

Electronic Supporting Information (ESI)

Li₃Co_{1.06(1)}TeO₆: Synthesis, single-crystal structure and physical properties of a new tellurate compound with Co^{II}/Co^{III} mixed valence and orthogonally oriented Li-ion channels

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Rietveld refinement of Li₃Co_{1.06(1)}TeO₆

Rietveld refinements were done with the Diffra^{plus}-TOPAS[®] 4.2 software package (Bruker AXS, Karlsruhe, Germany) based on the parameters derived from the single-crystal structure model. Peak shapes were modeled using modified Thompson-Cox-Hastings pseudo-Voigt profiles.^{1, 2} A measured instrument function for reflection profiles derived from the refinement of a LaB₆ standard³ took into account instrument contributions. The background was fitted with Chebychev polynomials up to the 8th order. Figure 1s displays the results of the Rietveld refinement of Li₃Co_{1.06(1)}TeO₆.

Figure S1:

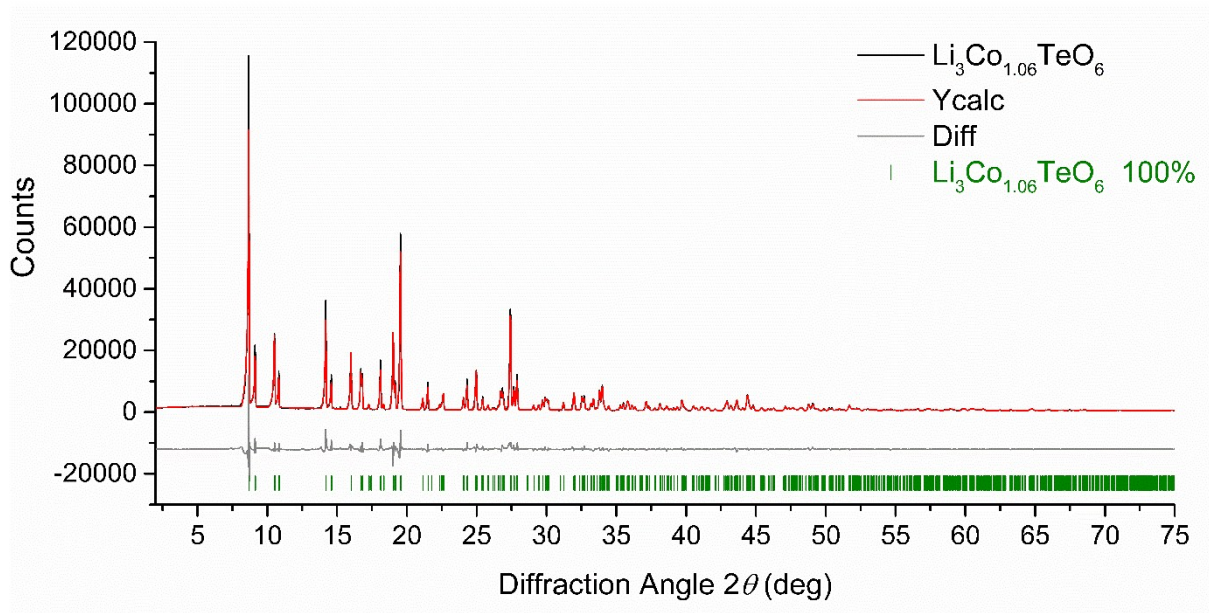


Figure S1. XRD pattern (Mo-K_{α1} radiation) and Rietveld refinement of X-ray pure Li₃Co_{1.06(1)}TeO₆ ($R_{\text{exp}} = 2.41$, $R_{\text{wp}} = 11.21$, $R_p = 8.34$, and $GOF = 4.65$).

Time-/temperature-dependent impedance measurements

Figure S2 A and C show that the heating and cooling curves of $\text{Li}_3\text{Co}_{1.06(1)}\text{TeO}_6$ in air between RT and 723 K hardly differ at all. At RT, an impedance value of $2.26 \cdot 10^7 \Omega$ is apparent. Upon heating to ~ 353 K the impedance starts to increase leading to a value of $8.27 \cdot 10^9 \Omega$. In the temperature region between 353 and 723 K, semiconductive behavior with a decreasing impedance value upon increasing the temperature is visible. Basically, the same impedance course is visible upon re-cooling to RT with slight differences between 371 K and RT. No directly visible phase transformation processes are apparent in Figure S2 A during the heating-cooling cycle. To check for eventual phase transformations, time- and temperature-dependent EIS experiments up to 1173 K were conducted as well as shown in Figure S2 C and D. During treatment of the sample up to 1173 K, a similar impedance course is pictured: lower impedance value at RT ($1.87 \cdot 10^6 \Omega$) at the beginning of the experiment, increase of between RT and 355 K ($1.55 \cdot 10^9 \Omega$ at 355 K), and semiconductive behavior between 355 and 1173 K. A very similar trend is visible upon cooling with slight differences in the impedance course between 382 and 320 K. However, if a closer look is taken at the temperature region around 940 K during heating in Figure 2s B, a small bump is visible (*c.f.* yellow trace in Figure 1D). This bump could indicate Li-ion segregation and a change in the structure of the $\text{Li}_3\text{Co}_{1.06(1)}\text{TeO}_6$ sample. Presumably the sample releases lithium, due to an observed corrosive attack of the silica glass sample chamber. Further studies concerning this point are still pending.

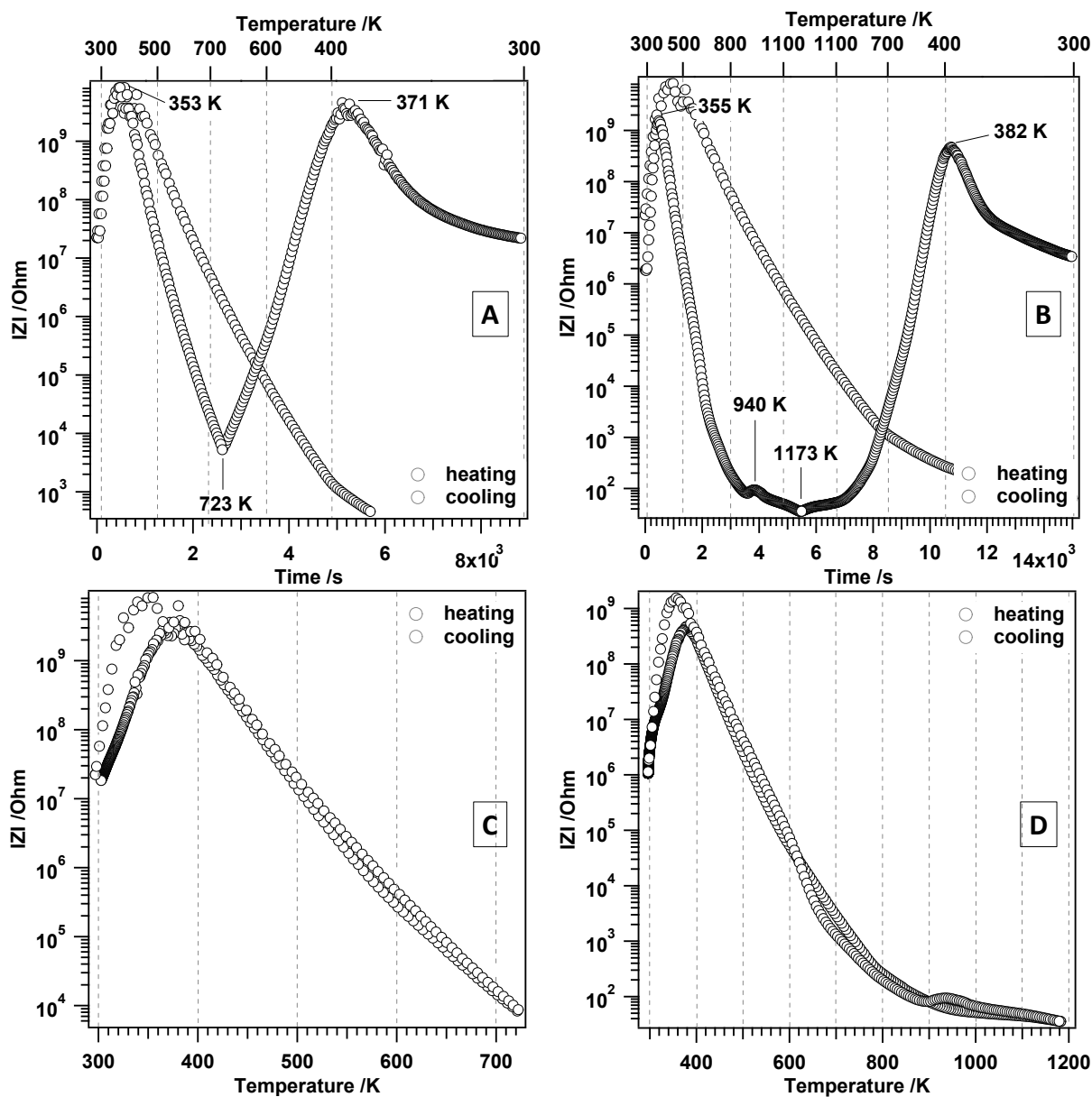


Figure S2. Time- and temperature-dependent *in-situ* EIS measurements of the $\text{Li}_3\text{Co}_{1.06(1)}\text{TeO}_6$ sample between RT and 723 K (panel A and C) and between RT and 1173 K (panel B and D) treated in air. The yellow traces indicate the heating procedure and the blue traces the cooling procedure. $|Z|$: impedance modulus value.

References

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2. P. Thompson, D. E. Cox and J. B. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79-83.
3. M. C. Morris, H. F. McMurdie, E. H. Evans, B. Paretzkin, H. S. Parker and N. P. Pyrrros, *Natl. Bur. Stand. (U.S.) Monogr.*, 1984, **25**, 62.