Article

Synthesis and Characterization of Ammonium Potassium Tellurium Polyoxomolybdate: $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ with One-Dimensional Anionic Polymeric Chain $[\text{TeMo}_6\text{O}_{22}]^{4-}$

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Abstract: A new tellurium polyoxomolybdate hydrate $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ was synthesized via the hydrothermal reaction method at 190 °C. The compound crystallizes in a one-dimensional tellurium polymolybdate $[\text{TeMo}_6\text{O}_{22}]^{4-}$ chain structure. The anionic polymeric chain is composed of Mo_6O_{22} hexamers bridged together through sharing four corner oxygen atoms on the electron lone-paired TeO_4 group. The Mo_6O_{22} hexamer cluster is assembled from six distorted MoO_6 octahedra in an edge-sharing manner. The ammonium and potassium cations distribute around the $[\text{TeMo}_6\text{O}_{22}]^{4-}$ chains and separate them from each other and maintain the charge balance. The thermal stability and optical properties of the compound were also investigated. The optical absorption data reveal that the compound is a wide band semiconductor with an optical band gap of 3.4 eV.

Keywords: tellurium polyoxomolybdate; $[\text{TeMo}_6\text{O}_{22}]^{4-}$ hexamolybdotellurate chain; crystal structure; hydrothermal synthesis

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1. Introduction

Molybdate materials have attracted considerable research interests in recent years owing to their diverse crystal structures and promising applications in the field of nonlinear optics [1,2], catalysis [3–5], medicine [6–8], and photochromism [9,10]. In most cases, molybdenum atoms can be coordinated with either four or six oxygen atoms into distorted tetrahedron or octahedron structural units, which usually makes molybdates possess large local polarizability. The six-coordinated molybdenum–oxygen octahedron may further be condensed into polyoxomolybdate clusters, based on which a large number of polyoxomolybdates have been synthesized. Tellurite units containing Te^{4+} lone pairs have flexible coordination patterns with oxygen atoms, such as TeO_3 pyramid, TeO_4 sphenoid, and TeO_5 square pyramid. The highly distorted acentric structural units of TeO_n ($n = 3, 4, 5$) cooperate with MoO_4 or MoO_6 polyhedra capable of forming new tellurium molybdates with interesting crystal structures and useful properties, such as piezoelectricity and nonlinear optics [11–16].

Currently, there have been only two inorganic hydrated molybdates reported in the K–Te–Mo–oxide system: $\text{K}_6(\text{TeMo}_6\text{O}_{24})\cdot 7\text{H}_2\text{O}$ [17] and $\text{K}_4(\text{Mo}_6\text{Te}_2\text{O}_{24})\cdot 5.8\text{H}_2\text{O}$ [18]. The former crystallizes in the orthorhombic space group Pbca , and the basic building blocks were confirmed to be the Anderson type flat hexamolybdotellurate complex ion $[\text{TeMo}_6\text{O}_{24}]^{6-}$ with TeO_6 octahedron centered [19]. The later crystallizes in the $[\text{Mo}_6\text{Te}_2\text{O}_{24}]^{4-}$ zero-dimensional aggregates composed of one hexamolybdic Mo_6O_{18} and two discrete TeO_3 units. Anderson–Evans polyoxometalates (POMs) containing heteroatom tellurium are known as one of the pioneering POM archetypes, which usually exist as a discrete $[\text{TeMo}_6\text{O}_{24}]^{6-}$ cluster in the crystal structures [20–30]. Polyoxometalates with one-dimensional chain-like, two-dimensional layer-like, or three-dimensional anionic extended framework

structures are relatively rare. Recently, rare earth elements have been introduced into the hexamolybdotellurate clusters as structural linkers to form one-dimensional chain-like architecture [31–33]. Another example in the A–Te–Mo–O system is the novel tellurium polymolybdate $A_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ ($A = \text{NH}_4, \text{Rb}$), which crystallize in the one-dimensional $[\text{TeMo}_6\text{O}_{24}]^{6-}$ anionic chains with $\text{NH}_4^+/\text{Rb}^+$ cations held together [34].

Encouraged by the surprising compositional variability and structural diversity of the tellurium molybdate system, we attempted to explore new compounds in the K–Te–Mo–oxide system. During the investigations, we synthesized a new tellurium polyoxomolybdate hydrate $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ by using the hydrothermal reaction method. The compound crystallizes in the $A_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ ($A = \text{NH}_4, \text{Rb}$) structure and displays a one-dimensional polymeric chain structure constructed by $[\text{Mo}_6\text{O}_{22}]^{8-}$ hexamer clusters with electron lone-paired $[\text{TeO}_4]^{4-}$ linkers connected alternatively. Here, we report the synthesis, crystal structure determination, and properties characterization of the compound.

2. Materials and Methods

2.1. Properties Characterization

The powder XRD patterns were recorded on a PANalytical Empyrean diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature in the 2θ range of $10\text{--}70^\circ$ with a step size of 0.026° . Figure S1 shows the experimental powder XRD patterns, which are consistent with the simulated ones from single crystal structure of $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ using the Powder Cell software [35]. The thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements were carried out on a NETZSCH STA 449F5 instrument under a flowing nitrogen atmosphere. The powder sample of the compound with mass about 16 mg was enclosed in an Al_2O_3 crucible, and heated from room temperature to 800°C with the heating rate of 15 K/min . The infrared spectra were recorded on a Nicolet 470 FT-IR spectrometer in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$. Several small crystal samples were ground with KBr and pressed into a transparent pellet for FT-IR absorption experiments. UV–Vis–NIR optical diffuse reflectance spectra were measured on a PerkinElmer Lambda 950 spectrophotometer. The spectral range was set from 2000 to 200 nm at room temperature. A BaSO_4 plate was used as the standard material (100% reflectance) for background correction. Optical absorption spectra were obtained through spectral conversion with the Kubelka–Munk function $\alpha/S = (1-R)^2/2R$ [36].

2.2. Synthesis

The title compound was synthesized via hydrothermal reactions. The stoichiometric mixture of TeO_2 (0.0798 g), KCl (0.1491 g), and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.5297 g) was loaded into a 15-ml Teflon liner and added to 2 ml of water. The above components were thoroughly mixed and sealed raw materials were heated to 190°C , held for 72 h, and then cooled to room temperature in 24 h. A lot of colorless prism-shaped crystals with single phase were obtained after several washes with deionized water. The overall yield ratio is around 60% based on TeO_2 in general.

2.3. Crystal Structure Determination

A transparent prism-shaped crystal with suitable size was selected for single crystal X-ray analysis. The diffraction data were collected at room temperature on a Bruker APEX II CCD X-ray diffractometer using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Lorentz and polarization corrections were applied, and absorption corrections were performed by multi-scan method. Lattice type and space group C2/c were first selected according to systematic absence conditions. The initial model of the structure was solved by the direct method with SHELXS-97 and subsequently refined by full-matrix least-squares on F^2 using SHELXL-2014 [37]. Hydrogen atoms on crystalline water were placed by residual peaks around oxygen atoms and further refined with DFIX and DANG restraint instructions with the O–H bond length of $0.85 \text{ \AA}$ and H–H distance of $1.35 \text{ \AA}$.

Hydrogen atoms on nitrogen atoms were not designated. The K and N atoms were refined with substitutional disorder at the same site occupied by K/N atoms under the restraint of the total occupation factor equaling to one. The final refined structures were checked on PLATON and no higher symmetry operation was suggested [38]. The final refined crystallographic data and details of structural refinement are summarized in Table 1. Some selected important bond lengths and angles are listed in Table 2. The atomic coordinates and equivalent isotropic displacement parameters are shown in Table S1. The crystal data has been deposited into the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures (accessed on 3 April 2021) with the CCDC 2069363.

Table 1. Crystal data and structure refinement for $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$.

Formula	$(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$
F.W.	1197.49
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	21.172(2)
<i>b</i> (Å)	7.660(0)
<i>c</i> (Å)	15.419(1)
β (deg.)	119.545(3)
<i>V</i> (Å ³), <i>Z</i>	2175.5(3), 4
Calculated density (g/mm ³)	3.656
<i>F</i> (000)	2208
Data collection range θ (deg.)	2.211 to 27.610
Limiting indices	$-27 \leq h \leq 26$ $-9 \leq k \leq 8$ $-20 \leq l \leq 20$
Reflections collected/unique, <i>R</i> _{int}	9472/2521, 0.0219
Completeness to $\theta = 25.242$	99.8%
GOF ^a on <i>F</i> ²	1.053
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^b	0.0180, 0.0485
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0189, 0.0489
Largest diff. peak and hole (eÅ ⁻³)	0.621 and −0.693

$$^a \text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (N_R - N_P)]^{1/2}; ^b R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table 2. Some selected bond lengths (Å) for $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$.

Atoms	Bond Lengths	Atoms	Bond Lengths
K(1)–O(10)#1	2.843(3)	Te(1)–O(5)	1.878(2)
K(1)–O(4)#2	2.855(3)	Te(1)–O(3)#9	2.113(2)
K(1)–O(9)#3	2.868(3)	Te(1)–O(3)#3	2.113(2)
K(1)–O(12)#2	2.879(4)	Mo(1)–O(9)	1.704(3)
K(1)–O(10)	2.925(3)	Mo(1)–O(11)	1.711(3)
K(1)–O(6)#4	2.958(3)	Mo(1)–O(3)	1.944(2)
K(1)–O(7)	3.029(3)	Mo(1)–O(6)	1.956(2)
K(1)–O(7)#4	3.103(3)	Mo(1)–O(1)#9	2.189(2)
K(1)–O(11)#3	3.252(3)	Mo(1)–O(8)	2.392(3)
K(1)–O(2)#4	3.300(3)	Mo(2)–O(4)	1.719(3)
K(2)–O(12)#2	2.770(4)	Mo(2)–O(8)	1.745(2)
K(2)–O(9)#5	2.829(4)	Mo(2)–O(2)	1.814(2)
K(2)–O(7)#4	2.912(3)	Mo(2)–O(1)	1.979(2)
K(2)–O(4)#6	2.922(3)	Mo(2)–O(3)#9	2.274(2)
K(2)–O(11)#7	2.968(3)	Mo(2)–O(1)#9	2.374(2)
K(2)–O(11)	3.012(3)	Mo(3)–O(10)	1.703(3)
K(2)–O(6)	3.073(3)	Mo(3)–O(7)	1.706(3)
K(2)–O(10)	3.373(3)	Mo(3)–O(6)	1.923(2)
K(2)–O(3)#7	3.401(3)	Mo(3)–O(5)	2.008(2)
K(2)–O(8)#5	3.426(3)	Mo(3)–O(1)#9	2.183(2)
Te(1)–O(5)#8	1.878(2)	Mo(3)–O(2)	2.234(2)

Symmetry codes: #1 $-x + 1/2, -y + 3/2, -z$; #2 $x - 1/2, y + 1/2, z$; #3 $x, -y + 1, z + 1/2$; #4 $-x + 1/2, -y + 1/2, -z$; #5 $-x + 1/2, y + 1/2, -z - 1/2$; #6 $x - 1/2, -y + 1/2, z - 1/2$; #7 $-x + 1/2, y - 1/2, z - 1/2$; #8 $-x + 1, y, -z + 1/2$; #9 $-x + 1, -y + 1, -z$.

3. Results and Discussion

3.1. Crystal Structure

Single crystal X-ray diffraction revealed that $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ crystallizes in the centrosymmetric $C2/c$ space group of monoclinic system with the cell parameters $a = 21.172(2) \text{ \AA}$, $b = 7.660(0) \text{ \AA}$, $c = 15.419(1) \text{ \AA}$, and $\beta = 119.545(3)^\circ$. The crystal structure of the compound viewed along b -axis direction of the unit cell is shown in Figure 1 left. There are two distinct (K1,N1) and (K2,N2) on Wyckoff general 8f sites, one tellurium on a twofold axis 4e site, three molybdenum on 8f sites and twelve oxygen atoms on 8f sites in the asymmetric cell. The overall feature of the $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ crystal structure is one-dimensional anionic polymeric chain of $[\text{TeMo}_6\text{O}_{22}]^{4-}$ formed of Mo_6O_{22} polyoxomolybdate hexamers joined together by the spenoid TeO_4 linkers through corner oxygen atoms along the c -axis (Figure 1 right). Six rows of charge-balanced potassium and ammonium cations distribute around the $[\text{TeMo}_6\text{O}_{22}]^{4-}$ chain and separate them from each other (Figure 2a). The crystalline water molecules are located around the tellurium atom as there is enough space to accommodate them between two neighboring Mo_6O_{22} clusters. When the electrovalent interaction of central potassium and ammonium cations with ligand oxygen atoms are considered, the $(\text{K}^+, \text{NH}_4^+)$ two-dimensional ionic layer can be viewed as the block barrier to separate and stabilize the $[\text{TeMo}_6\text{O}_{22}]^{4-}$ chains (Figure 2b).

Figure 1. Crystal structure of $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ viewed along the b -axis direction (left), and the $[\text{TeMo}_6\text{O}_{22}]^{4-}$ anionic chain formed by Mo_6O_{22} hexamers connected through TeO_4 linkers (right).

Figure 2. (a) Distribution of charge-balanced potassium and ammonium ions around the $[\text{TeMo}_6\text{O}_{22}]^{4-}$ chain running along the c -axis, and (b) the view of (K, N)-O polyhedra two-dimensional ionic layers (b) along the c -axis (left) and b -axis (right).

All three of the molybdenum atoms are coordinated by six oxygen atoms into distorted MoO_6 octahedra. The Mo–O distances vary widely from 1.703 to 2.392 Å, with two minimum (1.703–1.745 Å), two medium (1.814–2.008 Å), and two maximum (2.183–2.392 Å) Mo–O bond lengths, which are similar with the typical values found in other molybdates [18,39–41]. The average Mo–O bond lengths are 1.983, 1.984, and 1.959 Å for Mo1, Mo2, and Mo3, respectively—shorter than those found in the isostructural $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ ($d_{\text{Mo–O}} = 1.990, 1.988$, and 1.970 Å, respectively) and $\text{Rb}_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ ($d_{\text{Mo–O}} = 1.993, 1.972$, and 1.962 Å, respectively) [34]. Six neighboring Mo–O octahedra are assembled into the Mo_6O_{22} hexamers in an edge sharing manner and by TeO_4 sphenoïd bridging oxygen atoms on both side of the polymolybdic units into $[\text{TeMo}_6\text{O}_{22}]^{4-}$ chains. The electron lone-paired Te1 atom is sited on a two-fold axis and coordinated with four oxygen atoms with two shorter equivalent Te–O bonds and two longer equivalent Te–O bonds, forming the sphenoïd TeO_4 unit with the typical Te–O distances from 1.878 to 2.113 Å, falling into the range observed in some known tellurites [42–45]. The average Te–O distance is 1.995 Å, which is slightly shorter than that of the isostructural $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ ($d_{\text{Te–O}} = 2.005$ Å) and $\text{Rb}_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ ($d_{\text{Te–O}} = 2.008$ Å). Both of the crystallographically independent potassium (K1, N1) and (K2, N2) have similar polyhedral environments surrounded by ten oxygen atoms when the maximum (K1, N1)–O distances of 3.426 Å are extended. The average distances for (K1, N1) and (K2, N2) are 3.001 and 3.069 Å, respectively—both shorter than that of $\text{NH}_4\text{–O}$ ($d_{\text{N1–O}} = 3.060$ Å, $d_{\text{N2–O}} = 3.126$ Å) and Rb–O ($d_{\text{Rb1–O}} = 3.055$ Å, $d_{\text{Rb2–O}} = 3.116$ Å) in compounds $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ and $\text{Rb}_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$, respectively. It shows that the replacement of smaller (K, N) cations for NH_4^+ or Rb^+ with crystal structure unchanged leads to the shrinkage of cell volume from 2240.44 Å³ (for $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$), 2237.49 Å³ (for $\text{Rb}_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$), to 2175.49 Å³ (for $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$). Bond-valence sum (BVS) calculations using the empirical expression $V_i = \sum \exp(R_{ij} - d_{ij})/B$ were performed for the ordered central cations, where $B = 0.37$ Å, R_{ij} represents the bond-valence parameter for atom pairs, and d_{ij} corresponds to the bond length [46,47]. The calculated results give the BVSs of 4.28, 5.94, 5.98, and 6.07 for Te1, Mo1, Mo2, and Mo3, respectively, in agreement with their oxidation states suggested from the single crystal structure.

3.2. Dipole Moments and Local Distortion

The local dipole moments for TeO_4 and MoO_6 structural units were calculated in order to better understand the distortion of the electron lone-paired Te^{4+} and the second-order Jahn–Teller (SOJT) distorted Mo^{6+} cations in the compound, as all the above cations are in acentric coordination environments. The methodology for dipole moment has been reported in previous literature [48,49]. As the TeO_4 units contain lone-pair electrons, the lone pair is given a charge of -2 , and the $\text{Te–}E_{(\text{lone pair})}$ distance of 1.25 Å from the Te^{4+} cation is adopted in the calculation [50]. The total and component dipole moments for cations on one position along the crystallographic axis are listed in Table 3. The dipole moments for the same cations on other positions can be obtained by using the symmetry operation of the $\text{C2}/c$ space group, and are not listed here. In fact, all the dipole moments for all the cations are cancelled out, as the crystal structure is centrosymmetric. The calculation for TeO_4 units gives a dipole moment of 9.6 Debye along the positive b -axis direction. The result is intrinsically determined by the two-fold symmetrical axis site for tellurium atoms. The relatively large dipole moment of TeO_4 units is attributed to their high geometric distortion in this structure. The calculated dipole moments for Mo1, Mo2, and Mo3 are 7.0, 9.3, and 5.9 Debye, respectively, which are similar with previously reported values [11,51]. The magnitudes of out-of-center distortions of three distorted MoO_6 octahedra were investigated according to the method proposed by Halasyamani [52], giving the $\Delta d = 1.24, 1.43$, and 1.15 for Mo1, Mo2, and Mo3, respectively. It is seen that the out-of-center distortion of Mo3 is the largest among the three MoO_6 octahedra, consistent with the result of local dipole moment calculation.

Table 3. The calculated total and component dipole moments (Debye) along three crystal axes for TeO_4 and MoO_6 units.

Units	<i>a</i>	<i>b</i>	<i>c</i>	Total
Te1–O	0.000	9.610	0.000	9.610
Mo1–O	6.050	−2.245	7.013	6.999
Mo2–O	−1.693	8.539	2.490	9.281
Mo3–O	5.696	−1.596	−0.052	5.940

3.3. Thermal Stability

The TG-DSC measurement was carried out to test the thermal stability of the title compound. The TG-DSC curves versus temperature are shown in Figure S2. From the thermogravimetric curve, the weight loss process occurs in a relatively broad temperature range of 200–450 °C with several minor endothermic peaks, corresponding to the dehydration of crystalline water from around 190 to 300 °C (~3.1%) and the decomposition of ammonium from around 300 to 450 °C (~3.0%). It should be mentioned that the minor weight gains along with the flat exothermic band that occurred in the range of RT (room temperature)–200 °C may be caused by the N_2 absorption of the material. Two main endothermic peaks are observed at 290 and 330 °C, both lower than the corresponding decomposition temperatures of 310 and 378 °C of single ammonium phase $(\text{NH}_4)_4\text{Mo}_6\text{TeO}_{22}\cdot 2\text{H}_2\text{O}$ [34]. The total weight loss ratio was consistent with the theoretical one (total water and ammonium) of ~6.0%. No further weight loss occurred above 450 °C, although two high and strong endothermic peaks were observed, which may be related to the decomposition or melting of the remaining materials. In order to identify the decomposition product after heating, we handled another amount of the compound and heated it at 450 °C under flowing N_2 atmosphere. X-ray diffraction pattern indicated that the remains mainly contained two phases: $\text{K}_2\text{Mo}_4\text{O}_{13}$ and $\text{TeMo}_5\text{O}_{16}$ (see Figure S3) [53,54].

3.4. Optical Absorption Properties

UV–Vis–NIR optical absorption spectra converted from diffuse reflectance were plotted in Figure 3. It is seen that $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ is transparent from the 2000 to 400 nm band range. From 400 nm, the optical absorption edge gradually increases, and at around 360 nm the absorption abruptly rises to the maximum, which corresponds to the electron band transition. The optical band gap of 3.4 eV can be derived through extrapolating the tangent line with the largest slope value to the abscissa. Therefore, compound $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ is a wide bandgap semiconductor.

Figure 3. Optical absorption spectra for $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ polycrystalline sample.

The infrared absorption spectra from 4000 to 400 cm^{-1} range are shown in Figure 4. The several peaks in the band range of 3201–2767 cm^{-1} can be ascribed to the symmetric stretching vibrations of the tetrahedral ammonium ion, and the two sharp peaks at 1437 and 1396 cm^{-1} are related to the asymmetric stretching modes [18,22,34]. The strong and broad absorption around 3440 cm^{-1} is due to the stretching modes of water molecules, and the peaks at 1590 and 1637 cm^{-1} are caused by the H-O-H bending modes of crystalline water [55,56]. The two strong peaks at 935 and 920 cm^{-1} can be assigned to the symmetric stretching vibrations of Mo-O bonds, whereas the two strong peaks at 885 and 852 cm^{-1} could be due to the asymmetric stretching vibrations of Mo-O bonds. The bands at 756 and 644 cm^{-1} can be attributed to the Te-O vibrations. The peaks at 555, 488, 463, and 432 cm^{-1} may be ascribed to the Te-O-Te, Te-O-Mo, or Mo-O-Mo bending vibrations [34,43].

Figure 4. Infrared absorption spectra for $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$.

4. Conclusions

A new tellurium polyoxomolybdate hydrate $(\text{NH}_4)_2\text{K}_2\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ was synthesized from the hydrothermal reaction method and structurally characterized from single crystal X-ray diffraction at room temperature. The compound can be viewed as the structural evolution from $(\text{NH}_4)_4\text{TeMo}_6\text{O}_{22}\cdot 2\text{H}_2\text{O}$ through half replacement of ammonium with potassium cations. The crystal structure contains a novel one-dimensional anionic polymeric chain $[\text{TeMo}_6\text{O}_{22}]^{4-}$ formed of Mo_6O_{22} clusters with TeO_4 units linked alternatively. The local dipole moments and the magnitudes of out-of-center distortions for the electron lone-paired TeO_4 and the distorted MoO_6 octahedra were calculated, indicating that they are in highly distorted coordination environments. Thermal analysis showed that the compound decomposes in the temperature range of 200–450 $^\circ\text{C}$, corresponding to the removal of crystalline water and ammonium in the structure. The infrared absorption spectra in the range of 4000–400 cm^{-1} and the UV–Vis–NIR optical spectroscopy were investigated to understand the structure–properties relationship. It indicated that the optical bandgap is 3.4 eV, belonging to a wide band semiconductor. This work demonstrates an example of the synthesis of a new tellurium polyoxomolybdate through half substitution of ammonium with potassium cations.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst11040375/s1>: Table S1: Atomic coordinates, equivalent isotropic displacement parameters, and summary of bond-valence sum (BVS) calculations; Table S2: Typical bond lengths; Figure S1: The experimental and simulated powder XRD; Figure S2: Curves of thermogravimetric (TG) mea-

measurements and differential scanning calorimetric (DSC) measurements versus temperature; Figure S3: Powder XRD and phases of the remains after heating.

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