MITT.ÖSTERR.MINER.GES. 148 (2003)

NITRILOTRIACETATO ZIRCONATES OF ALKYL AND POLYALKYL AMINES: STRUCTURAL AND PHYSICAL PROPERTIES

E. Haussühl[1,2], S. Haussühl[3] & E. Tillmanns[1]

[1]Institut für Mineralogie und Kristallographie
Universität Wien, Althanstrasse 14, A-1090 Vienna, Austria
[2]Institut für Mineralogie, Abteilung Kristallographie
Johann Wolfgang Goethe-Universität, Senckenberganlage 30, D-60054 Frankfurt a. M., Germany
[3]Institut für Kristallographie
Zülpicherstrasse 49B, D-50674 Köln, Germany

A large percentage (> 40%) of the nitrilotriacetato zirconates $X_m(Zr[N(CH_2COO)_3]_2)_n \cdot yH_2O$ possesses an acentric structure within the so far investigated inorganic cations X. Therefore, we expected a considerable number of the zirconates formed by organic cations like amines to exhibit polar structures, too. Such crystals might be candidates for pyroelectric, piezoelectric and non-linear optical applications. The syntheses were successfully carried out employing the method of LARSON & ADAMS [1] with the alkyl monoamine cations $(C_rH_{2r+1}NH_3)^+$ for r = 1 to 8 and alkyl diamine cations $(C_rH_{2r}(NH_3)_2)^{2+}$ for r = 2 to 12. The structural properties of most of these species have already been reported as NCS in Z. Kristallogr. during the last years. Large single crystals of these compounds having optical quality could be grown from aqueous solutions by standard methods (controlled lowering of temperature or controlled evaporation). In the cases of larger r values the nitrilotriacetato zirconates possess plastic properties which impede the measurement of physical properties.

The following general results were obtained from the study of about 80 phases with different cations:

1. The nitrilotriacetato zirconates of the amines so far investigated crystallize exclusively in orthorhombic and monoclinic space groups.
2. The salts of the monoamines exhibit a rather high percentage of acentric structures (about 60 %), whereas the salts of the symmetric diamines form centrosymmetric structures, so far without exception.
3. The maximum pyroelectric and piezoelectric effects are in most cases considerably stronger than those found in tourmaline or α-quartz, respectively.
4. Despite a heavy anisotropy of expansion and elastic stiffnesses the volume thermal expansion and the mean elastic stiffness $C = (c_{11}+c_{22}+c_{33}+ c_{44}+c_{55}+c_{66}+c_{12}+c_{13}+c_{23})/9$ differ only slightly within these nitrilotriacetato zirconates. However, the salts of the diamines show distinct smaller values of α and larger values of C. An analogous behaviour is observed with the temperature dependence of the elastic properties.

These common properties stem from the similarity of the structural arrangement of the anionic layers.

Literature

[1] LARSEN, E. M. & ADAMS, A. C. (1967): Potassium bis (Nitrilotriacetato) Zirconate (IV). - Inorg. Synth. 10. 7-8.

The authors are gratefully indebted to the Austrian Fonds zur Förderung der wissenschaftlichen Forschung FWF (P14125-GEO) and the International Centre for Diffraction Data for financial support of this work (Grant 90-03 ET).