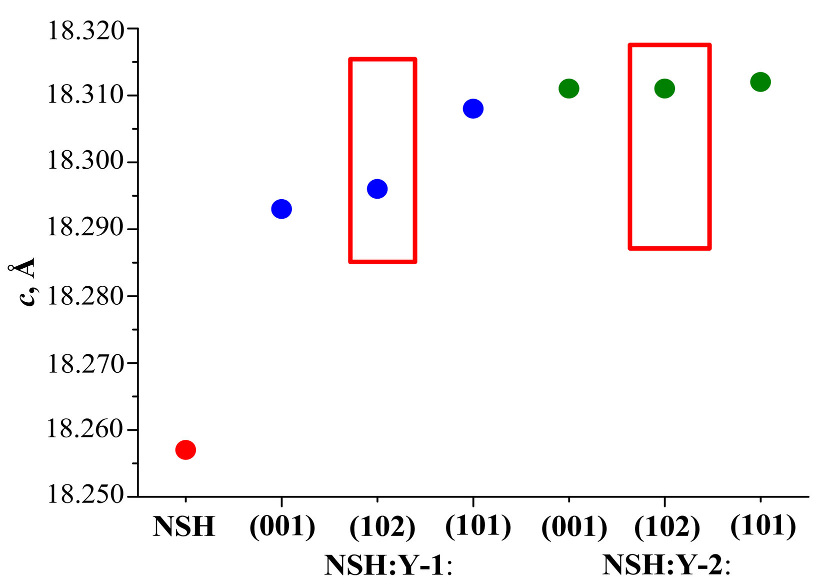


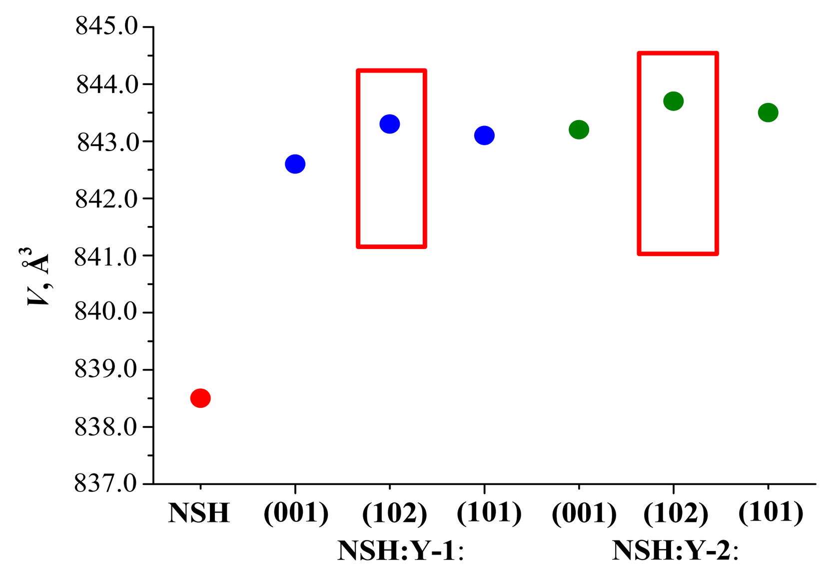
Sample/ Growth sector	Concentration (c_M) of Y^{3+}, ppm (mM/l) / mass spectrometry		
	(001)	(102)	(101)
NSH:Y-1	0.045 (0.045·10^-2^)	0.057 (0.057·10^-2^)	0.085 (0.085·10^-2^)
NSH:Y-2	0.091 (0.091·10^-2^)	0.092 (0.092·10^-2^)	0.094 (0.094·10^-2^)

RESULTS & DISCUSSION

The *a* and *c* unit cell parameters and crystal volume *V* of NSH, NSH:Y-1 and NSH:Y-2, taken from growth sectors (001), (102) and (101)







CONCLUSION

•Ratio for unit cell parameters and volume is *a, c, V* (NSH:Y) > *a, c, V* (NSH), which confirms entry of Y^{3+} into the NSH:Y structure ($^{VI}r(Y^{3+})$ = 0.90 Å > $^{VI}r(Ni^{2+})$ = 0.69 Å).

•For the NSH:Y-1 and NSH:Y-2, the largest *a*, Å parameter and relatively small *c*, Å parameter are found for the growth sector (102). For the NSH:Y-2, a smaller range of parameter's variation is observed, which is not consistent with the content of Y^{3+} ions in the growth sectors according to mass spectroscopy data. The absence of a regular increase in the unit cell parameters with the content of dopant ions is caused by different reticular density ρ ~ n/S (n, the number of material particles, in the present case, Y^{3+} ions; S, surface area): ρ (102)>>ρ(101) for NSH:Y-1 and ρ(102)>ρ(101) for NSH:Y-2. The combination of the large parameter *c*, Å and the small parameter *a*, Å is typical for a tetragonal crystal: an increase in the *a* parameter leads to a decrease in the *c* parameter.

• Y^{3+} ions occupy the interstitial site (Y_i) in NSH:Y with the formation of vacancies at the Ni site to maintain electroneutrality. Defect formation can be described by the quasi-chemical reaction **$0 \rightarrow V_{Ni}^{n'} + Y_i^{m\bullet}$** and the composition **$(Ni^{2+}_{1-x\frac{1}{2\pi}})(Y^{3+}_{i(x)})SO_4]·6H_2O$**. A decrease in the Y^{3+} content is accompanied by a decrease in the Y^{3+} interstitials ($Y_i^{m\bullet}$) and vacancies in the Ni^{2+} site ($V_{Ni}^{n'}$).

• The compositions of the NSH:Y growth sectors, on which the functional properties depend, are important for the application of the material: maximum antimicrobial activity in relation to 8 strains of bacteria and fungi was established for NSH:Y-1 (101), caused by the highest Y^{3+} ion content. This allows us to recommend NSH:Y-1 (101) crystal in the form of a low-concentration solution for use in medicine (wound dressings) both individually and in combination with medicinal products.

FUNDING

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