

NEUSTÄDTTELITE AND COBALTNEUSTÄDTTELITE,
TWO NEW MINERALS OF THE MEDENBACHITE-GROUP

by

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The minerals of the medenbachite group have space-group symmetry $P\bar{1}$ and have the chemical formula $Bi_2M_1M_2(O,OH)_2(OH)_2(AsO_4)_2$: end-member composition of medenbachite [1] / cobaltneustädtelite / neustädtelite is $M_1 = Fe^{3+}$, $M_2 = Cu^{2+} / Co^{2+} / Fe^{3+}$. On the average, the three minerals have the same crystal structure. Medenbachite is isotypic with cobaltneustädtelite; neustädtelite is isostructural. The medenbachite-group minerals with M_2^{3+} , two OH groups, and two oxo-oxygen groups p.f.u. have a "small" unit cell with $Z = 1$ (neustädtelite); in cases with M_2^{2+} , three OH groups, and one oxo-oxygen atom p.f.u. the unit cell is "large", $Z = 2$ (medenbachite and cobaltneustädtelite). The intensities of the superstructure reflections responsible for the change of the unit cell originate from order phenomena of the split Bi site.

Neustädtelite and cobaltneustädtelite were found on samples from the dumps of the Guldener Falk Mine (Schneeberg-Neustädtel, Saxony, Germany). The appearance of the two new minerals is very similar: small tabular crystals up to 0.2 mm in diameter, transparent to translucent, with a brown color and a light brown streak; the lustre is adamantine. Both minerals are biaxial negative, $2V = 65(5)^\circ$, $n_x = 2.02(2)$, $n_y = 2.09$ (calc.), $n_z = 2.12(2)$; pleochroism is strong with $X =$ brown to opaque, $Y =$ yellow, $Z =$ pale yellow. Mohs' hardness is $4\frac{1}{2}$. The cleavage parallel to $\{001\}$ is good. The chemical composition was derived by means of electron-microprobe analyses. Average contents for neustädtelite / cobaltneustädtelite are (in wt.%): Bi_2O_3 52.58/51.54, PbO 0.08/0.08, CaO 0.15/0.32, Fe_2O_3 13.92/10.90, Al_2O_3 0.29/0.07, CoO 3.35/5.47, NiO 0.34/1.61, ZnO 0.09/0.39, CuO 0.07/0.00, As_2O_5 26.82/25.91, P_2O_5 0.23/0.43, H_2O (calc.) 2.56/3.01, total 100.48/99.73.

Based on 12 oxygen atoms the empirical formulas for the neustädtelite and cobaltneustädtelite type material are

$Bi_{1.94}Ca_{0.02} \Sigma_{1.96} Fe_{0.99}(Fe_{0.51}Co_{0.38}Ni_{0.04}Al_{0.05}Zn_{0.01}Cu_{0.01}) \Sigma_{1.00} [(OH)_{2.44}O_{1.54}] \Sigma_{3.98} [(AsO_4)_{2.01}(PO_4)_{0.03}] \Sigma_{2.04}$
and

$(\text{Bi}_{1.91}\text{Ca}_{0.05})_{\Sigma 1.96}\text{Fe}_{1.02}(\text{Co}_{0.63}\text{Fe}_{0.16}\text{Ni}_{0.19}\text{Zn}_{0.04}\text{Al}_{0.01})_{\Sigma 1.03}[(\text{OH})_{2.88}\text{O}_{1.14}]_{\Sigma 4.02}[(\text{AsO}_4)_{1.95}(\text{PO}_4)_{0.05}]_{\Sigma 2.00}$ respectively. Extensive solid solution is observed between these two minerals.

The valence state of iron in cobaltneustädteelite and medenbachite was investigated by Mössbauer spectroscopy. Both spectra were fitted to two Lorentzian doublets. The doublets in the medenbachite spectrum are sufficiently resolved to conclude that there are at least two distinct environments for Fe^{3+} , which are octahedral based on the centre shifts. These could tentatively be assigned to M1 and M2 in the structure, where $\text{Fe}^{3+}(\text{I})$ corresponds to M1 and $\text{Fe}^{3+}(\text{II})$ corresponds to M2 based on the values of quadrupole splitting and the relative site distortion. Fe^{3+} is therefore preferentially partitioned into the M1 site, although some Fe^{3+} appears to occupy also the M2 site, which is mainly occupied by Cu. Determining accurate site occupancies is not possible, however, due to the line overlap. For the cobaltneustädteelite spectrum the linewidths of both doublets were constrained to be equal since the doublets were not sufficiently resolved; the fitting to two Lorentzian doublets is consistent with the observations of medenbachite.

Neustädteelite / cobaltneustädteelite have space group $\text{P}\bar{1}$: $a = 4.556(1) / 9.156(1)$, $b = 6.153(2) / 6.148(1)$, $c = 8.984(2) / 9.338(1)$ Å, $\alpha = 95.43(2) / 83.24(1)$, $\beta = 99.22(2) / 70.56(1)$, $\gamma = 92.95(3) / 86.91(1)^\circ$, $V = 246.9 / 492.2$ Å³, $Z = 1 / 2$. Structure investigations were performed on single-crystal X-ray data. A structural reinvestigation of medenbachite proved isotypy with cobaltneustädteelite: $a = 9.162(2)$, $b = 6.178(1)$, $c = 9.341(2)$ Å, $\alpha = 83.50(1)$, $\beta = 71.04(1)$, $\gamma = 85.15(1)^\circ$, $V = 496$ Å³, $Z = 2$. The crystal structure investigations of neustädteelite / cobaltneustädteelite / medenbachite was based on 873 / 1729 / 1749 unique data; 796 / 1579 / 927 had $F_o > 4\sigma(F_o)$. R1 was 0.047 / 0.090 / 0.083 and $\omega R2$ was 0.107 / 0.192 / 0.233 after refinement of the 95 / 108 / 108 free variables.

In neustädteelite the Bi atoms feature a site disorder; they are split onto two half occupied positions separated by 0.486(3) Å. No indications for ordering of the Bi atoms were detected. A trial to obtain order by reducing the symmetry to P1 failed. Superstructure reflections were not seen even after long exposed X-ray investigations. Cobaltneustädteelite and medenbachite display topologically the same building principles as found in neustädteelite, but the unit-cell volume is twice as large. Their average cells correspond with the neustädteelite cell. The most striking difference concerns the actual position of the Bi atoms and the environment of one of the oxygen atoms with respect to its coordination by Bi and H atoms. In cobaltneustädteelite and medenbachite all atoms except Bi exhibit an exact translation vector $[\frac{1}{2} 0 0]$. 50 % of the Bi atoms show a site disorder; their separation is larger as compared to neustädteelite and amounts to 0.587(3) and 0.762(4) Å, respectively. The other half of the Bi atoms are on a fully occupied atomic site (Bi12). This fully occupied Bi site corresponds approximately to the average position between Bi1 and Bi2 after application of the pseudotranslation vector (the deviations are 0.017(4) and 0.019(7) Å in the two minerals).

The coordination of the $\text{Bi}^{(3+4)}$ and $\text{Bi}^{(4+3)}$ atoms is irregular. The nearest ligands are in the range of 2.02 to 2.34 Å, additional ligands are up to 2.91 Å. The gaps between nearest and next-nearest neighbour environments as well as the spreading of the outer coordination sphere are unequally developed. Half of the O atoms not belonging to an arsenate tetrahedron are linked to a $\text{M1}\text{O}_6$ and a $\text{M2}\text{O}_6$ octahedron; bonds to Bi atoms are ≥ 2.70 Å. Despite the actual position of the Bi atom, the cations yield a too small contribution to the bond strength reaching this O atom to compensate for its valence (1.05 to 1.19 v.u.) and it has to be considered as a hydroxyl group.

The other oxygen atoms not belonging to $[\text{AsO}_4]$ are oxo-oxygen atoms in neustädteelite but they are half oxo-oxygen atoms and half hydroxyl groups in cobaltneustädteelite and medenbachite. They balance the charge according to the formula $\text{M}^{3+} + \text{O}^{2-} \leftrightarrow \text{M}^{2+} + (\text{OH})^-$. These O atoms are exclusively coordinated by two or three Bi atoms, featuring a varying distribution of the O-Bi bond lengths; two O-Bi bonds are $\leq 2.21 \text{ \AA}$. For compensation of the bond valences the Bi-O bond lengths are adopted by shifting the Bi atoms. The actual bond length to the coordinating cations depends on the respective position of the Bi atom due to site disorder. Fe^{3+} , Co^{2+} , and Cu^{2+} atoms occupy two six-coordinated M positions. The average bond lengths indicate that M1 is Fe^{3+} and M2 is (Fe^{3+} , Co^{2+} , Cu^{2+}).

The medenbachite-type structures are characterized by chains of edge-connected MO_6 octahedra (neustädteelite and cobaltneustädteelite) and of alternating octahedra and tetragonal bipyramids (medenbachite) running parallel to $[010]$. Layers in (001) are formed by corner connection of the chains with the arsenate tetrahedra. The layers may be described as formed by densely packed oxygen atoms in (001) . Half of the octahedral sites are occupied by M atoms. The other sites are vacant; however an arsenate tetrahedron is alternately at the top and bottom face of the vacant tetrahedra, which results in $\text{M}^{6l}(\text{OH})(\text{XO}_4)$ layers. They are linked by Bi atoms. The structure may also be regarded as columns of edge-sharing octahedral columns $\infty^1[\text{MO}_4]$ running parallel to $[010]$ and by $\infty^1[\text{Bi}(\text{O},\text{OH})]$ chains running parallel to $[100]$, i.e., the two chemically different chains are approximately perpendicular to each other.

References

- [1] KRAUSE, W., BERNHARDT, H.-J., GEBERT, W., GRAETSCH, H., BELENDORFF, K. & PETITJEAN, K. (1996): *Amer. Miner.* 81, 505-512.