This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Multianvil High-Pressure/High-Temperature Synthesis and Characterization of magnetoelectric HP-Co₃TeO₆

Elisabeth Selb, Toni Buttlar, Oliver Janka, Martina Tribus, Stefan G. Ebbinghaus and Gunter Heymann

By high-pressure/high-temperature multianvil synthesis a new high-pressure (HP) phase of Co₃TeO₆ was obtained. The compound crystallizes in the acentric trigonal crystal system of the Ni₃TeO₆-type structure with space group R3 and the following unit cell parameters and refinement results: a = 519.37(6) pm, c = 1382.4(2) pm, V = 322.93 Å³, R1 = 0.0150, wR2 = 0.0374, Goof = 1.114 and a Flack parameter of 0.04(5). High-temperature powder X-ray diffraction (PXRD) measurements showed an exceptionally high-temperature stability of the HP-modification up to 1070 K. Magnetic measurements revealed an antiferromagnetic ordering below \( T_N = 58.2(1) \) K and a spin-flop-type transition at \( T = 3 \) K with a critical magnetic field of \( H_{\text{cr}} = 10.8(1) \) kOe. Magnetic and magnetoelectric (ME) transition temperatures were determined by specific heat measurements and exhibited a non-hysteretic behavior of the magnetoelectric coupling. Additionally, from the UV-Vis reflectance spectra a direct and an indirect band gap of \( E_g = 1.88 \) eV and \( E_g = 1.91 \) eV were calculated, underlining the semiconducting nature of HP-Co₃TeO₆.

1 Introduction

In recent years, research on magnetoelectric (ME) compounds has exerted enormous attraction in material science and condensed matter physics. Without magnetic and magnetoelectric materials many forms of current technology in particular microelectronics would be unimaginable. To further enhance the performance of the corresponding devices, new technologies are required. For example, materials that combine ferroelectricity and ferromagnetism allow a fast and energy efficient electric writing of a magnetic information. Therefore, there is great demand for multiferroics, where these two phenomena are intimately coupled.1-3

In this regard, novel metal tellurates \( M_3\text{TeO}_6 \) \((M = \text{Ni, Co, Mn, Cu})\) have gained great importance. These materials are classified as type-II multiferroics and show antiferromagnetic ordering at low temperatures.4 Remarkably, the ME effect is stronger in type-II multiferroics, because the order parameters are closely linked and not decoupled as in type-I multiferroics.5, 6

Despite their same stoichiometry (transition metal to tellurium ratio of 3:1) the tellurates \( M_3\text{TeO}_6 \) \((M = \text{Ni, Co, Mn, Cu})\) exhibit different crystal structure-types and different magnetic structures.4 A brief overview is given in the following. The longest known tellurate of this composition is \( \text{Ni}_3\text{TeO}_6 \). Its crystal structure was already investigated in the year 1967.7 Current research on this compound revealed spin driven pyroelectricity and a so-called colossal magnetoelectric effect (CME) below the antiferromagnetic (AFM) ordering temperature of \( T_N = 52 \) K.8-11 Exceptional about \( \text{Ni}_3\text{TeO}_6 \) is the possibility of a magnetoelectric switching without hysteresis. Thus already small changes in electric and magnetic fields are sufficient for a spin-flop transition.11

Hostachy and Coing-Boyat et al.12 reported on cubic (123) \( \text{Cu}_3\text{TeO}_6 \), also a type-II multiferroic tellurate, which adopts a bixbyte-type structure and orders in a “three-dimensional spin web” with hexagonal arrangements of the magnetic moments.13 One decade later \( \text{Mn}_3\text{TeO}_6 \) was discovered, crystallizing in the rhombohedral \( \text{Mg}_3\text{TeO}_6 \)-type structure.14, 15

Here, the multiferroic ordering arises from two coexistent incommensurate spin structures with a cycloidal and a helical ordering.16 Recently Attfield et al. reported on a magnetically frustrated high-pressure \( \text{Mn}_2\text{MnTeO}_6 \) with double perovskite-type structure and antiferromagnetic ordering at 36 K.17 One of the most complex \( \text{M}_3\text{TeO}_6 \) compounds is \( \text{Co}_3\text{TeO}_6 \), which crystallizes in a monoclinic lithium cryolite-type structure (C2/c) with 5 independent Co sites and shows a complex temperature-dependent incommensurate magnetic behavior.18-20 Due to the good multiferroic properties of \( \text{Co}_3\text{TeO}_6 \) this compound has arisen a lot of interest in the last few years and has been well investigated in numerous publications.18-24 Later, we succeeded in the synthesis of a high-pressure polymorph of \( \text{Co}_3\text{TeO}_6 \) at a pressure of 6.5 GPa and a temperature of 1070 K. It crystallizes in the \( \text{Ni}_3\text{TeO}_6 \)-type...
structure. Besides normal-pressure (NP) Co$_3$TeO$_6$ and a monoclinic CoTeO$_6$, that is related to the rutile structure, HP-Co$_3$TeO$_6$ is the third existing cobalt tellurate modification. This work presents the synthesis, single-crystal structure and magnetic as well as magnetoelectric characterization of HP-Co$_3$TeO$_6$.

2 Experimental

2.1 Synthesis

The high-pressure phase of Co$_3$TeO$_6$ was obtained via high-pressure/high-temperature multianvil synthesis. In the first step single phase NP-Co$_3$TeO$_6$ was prepared by conventional solid state synthesis, starting from Co(NO$_3$)$_2$ · 6 H$_2$O (Merk, 99% p.a) and H$_2$TeO$_3$ (TCI, >99.0%). The stoichiometric mixture was homogenized and calcined at 770 K for 7 h. The intermediate product was powdered and annealed multiple times (7 h per temperature step) with temperature intervals of 100 K up to 970 K, as described in literature.$^{26}$

For the high-pressure/high-temperature experiment, the polycrystalline precursor was surrounded by platinum foil and placed in an 18/11-assembly crucible made of hexagonal boron nitride. The Walker module of the multianvil press, which contained the sample inside of an octahedral pressure medium, was compressed with a ramp of 72 bar/h to a pressure of 1070 K within 5 min and kept at this temperature for another 20 min. Subsequently, the sample was steadily cooled down to 670 K during 120 min to preserve better crystal quality. As soon as the heating process was terminated, the pressure was released with a ramp of 24 bar/h. Afterwards, the sample was isolated by breaking the octahedral pressure medium. The powdered sample appears dark greyish to purple and is stable in air. Further information about the multianvil technique and the construction of the various assemblies can be found in literature and references therein.$^{27, 28}$

2.2 Characterization

Elemental analysis by EDX
By the use of a Jeol JSM-6010LV scanning electron microscope with a Quantax (Bruker Nano) energy-dispersive X-ray detector (EDX) for element identification, several crystals of HP-Co$_3$TeO$_6$ were semiquantitatively analyzed. Three suitable regions of each crystal were selected as measurement points. The averaged experimentally observed element quantification for HP-Co$_3$TeO$_6$ (32±3 at% Co : 11±2 at% Te : 57±3 at% O) was near to the expected one (30.0 at% Co : 10.0 at% Te : 60.0 at% O). No additional elements were detected.

Powder and single crystal X-ray diffraction
A polycrystalline sample of HP-Co$_3$TeO$_6$ was characterized by X-ray powder diffraction on a STOE Stadi P diffractometer with (111) curved Ge monochromatized MoK$_\alpha$ radiation ($\lambda$ = 70.93 pm). The powdered sample was mounted between two thin acetate films with high-vacuum grease and measured in transmission geometry. The diffraction intensities were collected by a Dectris MYTHEN2 1K microstrip detector with 1280 strips. For the Rietveld refinements the software package DiffraX,$^{29}$ Topas $^{4.2}$ (Bruker AXS, Karlsruhe, Germany) was used. The refinement is based on the parameters derived from the single-crystal structure model and the peak shapes were modeled using modified Thompson-Cox-Hastings pseudo-Voigt profiles.$^{29, 30}$ Instrumental contributions on reflection profiles were corrected from the refinement of a LaB$_6$ standard.$^{31}$ The background was fitted with Chebychev polynomials up to the 8th order. Figure S1 displays the results of the Rietveld refinement of HP-Co$_3$TeO$_6$. The lattice parameters derived from the refinement are comparable with those received by single-crystal X-ray diffraction (see Table 1). The sample was single-phase apart from a small contamination from the BN assembly crucible.

High-temperature X-ray powder diffraction data (HT-PXRD) of HP-Co$_3$TeO$_6$ were recorded with a STOE Stadi P diffractometer system (Mo-K$_\alpha$, $\lambda$ = 70.93 pm) equipped with an image-plate detector (120°) and a STOE furnace. A milled polycrystalline sample of HP-Co$_3$TeO$_6$ was filled in a silica glass capillary with a diameter of 0.3 mm and a wall thickness of 0.01 mm. The furnace was heated and cooled in the range from 298 K to 673 K in steps of 100 K. From 673 K to the maximum temperature of 1373 K the sample was heated and cooled in steps of 50 K. The heating rate was set to 5 K min$^{-1}$. After every temperature step, a diffraction pattern was recorded in the region 2-52° 2θ. Several fragments of the crushed sample were embedded in polyfluoropolyalkylether (viscosity 1800) and suitable single-crystal fragments were isolated under the microscope and fixed on the tip of MicroMounts™ (MiTeGen, LLC, Ithaca, NY, USA) with a diameter of 30 μm. Diffraction data was collected on a Bruker D8 Quest diffractometer with a Photon 100 detector system and an Incoatec microfocus source generator (multi-layered optic, monochromatized MoK$_\alpha$ radiation, $\lambda$ = 71.073 pm). To optimize the collection strategies concerning $ω$- and $φ$-scans, the Apex 3 program package$^{32}$ was used. As a result, a data set of the complete reciprocal sphere up to high angles ($θ$ = 37.7°) with a high redundancy (9.28) was received. The program Saint$^{32}$ was used for data processing and data reduction. Finally, an absorption correction was carried out on the semi-empirical “multi scan” approach with the program Sadabs.$^{32}$

Vibrational spectroscopy
FTIR-ATR
The polycrystalline sample of HP-Co$_3$TeO$_6$ was characterized by FTIR-ATR (Fourier Transformed IR - Attenuated Total Reflection) spectroscopy using a Bruker ALPHA Platinum-ATR spectrometer (Bruker, Billerica, USA) equipped with a 2 x 2 mm diamond ATR-crystal and a DTGS detector, in the spectral range of 400-4000 cm$^{-1}$. For the measurement, 320 scans were acquired and a data correction for atmospheric influences was performed using the Opus 7.2 software.$^{33}$

UV-Vis
A diffuse reflectance spectrum of the powdered sample was recorded in the range of 360 to 830 nm, using an Agilent Cary 5000 UV-Vis spectrometer equipped with an integrating sphere.
(DRA-2500), a D65 as standard illuminant and a 10° complementary observer. A scan rate of 600 nm · min⁻¹ and a data interval of 1 nm were applied and BaSO₄ was used as white standard. Via the Kubelka-Munk (KM) function the optical absorbance was calculated from the generated reflectance data and the band gap was determined using Tauc-plots.³⁴, ³⁵

**Physical property measurements**

Magnetic properties

The polycrystalline sample of HP-Co₃TeO₆ was enclosed in a polyethylene (PE) capsule. Magnetization M(T, H) measurements were performed on a Quantum Design Physical Property Measurement System (PPMS) using the Vibrating Sample Magnetometer (VSM) unit. The sample was investigated in the temperature range of 2.5-300 K with magnetic fields up to 80 kOe.

Heat capacity

The specific heat of a HP-Co₃TeO₆ specimen with m = 16.03(2) mg was measured in a PPMS-9 at magnetic fields of 0 Oe, 100 Oe and 10 kOe, respectively. A step width of 5 K was chosen in the temperature range 300-80 K, whereas between 80 and 3 K Cv values were recorded with 1 K steps. The contribution of the thermal conduction grease (0.13 mg Apiezon N) was subtracted prior to data evaluation.

Magnetoelectric properties

For the magnetoelectric investigations gold contacts of 100 nm thickness were sputtered on both sides of the disk-shaped Co₃TeO₆ sample (Ø = 3 mm, h = 1 mm) using a Cressington Sputter Coater 108auto. ME measurements were carried out in the temperature range 65 K to 10 K with 5 K intervals in a PPMS-9, using the self-designed setup described in literature.³⁶ The static magnetic field was varied between -17 kOe and 17 kOe and a collinear ac field of Hₜₐₚ = 10 Oe with a frequency of 900 Hz was superimposed. The ME coefficient α_ME was calculated from the real part (in-phase) of the ac-voltage U_ac according to equation 1 using a lock-in technique.

\[
\alpha_{ME} = \frac{U_{ac}}{I_{ac}\cdot h} \quad (1)
\]

Data analysis was carried out using the peak analyzing tool of OriginPro 2018G.³⁷

### 3 Results and discussion

#### 3.1 Structure refinements

HP-Co₃TeO₆ crystallizes in the trigonal crystal system and the systematic extinctions were in agreement with the acenctic space group R3. The initial positional parameters were determined by the “Intrinsic Phasing” method,³⁸ implemented in the Apex 3 program package.³¹ Full-matrix least-squares refinements based on F², yielded the exact atom positions.³⁹, ⁴⁰ Finally, all atoms were refined with anisotropic displacement parameters and the occupation parameters were refined in separate series of least-squares cycles in order to verify the correct composition. The correctness of the space group was checked with the Addsym⁴¹ routine of the Platon program package.⁴² Addsym detected a pseudo centre of symmetry which implicates the structural relationship of HP-Co₃TeO₆ to corundum (R̅₃c). In contrast to corundum, the oxygen ions of HP-Co₃TeO₆ are only approximately hexagonally close-packed. Co and Te occupy four 37 sites (corresponding to the 12c site of Al in the corundum structure) in an ordered manner. The oxygen atoms in Co₃TeO₆ occupy two general positions (9b) breaking the inversion symmetry and leading to space group R3. Furthermore, the Flack parameter of 0.04(5) verifies the presence of an acenctic crystal structure. Experimental details, the positional parameters, anisotropic displacement parameters, interatomic distances, and angles are listed in Table 1, 2 and in Table S11–S13 of the Supporting Information. CSD 2032321 (HP-Co₃TeO₆) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

| Table 1. Crystal data and structure refinement of HP-Co₃TeO₆ (standard deviations in parentheses). |
|---------------------------------------------------------------|
| **Empirical formula** | Co₃TeO₆         |
| **Molar mass, g mol⁻¹** | 400.39         |
| **Crystal system** | trigonal      |
| **Space group** | R3 (no. 146)   |
| **Formula units per cell, Z** | 3               |
| **Powder diffractometer** | STOE Stadi P  |
| **Radiation** | Mo-Kα, (λ = 70.93 pm) |
| **Powder data** |                                        |
| a, pm | 518.97(1)          |
| c, pm | 1381.56(1)         |
| V, Å³ | 322.24             |
| **Single-crystal diffractometer** | Bruker D8 Quest |
| **Radiation** | Mo-Kα, (λ = 71.07 pm) |
| **Single-crystal data** |                         |
| a, pm | 519.37(6)          |
| c, pm | 1382.4(2)          |
| V, Å³ | 322.9              |
| **Calculated density, g cm⁻³** | 6.18            |
| **Crystal size, mm²** | 0.04 × 0.03 × 0.03 |
| **Temperature, K** | 297(2)           |
| **Absorption coefficient, mm⁻¹** | 18.0            |
| F (000), e | 543               |
| **Detector distance, mm** | 40              |
| **β range, deg** | 4.4–37.7         |
| **Range in hkl** | ±8, ±8 ±23       |
| **Reflections total** | 3596            |
| **Data/ref. parameters** | 773/32          |
| **Reflections with I ≥ 2σ(I)** | 773             |
| **R_ave, R_b** | 0.0236, 0.0176    |
| **Goodness-of-Fit on F²** | 1.114           |
| **Absorption correction** | Multi-scan       |
| R1 / wR2 for I ≥ 2σ(I) | 0.0150/0.0374  |
| R1 / wR2 (all data) | 0.0150/0.0374    |
| **Flack parameter** | 0.04(5)          |
| **Largest diff. peak/hole, e Å⁻³** | 0.94 / -0.80  |
| **Extinction coefficient** | 0.0035(4)       |
| **Transmission min./max.** | 0.6489/0.7474  |
The coordination spheres of the CoO\textsubscript{6} and the TeO\textsubscript{6}-octahedra. Distances are given in [pm].

In the following, the crystal structure of HP-Co\textsubscript{3}TeO\textsubscript{6} is compared to the crystal structure of NP-Co\textsubscript{3}TeO\textsubscript{6} and to the isotopic compound Ni\textsubscript{3}TeO\textsubscript{6}. Moreover, the pressure-induced phase transition is discussed concerning the observed structural changes.

At ambient conditions, NP-Co\textsubscript{3}TeO\textsubscript{6} crystallizes in a monoclinic lithium cryolite-type structure with the space group \textit{C2/c}. In contrast to HP-Co\textsubscript{3}TeO\textsubscript{6}, the oxygen atoms of NP-Co\textsubscript{3}TeO\textsubscript{6} are not only hexagonally closed packed, but also show cubic packing elements, which results in a mixed approximately double hexagonal-cubic close packed \textit{hhchhc} six-layer sequence along the \textit{a}-axis,\textsuperscript{18} as shown in Figure 2-a. Due to the different packing of the oxygen atoms, there are nine distinct crystallographic oxygen sites, three are located on the \textit{c}-layers and six on the \textit{h}-layers. The tellurium cations, which both have an octahedral coordination geometry in NP- and HP-Co\textsubscript{3}TeO\textsubscript{6}, split into two distinct crystallographic sites for NP-Co\textsubscript{3}TeO\textsubscript{6}. Oxygen atoms coordinate only three of the five crystallographically distinct cobalt sites of NP-Co\textsubscript{3}TeO\textsubscript{6} in a more or less distorted octahedral manner. As a result of a markedly extended Co3–O2 distance, the Co3 site is described in a square-pyramidal coordination geometry and Co5 even exhibit only a tetrahedral coordination sphere.\textsuperscript{18}

Due to the pressure impact, the coordination numbers of cobalt and oxygen partially increase to form the higher symmetric Ni\textsubscript{3}TeO\textsubscript{6}-type structure of HP-Co\textsubscript{3}TeO\textsubscript{6}, which is built by less distorted CoO\textsubscript{6}- and TeO\textsubscript{6}-octahedra (see Figure 2-b, -c, -d). This increase in the coordination number is in line with the pressure coordination rule, the subsequent increase in the interatomic distances of cobalt and oxygen satisfies the pressure distance rule.\textsuperscript{44} This is most evident from the shortest Co–O contacts of the tetrahedral Co5 site of NP-Co\textsubscript{3}TeO\textsubscript{6} which differ from 192.9(4) to 199.8(3) pm. While adapting the Ni\textsubscript{3}TeO\textsubscript{6}-type structure, the contacts elongate to an average Co–O distance of 212.7 pm in octahedral coordination sphere.\textsuperscript{18} This is accompanied by a density increase of approximately 5%. The TeO\textsubscript{6}-octahedra are isolated, i.e., not paired or linked to other TeO\textsubscript{6}-octahedra in both NP- and HP-Co\textsubscript{3}TeO\textsubscript{6}. The layer sequence of the nearly hexagonal layers can be seen in Figure 2-c, -d. As a result of the high valence of tellurium, the Te\textsuperscript{6+}-cations are located at a maximum distance from the cobalt and nickel cations. Therefore, the shared edges and faces of the TeO\textsubscript{6}-octahedra with CoO\textsubscript{6} or NiO\textsubscript{6}-octahedra of NP-Co\textsubscript{3}TeO\textsubscript{6}, HP-Co\textsubscript{3}TeO\textsubscript{6} and Ni\textsubscript{3}TeO\textsubscript{6} show significantly shorter O–O distances of 258.3(5)-264.6(5) pm, 262.3(8)-266.6(5) pm and 260.9(8)-266.6(8) pm than the non-shared edges and faces of 269.5(5)-286.8(5) pm, 277.1(5)-286.0(7) pm, and 278.7(8)-288.1(9) pm, respectively.\textsuperscript{18, 45}

Table 3. Charge distributions according to the bond length/bond-strength (\textit{ΣV}) and the CHARDI (\textit{ΣQ}) concept of HP-Co\textsubscript{3}TeO\textsubscript{6}.

\begin{table}[h]
\centering
\begin{tabular}{ccccccc}
\hline
\textbf{At} & \textbf{Co} & \textbf{Co} & \textbf{Co} & \textbf{Te} & \textbf{O} & \textbf{O} \\
\hline
\textbf{ΣV} & +1.84 & +1.89 & +1.98 & +5.72 & -1.92 & -1.89 \\
\textbf{ΣQ} & +2.00 & +2.00 & +2.00 & +6.00 & -2.02 & -1.98 \\
\hline
\end{tabular}
\end{table}

The Madelung part of lattice energy of HP-Co\textsubscript{3}TeO\textsubscript{6} (\textit{MAPLE}_{\text{lar}} = 39195 kJ·mol\textsuperscript{-1}) was estimated by \textit{MAPLE} value calculations\textsuperscript{10, 51} and was compared to the sum of the \textit{MAPLE} values of the binary educts CoO\textsubscript{52} (CoO: 4555 kJ·mol\textsuperscript{-1}) and TeO\textsubscript{3}\textsuperscript{13} (TeO\textsubscript{3}: 25794 kJ·mol\textsuperscript{-1}) as described in equation 2.

\begin{equation}
\textit{MAPLE}_{\text{bin}} = 3 \cdot \textit{MAPLE}_{\text{CoO}} + \textit{MAPLE}_{\text{TeO}_3} = 39459 \text{ kJ·mol}^{-1} \tag{2}
\end{equation}

A discrepancy of \textit{MAPLE}_{\text{lar}} = \textit{MAPLE}_{\text{bin}} of \Delta = 264 \text{ kJ·mol}^{-1}, or 0.7% was observed.
3.3 Temperature-dependent X-ray diffraction

In general, the heating of metastable high-pressure phases leads to a back-transformation to the normal-pressure modifications or to a decomposition. Temperature dependent powder X-ray investigations are an excellent method to follow these transformations. As displayed in Figure 3, HP-Co$_3$TeO$_6$ (R3) converts to NP-Co$_3$TeO$_6$ (C2/c) within a small temperature range above 1070 K. Both phases coexist within a temperature interval of 50 K and above 1120 K only NP-Co$_3$TeO$_6$ (C2/c) reflections can be observed. At a temperature of 1270 K, the compound starts to decompose to CoTeO$_3$. A subsequent reaction with the silica glass capillary finally leads to silicon dioxide, cobalt(II)oxide and Co$_2$SiO$_4$. During cooling, no reflections could be assigned to tellurium containing phases, indicating that either amorphous compounds are formed or that tellurium has completely evaporated due to the open system.

3.4 Spectroscopic characterization

FT-IR

The FT-IR spectra in Figure 4 shows three strong bands in the range of 400-700 cm$^{-1}$, that can be assigned to $\nu_3$, $\nu_4$ and $\nu_5$ modes (C$_3$ site symmetry) of the TeO$_6$-octahedra. The assignment of the bands was done according to the isotypic compound Mg$_3$TeO$_6$ and Ni$_3$TeO$_6$. As a consequence of the acentric space group R3, the site symmetry of the TeO$_6$-octahedra is C$_3$ instead of O$_h$ and the $\nu_3$, $\nu_4$, and $\nu_5$ vibrations are split. Furthermore, due to the acentric crystal structure the $\nu_3$, $\nu_5$, and $\nu_6$ vibrations are also IR active but the infrared intensities are expected to be low. The $\nu_1$ mode is only visible as a weak absorption at 579 cm$^{-1}$ and the $\nu_1$ overlap with the strong $\nu_3$ modes.

Figure 2. The crystal structure of NP-Co$_3$TeO$_6$ is shown in (a). The five different Co coordination polyhedra are marked. The crystal structure of HP-Co$_3$TeO$_6$ with a view along the b-axis and view along the c-axis are given in (b) and (d), respectively. TeO$_6$- and CoO$_6$-octahedra are drawn in violet and teal. Figure (c) illustrates the stacking of the honeycomb-ordered layers along the c-axis.

Figure 3. Temperature dependent X-ray powder diffraction of HP-Co$_3$TeO$_6$. A precise identification is thereby impeded. At 510 cm$^{-1}$ the Co–O stretching modes of the CoO$_6$-octahedra along the ab plane and the $\nu_3$ modes of the TeO$_6$-octahedra overlap. It should be kept in mind that the modes are complex framework vibrations and an allocation to isolated stretching or bending modes of the TeO$_6$- and CoO$_6$-units is only possible in a first approximation, as calculations showed.
energies was chosen. The onset which led to the lowest band gap in Figure 5 (inset). Since the reflectance spectra exhibited two reflectance, the Tauc plot was set to \( R(\nu) = \frac{K}{S} \) is the absorption coefficient and \( (1 - R)^{2} \) is the factor calculated according to equation 3, in which \( R \) represents the reflectance, \( K \) the absorption coefficient and \( S \) the scattering coefficient. To generate the Tauc plots, the factor \( (F(R) \cdot h\nu)^{n} \) was plotted against the photon energy. For indirect and direct band gaps, \( n \) was set to \( n = 2 \) and \( n = 0.5 \), respectively. The band gap values \( E_{g} \) were determined by the tangent method as shown in Figure 5 (inset). Since the reflectance spectra exhibited two absorption peaks, the onset which led to the lowest band gap energies was chosen.

**3.5 Physical properties**

**Magnetic properties**

Magnetic susceptibility measurements were conducted in a zero-field-cooled (ZFC) mode between 3 and 300 K with an external field strength of 10 kOe. A data correction was performed to account for diamagnetic contributions of the PE capsule and of the constituent ions leading to \( \chi_{\text{dia}}^{\text{Co}_{3}TeO_{6}} = -120 \times 10^{-6} \text{emu} \cdot \text{mol}^{-1}; \chi_{\text{dia}}^{\text{TeO}_{6}} = -12 \times 10^{-6} \text{emu} \cdot \text{mol}^{-1} \); \( \chi_{\text{dia}}^{\text{O}_{2}^{2-}} = -12 \times 10^{-6} \text{emu} \cdot \text{mol}^{-1} \). The temperature dependent values of \( \chi \) and \( \chi^{'1} \) are illustrated in Figure 6 (top). Beneath 50 K two phenomena are apparent, while between 100 K and 300 K a Curie-Weiss behavior is observed. Based on the inverse susceptibility the effective magnetic moment was calculated and a value of \( \mu_{\text{eff}} = 5.28(1) \mu_{B} \) was obtained. This magnetic moment is higher than the expected moment of Co\(^{2+}\) (3\(^{d}\) high-spin) of 3.88 \( \mu_{B} \). Therefore, a high degree of spin-orbit interactions can be assumed. A Weiss constant of \( \theta = -63.4(1) \) K indicates an antiferromagnetic interaction in the paramagnetic region.

Low-field measurements (100 Oe) between 2.5 and 100 K (Figure SI3) revealed four anomalies at \( T_{1} = 21 \) K, \( T_{2} = 52 \) K, \( T_{3} = 58.2(1) \) K and \( T_{4} = 80 \) K. The anomaly at \( T_{4} = 58.2(1) \) K can be clearly assigned to an antiferromagnetic ordering, the other phenomena still have to be clarified.

The magnetization isotherms (see Figure 6, middle) below \( T_{4} = 58.2(1) \) K show a sigmoidal shape due to a spin-flop-type transition (meta-magnetic step, spin reorientation). The negative peak of the derivation of the magnetic isotherm at 3 K reveals a critical field of \( H_{c} = 10.8(1) \) kOe required for the spin-flop-type transition (\( \uparrow \downarrow \uparrow \downarrow \rightarrow \uparrow \uparrow \uparrow \uparrow \)). At even higher fields another kink of the magnetization is visible, leading to a flattening of the trace of the magnetization. The magnetization continuously rises after the meta-magnetic step, due to an ongoing reorientation of the spins in the polycrystalline material. Around \( \approx 55 \) kOe, it seems like the majority of the spins has been parallelized causing saturation. The saturation magnetization of \( \mu_{\text{sat}} = 0.88(1) \mu_{B} \) at 3 K and 80 kOe is far beneath the estimated value of \( \mu_{\text{cal,sat}} = 3.87 \mu_{B} \) originating from the polycrystalline sample.

**Specific heat**

To further examine the magnetic and magnetoelectric transition (see below) temperatures of HP-Co\(_{3}\)TeO\(_{6}\), measurements of the heat capacity were performed at 0 Oe, 100 Oe and 10 kOe. The results were very similar and shown in comparison in the supplemental Figure SI4. At 300 K the specific heat of 211(1) J · mol\(^{-1}\) K\(^{-1}\) comes close to the Dulong-Petit value of \( C_{p} = 3R \cdot N \approx 250 \) J · mol\(^{-1}\) K\(^{-1}\) (\( N = 10 \), reflecting the 10 atoms per formula unit of Co\(_{3}\)TeO\(_{6}\)).

Figure 6 (bottom) shows the magnetization isotherms of Co\(_{3}\)TeO\(_{6}\) for the measurement at zero field. To account for the lattice (phonon) contribution the data was fitted...
using a model with one Debye and two Einstein terms with a weighting of 4:3:3, similar to the ones described in literature. The weighting scheme was chosen to keep the model as simple as possible (i.e., to reduce the number of refinable parameters) while being physically meaningful. The fourfold Debye term can be considered to reflect the motion of the heavy atoms (3 Co, 1 Te), while the two threefold Einstein terms may be assigned to the bending and stretching modes of oxygen atoms. We emphasize, though, that we do not attempt to derive any physical information from the fit. The temperature interval 10-80 K in which the magnetic transitions occur was excluded from the fit. For the Debye and Einstein contributions, the following characteristic temperatures were obtained: \( \Theta_D = 247 \) K, \( \Theta_{E1} = 494 \) K, \( \Theta_{E2} = 795 \) K.

The difference between \( C_p \) and \( C_V \) was considered using the Nernst-Lindemann relation \( C_p - C_V = A C_p T \) resulting in A = \( 8.76 \times 10^{-7} \) mol \( \cdot \) K\(^{-2}\). As shown in Figure 6 (bottom), a sharp and intense signal occurs around 56 K and a second smaller, broader one at ca. 20 K. These transitions can more clearly be seen as peaks in Figure 7, which shows on the left scale the magnetic contribution \( C_{P\text{,mag}}/T = C_p/T - C_{P\text{lattice}}/T \). The obtained characteristic temperatures (taken from the peak maxima) are listed in Table 4 and are in good accordance with the values of \( T_N \) and \( T_1 \) determined from the magnetic investigations. Around 80 K, where an additional magnetic anomaly was observed (Figure S13), a tiny step-like feature appears.

Compared to the NP-modification of \( \text{Co}_3\text{TeO}_6 \) remarkable differences are found. NP-\( \text{Co}_3\text{TeO}_6 \) shows a rather small and diffuse \( C_p \) peak at 26 K and a sharp, much more intense one at 16 K. On the other hand, the antiferromagnetic ordering temperature of \( \text{HP-Co}_3\text{TeO}_6 \) is comparable to the one of \( \text{Ni}_3\text{TeO}_6 \) (\( T_N = 52 \) K), which possesses a similar structure, indicating a strong correlation between crystal structure and Néel-temperature of the tellurates as reported.

It is to be noted that the \( C_p \) measurements of \( \text{HP-Co}_3\text{TeO}_6 \) are closely related to the magnetoelectric investigations described below, in which measurable ME voltages were only detected in the temperature regime between \( T_N \) and \( T_1 \). The values listed in Table 4 show that \( T_N \) of \( \text{HP-Co}_3\text{TeO}_6 \) remains unaffected by the external magnetic field (56±0.5 K) although the corresponding peak in \( C_p \) clearly broadens at 10 kOe. In contrast, the value of \( T_1 \) decreases by ca. 2 K when \( H \) is raised from 100 Oe to 10 kOe.

Figure 6. Magnetic properties of HP-\( \text{Co}_3\text{TeO}_6 \): susceptibility and inverse susceptibility (\( \chi \) and \( \chi^{-1} \)), measured in an external field strength of 10 kOe (top); magnetization isotherms recorded at 3, 10, and 50 K, the derivative \( dM/dH \) is depicted in red (middle); Temperature dependence of \( C_p/T \) of HP-\( \text{Co}_3\text{TeO}_6 \) at zero field (blue line and circles) with the corresponding Einstein-Debye fit (red line) (bottom).

Figure 7. Magnetic contribution to \( C_p/T \) (solid lines, left scale) and magnetic entropy (dashed lines, right scale).
The right scale of Figure 7 shows the low temperature region of the magnetic contribution to the entropy according to $\Delta S_{\text{mag}} = \int_0^T \frac{\partial S}{\partial T} \, dT$ and in Table 4 the numerical values are listed. The two transitions at $T_1$ and $T_2$ correspond to entropy changes of $\approx 1.4 \, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $\approx 3.5 \, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively, resulting in a total $\Delta S_{\text{mag}} \approx 4.9 \, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. As visible from Figure SI4 and Table 4 very similar values were obtained for the magnetic entropy change for all three external magnetic fields.

For an ordering spin moment $S$, the theoretical entropy change is given by $\Delta S_{\text{mag}} = R \ln(2S+1)$, for $S = \frac{1}{2}$ value of $\Delta S_{\text{mag}} = 5.76 \, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ results, which is larger than our experimental finding. On the other hand, due to the rather extended temperature range that had to be excluded from the fit, we cannot completely rule out the possibility of slightly larger values. Nevertheless, the obtained values are far from the expected ones, considered that $\Delta S_{\text{mag}}$ was calculated with respect to one formula unit (not per Co atom). Our specific heat measurements may be explained assuming that only the spin of one electron of one Co$^{2+}$ per formula unit participates in the magnetic ordering. This interpretation agrees with the rather low saturation magnetization (Figure 6, middle). At 50 K (i.e. in the region between $T_1$ and $T_2$) the $M_s$ accounts to $\approx 0.33 \, \mu_B$/Co, respectively $\approx 1 \, \mu_B$ f.u. According to $M_s/M_H = 2 \times S$ this value reflects a spin of $S = \frac{1}{2}$ (Please note that this value corresponds to the ordered spin moment only and not to the total). While this value might be somewhat too small as the temperature is close to $T_N$, the general statement that the ordered magnetic moment is much smaller than the total one remains valid. Additional neutron diffraction experiments may be helpful to further examine the temperature dependence of the magnetic ordering in HP-Co$_2$TeO$_3$.

**Magnetoelastic properties**

The field-dependent magnetoelastic signal was measured between 65 and 10 K. As visible in Figure 8, no significant ME-response was found for temperatures down to 60 K, while at 55 K a negative peak appears at approximately $+4.5$ kOe and symmetrically a positive peak at the corresponding negative field. With decreasing temperature, the peaks shift to higher fields and their intensities reach a maximum at 45 K. In addition, the peaks become broader and vanish below 25 K. These temperatures correlate with the Néel temperature ($T_N = 58.2$ K) and with $T_1$ (21 K) determined from magnetic- and specific heat measurements described above.

**Table 4.** Transition temperatures ($T_0$, $T_1$) and calculated entropy values for HP-Co$_2$TeO$_3$.

| Substance  | $H$ (Oe) | $T_0$ (K) | $\Delta S_0$ ('') | $T_1$ (K) | $\Delta S_1$ ('') | $\Delta S_{\text{mag}}$ ('') |
|------------|----------|-----------|-------------------|-----------|-------------------|---------------------------|
| HP-Co$_2$TeO$_3$ | 0        | 56.5(5)   | -3.5              | 20.2(5)   | 1.3               | 4.8                       |
| HP-Co$_2$TeO$_3$ | 100      | 56.5(5)   | -3.5              | 20.2(5)   | 1.3               | 4.8                       |
| HP-Co$_2$TeO$_3$ | 10000    | 55.5(5)   | -3.5              | 18.2(5)   | 1.4               | 4.9                       |
| Ni$_2$TeO$_3$  | 0        | 26        | -16               | -         | -                 | 8.9                       |
| Ni$_2$TeO$_3$  | 52       | -         | -                 | -         | -                 | -                         |

$^* (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$

For a quantitative analysis the peaks were fitted using the asymmetric function given in equation 4.

$$\alpha_{\text{ME}} = \alpha_{\text{ME,0}} + \frac{1}{1+e^{-\frac{H-H_{\text{ME,max}}}{w_1}}} - \frac{1}{1+e^{-\frac{H-H_{\text{ME,0}}}{w_2}}}$$

(4)

Here, $\alpha_{\text{ME,0}}$ is the offset, and $w_1$ and $w_2$ are the shape parameters. The obtained characteristic values, i.e. the position of the peak maximum/minimum ($H_{\text{MAX}}$), its full width at half maximum (FWHM) and values at the maximum/minimum of the peaks ($\alpha_{\text{ME,max}}$) are shown in Figure 9. It turned out that the two peaks at positive and negative magnetic fields are centro symmetric with respect to $H = 0$. Therefore, averaged values are depicted. In the temperature regime $T_N \leq T \leq T_1$ $\alpha_{\text{ME,MAX}}$ increases with decreasing temperature from 6.4 to 12.7 $\mu$V Oe$^{-1}$ cm$^{-1}$ at 45 K and re-decreases to 2.1 $\mu$V Oe$^{-1}$ cm$^{-1}$ at 25 K. In contrast, both the magnetic field of the peak maximum and its FWHM increase continuously with decreasing temperature. For all three values, the change between 55 and 50 K is strongest.
In the ME investigations described so far, the voltage was measured parallel to the applied magnetic field. Figure S15 shows additional measurements, in which the ME voltage generated perpendicular to the magnetic field was recorded by positioning the disk-shaped samples upright. The general trend is similar to the parallel orientation but there are also distinct differences: The sign of $\alpha_{ME}$ is inverted, i.e., a positive peak occurs at positive fields and the magnitudes of the peaks are clearly smaller. At 20 K the ME signal has not completely vanished but a step-like feature remains. Figure S16 shows the results of the peak fitting for the perpendicular orientation. The magnetic field at which the ME-peaks occur ($H_{\text{max}}$) are very similar compared to the parallel orientation and $\alpha_{ME,\text{max}}$ has its highest value at 45 K, too. On the other hand, the absolute values of $\alpha_{ME,\text{max}}$ are about 40% smaller for the perpendicular orientation and the FWHM values are reduced. Due to the small signals the values of $\alpha_{ME,\text{max}}$ and in particular of the FWHM possess a larger uncertainty and therefore for the latter no clear trend can be determined.

The reversed sign and smaller magnitude of $\alpha_{ME}$ in perpendicular orientation of H and P can be explained assuming that the magnetoelectric coupling in HP-Co$_3$TeO$_6$ is mediated by mechanical deformation, i.e., magnetostriction. If the cell volume remains constant, an elongation in direction of the magnetic field results in a shortening perpendicular to it (respectively vice versa). For small magnetostriction (typically in the order 10$^{-5}$) the value of the transverse deformation is about half of the one in field direction. In turn, the perpendicular ME voltage is expected to be roughly ~1/2 of the parallel one in good agreement with experiment. It is to be noted that we have observed this relation between $\alpha_{ME,||}$ and $\alpha_{ME,\perp}$ in composite multiferroics like CoFe$_2$O$_4$/BaTiO$_3$ or Ni/BaTiO$_3$, too.$^{55,56}$

At selected temperatures the ME voltage was measured with different field sweep directions. No significant deviations were found between the data recorded at increasing and decreasing field, respectively, proving a non-hysteretic behavior of the magnetoelectric coupling. In addition, measurements at different frequencies of the ac-magnetic field were carried out at 45 K for both orientations. As shown in Figure 10, a significant increase by a factor of roughly 2.5 in the range 100 to 900 Hz was observed for both parallel and perpendicular orientation. The reasons for this increase as well as for the loss of the ME effect below 20 K need to be established in further experiments.

For the parallel orientation a second set of measurements was carried out after applying an electric field of 800 V to the sample for 24 hours at room temperature. Such an electrical poling was found to be essential for the detection of an ME signal in type-I magnetoelectric composites, e.g. BaTiO$_3$/CoFe$_2$O$_4$ or BaTiO$_3$/CoFe$_3$.$^{57}$ In case of HP-Co$_3$TeO$_6$, the results were almost identical with the ones without poling. Additionally, the shape of the ME response of HP-Co$_3$TeO$_6$ with its well-defined rather sharp peaks is completely different from the ones of magnetoelectric composites, e.g. the above-mentioned BTO/CFO system. Finally, we emphasize that in HP-Co$_3$TeO$_6$ the ME voltage was not detected for $T > T_N$, thus it is coupled to the occurrence of the magnetic ordering. These findings clearly indicate that HP-Co$_3$TeO$_6$ is type-II magnetoelectric.

![Image](https://example.com/image.png)

**Figure 10.** Amplitude of the magnetoelectric signal measured with different frequencies of the $H_{\text{ac}}$-driving field.

### 4 Conclusions

Under high-pressure/high-temperature conditions of 6.5 GPa and 1073 K, Co$_3$TeO$_6$ transforms from a monoclinic lithium cryolite-type structure (C2/c) to the acentric Ni$_3$TeO$_6$-type structure (R3). The high-pressure modification of Co$_3$TeO$_6$ is stable up to a maximum temperature of 1070 K at ambient conditions and was characterized by powder and single-crystal X-ray diffraction. Comparable to Ni$_3$TeO$_6$ an antiferromagnetic ordering below $T_N = 58.2(1)$ K as well as a spin-flop-type transition at $T = 3$ K and a critical magnetic field of $H_{\text{crit}} = 10.8(1)$ kOe, was observed. Both compounds, Ni$_3$TeO$_6$ ($T_N = 52$ K)$^9$ and Co$_3$TeO$_6$, show a strong correlation between crystal structure and Néel-Temperature. Furthermore, there is a clear dependence of the occurrence of ME effects on the presence of a magnetic order, proving that HP-Co$_3$TeO$_6$ is a type-II magnetoelectric material. In the temperature regime between $T_N$ and $T_L = 21$ K considerable ME voltages were detected and no significant deviations between increasing and decreasing field proved a non-hysteretic behavior of the magnetoelectric coupling. The magnetic entropy changes at the two transitions ($T_N, T_L$) as well as the low saturation magnetization can be explained assuming that the spin of only one electron of one Co$^{2+}$ per formula unit is involved in the magnetic order. This has to be verified by neutron diffraction experiments in future.

**Author contributions**

E. Selb: investigation, visualization, writing - original draft; T. Buttlar: investigation, visualization; O. Janka: investigation, visualization, supervision, writing - review & editing; M. Tribus: investigation; S. G. Ebbinghaus: data analysis, supervision, writing - review & editing and G. Heymann: data analysis, conceptualization, supervision, writing - review & editing.
ARTICLE

Conflicts of interest

“There are no conflicts to declare”.

Acknowledgements

We would like to thank Prof. Dr. H. Huppertz for continuous support and usage of all the facilities of the Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck. Furthermore, we thank T. Miller and Prof. Dr. W. Schnick (LMU Munich) for recording the temperature-dependent X-ray diffraction data.

Notes and references

1. W. Eerenstein, N. D. Mathur and J. F. Scott, Nature, 2006, 442, 759-765.
2. M. Fiebig, T. Lottermoser, D. Meier and M. Trassin, Nat. Rev. Mater., 2016, 1, 16046.
3. N. A. Spaldin and M. Fiebig, Science, 2005, 309, 391-392.
4. R. Mathieu, S. A. Ivanov, P. Nordblad and M. Weil, Eur. Phys. J. B, 2013, 86, 361.
5. D. Khomskii, Physics, 2009, 2.
6. S.-W. Cheong and M. Mostovoy, Nat. Mater., 2007, 6, 13.
7. R. E. Newnham and E. P. Meagher, Mater. Res. Rev., 1967, 2, 549-554.
8. L. Zhao, C. H. Du and A. C. Komarek, Phys. Status Solidi RRL, 2017, 11, 1700073.
9. J. W. Kim, S. Artyukhin, E. D. Mun, M. Jaime, N. Harrison, A. Hansen, J. J. Yang, Y. S. Oh, D. Vanderbilt, V. S. Zapf and S. W. Cheong, Phys. Rev. Lett., 2015, 115, 137201.
10. I. Živković, K. Prša, O. Zaharko and H. Berger, J. Phys.: Condens. Matter, 2010, 22, 056002.
11. Y. S. Oh, S. Artyukhin, J. J. Yang, V. Zapf, J. W. Kim, D. Vanderbilt and S.-W. Cheong, Nat. Commun., 2014, 5, 3201.
12. A. Hostachy and J. Coing-Boyat, C. r.hebd. seanc. Acad. Sci. B, 1968, 267, 1435 - 1438.
13. K. Y. Choi, E. D. Politova, V. V. Chetchkin, E. A. Myzgin, B. S. Medvedev and Y. N. Venetsev, Inorg. Mater., 1982, 18, 1616-1619.
14. S. A. Ivanov, P. Nordblad, R. Mathieu, R. Tellgren, C. Ritter, N. V. Golubko, E. D. Politova and M. Weil, Mater. Res. Bull., 2011, 46, 1870-1877.
15. A. M. Arévalo-López, E. Solana-Madurga, C. Aguilar-Maldonado, C. Ritter, O. Menté and P. J. Attfield, Chem. Commun., 2019, 55, 14470-14473.
16. R. Becker, M. Johnsson and H. Berger, Acta Crystallogr. C, 2006, 62, i67-i69.
17. M. Hudl, R. Mathieu, S. A. Ivanov, M. Weil, V. Carolus, T. Lottermoser, M. Fiebig, Y. Tokunaga, Y. Taguchi, Y. Tokura and P. Nordblad, Phys. Rev. B: Condens. Matter Mater. Phys., 2011, 84, 180404.
18. S. A. Ivanov, R. Tellgren, C. Ritter, P. Nordblad, R. Mathieu, G. André, N. V. Golubko, E. D. Politova and M. Weil, Mater. Res. Bull., 2012, 47, 63-72.
51. R. Hoppe, Angew. Chem. Int. Ed., 1966, 5, 95-106.
52. S. Sasaki, K. Fujino, Tάk, Eacute and Y. Uchi, Proc. Jpn. Acad., Ser. B, Phys. Biol. Sci., 1979, 55, 43-48.
53. M. Dusék and J. Loub, Powder Difffr., 1988, 3, 175-176.
54. K. Kohn, K. Inoue, O. Horie and S.-I. Akimoto, J. Solid State Chem., 1976, 18, 27-37.
55. E. Selb, L. Declara, L. Bayarjargal, M. Podewitz, M. Tribus and G. Heymann, Eur. J. Inorg. Chem., 2019, 2019, 4668-4676.
56. G. Blasse and W. Hordijk, J. Solid State Chem., 1972, 5, 395-397.
57. C.-W. Tang, C.-B. Wang and S.-H. Chien, Thermochim. Acta, 2008, 473, 68-73.
58. P. Yasodha, M. Premila, A. Bharathi, M. C. Valsakumar, R. Rajaraman and C. S. Sundar, J. Solid State Chem., 2010, 183, 2602-2608.
59. G. A. Bain and J. F. Berry, J. Chem. Educ., 2008, 85, 532.
60. S. G. Ebbinghaus, E.-W. Scheidt and T. Götzfried, Phys. Rev. B: Condens. Matter, 2007, 75, 144414.
61. S. Riegg, A. Günther, H. A. Krug von Nidda, A. Loidl, M. V. Eremin, A. Reller and S. G. Ebbinghaus, Phys. Rev. B: Condens. Matter, 2012, 86, 115125.
62. S. Riegg, A. Günther, H. A. Krug von Nidda, M. V. Eremin, A. Reller, A. Loidl and S. G. Ebbinghaus, Eur. Phys. J. B, 2012, 85, 413.
63. J. L. Her, C. C. Chou, Y. H. Matsuda, K. Kindo, H. Berger, K. F. Tseng, C. W. Wang, W. H. Li and H. D. Yang, Phys. Rev. B: Condens. Matter, 2011, 84, 235123.
64. R. Mathieu, S. A. Ivanov, P. Nordblad and M. Weil, Eur. Phys. J. B, 2013, 86, 361.
65. M. Breitenbach, H. Deniz and S. G. Ebbinghaus, J. Phys. Chem. Solids, 2019, 135, 109076.
66. T. Buttlar, T. Walther, K. Dörr and S. G. Ebbinghaus, Phys. Status Solidi B, 2020, 257, 1900622.
67. M. Breitenbach and S. G. Ebbinghaus, J. Cryst. Growth, 2018, 483, 81-88.
68. T. Walther, R. Köferstein and S. G. Ebbinghaus, J. Am. Ceram. Soc., 2017, 100, 1502-1507.