

Anharmonic thermal vibrations and disorder of atoms in tourmaline

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Elbaite (space group R3m), a Li-bearing tourmaline with general formula of $XY_3Z_6(BO_3)_3Si_6O_{18}W_4$, has 5 kinds of cations and 8 kinds of O (including W). Of the structural studies of tourmaline, those of Gabrielle Donnay and her group were unique in focusing on the structural aspects of the primary pyroelectricity (Donnay, 1977¹ etc). Donnay (1977) refined the structure of elbaite, and found that the magnitudes of u values for O₁ and, to a lesser degree for X and O₂, point to abnormalities in the thermal vibrations. From the atomic coordinates at two different temperatures, she noticed that, while neither X nor O₂ has shifted significantly, O₁ has. In the present study, we attempted least-squares refinement with a generalized structure factor expression, based on the Gram-Charlier expansion of atomic probability density functions (PDF), to examine the anharmonic characters of atoms in elbaite at room temperature, suggested by Donnay (1977).

The chemical formula of a green prismatic crystal from Lahgman (Afghanistan) was $X = (Na_{0.52}Ca_{0.13}K_{0.01034})_{\Sigma=1}$, $Y = (Li_{1.26}Al_{0.95}Fe_{0.50}Mn_{0.20}Mg_{0.01}Ti_{0.08})_{\Sigma=3}$, $Z = Al_{6.00}$ and $W = ([O_1(OH)]_{3.97}F_{0.03})_{\Sigma=4}$. All the diffraction data were obtained at room temperature with a spherical specimen of diameter about 0.3 mm. The unit-cell dimensions are $a = 15.874(3)$ and $c = 7.116(3)$ Å. All the refinement cycles were performed using the 3061 F_o without omitting any reflection from the measured. The polarity of our spherical specimen was determined with respect to the structure of Donnay (1977).

The harmonic least-squares refinement with 88 variables, initiated with the positional parameters of Donnay (1977), converged at $R = 0.0337$, showing considerably large thermal parameters for X, Y, O₁ and O₂ atoms (First group) compared to the rest atoms (Second group). The further refinements with additional 63 variables for the third and fourth order coefficients for the first-group atoms converged at $R = 0.0294$, resulting in significantly anharmonic or multimodal PDFs for the first-group atoms. These PDFs are clearly asymmetric along c with the modes shifted toward the positive side for the O atoms and toward the negative side for the cation sites from the corresponding means. Our result of the single-temperature measurement, particularly for O₁, is just concordant with Donnay (1977)'s two-temperature measurement of atomic shift. The present study further indicated that O₁ was disordered over three potential energy minima in the plane perpendicular to the 3-fold axis.

1) Donnay G. Acta Cryst. A33, 927-932, 1977

Software For Identification and Refinement of Cell Parameters From Powder Diffraction Data of Minerals Using the RRUFF Project and American Mineralogist Crystal Structure Databases

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The RRUFF project is dedicated to the identification and characterization of all minerals through X-ray powder diffraction, single crystal diffraction, Raman spectroscopy, and chemical analysis. Crystal Sleuth software was developed as an analytical tool for the RRUFF project and shares the common goal of providing a worldwide resource for identification of minerals and general advancement of the mineral sciences by providing an interactive environment for X-ray powder refinement and mineral spectra identification using the RRUFF project database and American Mineralogy Crystal Structure Database (AMCSD). Among the many utilities that have proven to be invaluable in the reduction and analysis of diffraction patterns and Raman spectra, Crystal Sleuth gives the user the ability to remove cosmic rays, correct the spectral baseline, allows for the visualization and comparison of several spectra, and forms mathematical models of peaks. The true power of this software is illustrated when it works symbiotically with AMCSD to identify and refine X-ray powder diffraction patterns to high precisions, and when it houses the efforts of the RRUFF project database within a library to provide a rapid method of mineral identification through Raman spectroscopy.

This presentation will focus on the usefulness of Crystal Sleuth in the area of X-ray diffraction. In this arena, the software's ability to correct spectral baselines, auto-fit and index peaks, search and identify the mineral, and refine cell parameters plays the largest role. The program gives the user the versatility to fit and index $K\alpha_1$ and $K\alpha_2$ doublets and singlet peaks and has been tested on patterns both from traditional lab and synchrotron sources. Moreover, the technique which all these features are integrated into an analytical tool has proven time and again to be able to produce cell parameters in X-ray refinement with a precision of four or more decimal places through a nearly automated routine which can take under a minute. This quick automation and high accuracy produced by Crystal Sleuth is clearly a method adapted to unravel mineral data with minimal human intervention for use in such ventures as exploring our Solar System on a Mars Rover.

Continuous crystal chemical space for the dioctahedral iron-rich micas and related phases (celadonite, glauconite, Fe-illite)

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The dioctahedral iron-rich mica-related phases, the celadonite-glauconite group minerals (CGGM), have been defined and differentiated upon all of their possible crystal chemical positions, namely interlayer charge (IMA nomenclature, 1998), octahedral charge (AIPEA nomenclature, 1986) and tetrahedral charge (AIPEA nomenclature, 1980). The multitude of crystal chemistry based nomenclatures already forecasts that these minerals are difficult to distinguish on a crystal chemical basis. The routinely used formal identification methods (d_{060} and FTIR) do have strong limits. CGGM have also been separated, from the second half of the 19th century on, on formation environment: celadonite was supposed to have magmatic, while glauconite sedimentary origin. However, data accumulating in the literature suggest that minerals of magmatic and sedimentary origin may have overlapping chemical composition. For comparison the chemical data set (>350 analysis) we collected on CGGM we started by building up a second database on all chemical data on CGGM available in the literature, with some outlook on their iron containing aluminous counterparts, too. At the moment, that second database contains more than 700 entries. Chemical data were filtered on the presence/absence of measured Fe^{2+}/Fe^{3+} ratios and some crystal chemical constraints. The filtering process outlawed more than half of the data, leaving about 310 entries in the database for iron-rich dioctahedral micaceous phases. The valid(ated) data were plotted into different graphical representation systems to check the crystal chemical range of these minerals. We found that the crystal chemical space occupied by these minerals is continuous. The celadonite field of the IMA nomenclature is more populated towards the Fe^{3+} -rich side, while the glauconite field at lower interlayer charges is more populated on the Al-rich side. The transition towards the Al-rich regions is continuous in the low interlayer charge regions, pointing out the need for enlarging the IMA definition of illite. These findings agree well with the predicted trend of glauconitisation: an Al-Mg-rich smectitic material is gradually turning into an Fe^{3+} -Mg-rich mica, where the charge consequence of the K uptake is compensated by the decrease of octahedral occupancy and by Al- Fe^{2+} substitution in the octahedral layer.

Graphical representation systems for TOT layer silicates: a case study for iron-rich dioctahedral phases (celadonite, glauconite)

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We compare numerous graphical representations for the chemistry of TOT layer silicates, with special emphasis on the iron-rich dioctahedral mica and the related interlayer-deficient micas (celadonite-glauconite group minerals, CGGM). These minerals have been differentiated upon all of their possible crystal chemical positions, namely interlayer (IMA, 1998), octahedral (AIPEA, 1986) and tetrahedral (AIPEA, 1980) charge. In literature both 2D and 3D plots were designed to visualise the chemical composition of micas, applying 2-4 or even more variables. Special coefficients were created from individual cation numbers to reduce the number of variables. Ternary plots are widespread, but can be misleading, if normalised; source data normally cannot be read from the plots. Plots designed for micas often have the starting condition $X_{IL} = 1$ (X_{IL} : interlayer cation charge), rendering them limited use for interlayer-deficient micas. In CGGM tetrahedral cation charge (X_T) is defined by Si a.p.f.u., X_{IL} by K (+Ca,Na) a.p.f.u. (note sample impurity/homogeneity and H_2O). Octahedral cation charge (X_O) is defined by $X_O = 22 - (X_T + X_{IL})$. X_O can also be expressed as $X_O = {}^{VI}R^{3+} * 3 + {}^{VI}R^{2+} * 2$ (Li-free; ${}^{VI}R^{3+}$, ${}^{VI}R^{2+}$ is a.p.f.u. of trivalent (Fe^{3+} , Al) and divalent (Mg, Fe^{2+}) octahedral cations). An additional parameter, normally omitted, is octahedral site occupancy (SO_0): $SO_0 = {}^{VI}R^{3+} + {}^{VI}R^{2+}$ (Li-free). SO_0 gives a direct relationship between X_O and the ratio of the di- and trivalent octahedral cations (${}^{VI}R^{2+}/({}^{VI}R^{2+} + {}^{VI}R^{3+})$). At the particular case of "ideal" dioctahedrality ($SO_0 = 2.00$) ${}^{VI}R^{2+}/({}^{VI}R^{2+} + {}^{VI}R^{3+}) = (6 - X_O)/2$. SO_0 is frequently, and arbitrarily, fixed at 2.00 when calculating formulae from analyses (e.g. EPMA) where iron valence state is not measured. However, as we showed elsewhere, for CGGM SO_0 cannot be fixed, and especially cannot be fixed for 2.00 (may go up to 2.08-2.15). Because of that (1) even good chemical data may plot outside of the "definition boxes" (IMA, 1998); (2) phases differing chemically may plot close; (3) these plots are very sensitive to SO_0 vs. Fe^{2+}/Fe^{3+} calculations. Diagrams (e.g. IMA, 1998) using ${}^{VI}R^{2+}/({}^{VI}R^{2+} + {}^{VI}R^{3+})$ type variables can be regarded not only chemical, but also crystal chemical (= where chemical formulae can be reconstructed from the plots - ${}^{VI}R^{2+}$ type cations still not distinguished), only if SO_0 is added. Conclusion: the graphical representation of crystal chemistry of the CGGM needs four dimensions (quality of ${}^{VI}R^{2+}$ disregarded). Additionally a new, easy to use, combined plot is presented, where e.g. the glauconitisation process can be well visualised.