

carbonate materials. The reaction begins faster in Lk compared to the other carbonate rocks. For all materials the decomposition was completed at 900°C. For Lk completion of decomposition is observed after 1½ hour, whereas for the remaining samples the reaction is completed after 2 hours.

The isothermal curves were obtained in the temperature range 640-900°C. The time required achieving maximum decomposition decreased with temperature and the isothermal curves converge at higher temperatures. Moreover the shape of isothermal curves changed from almost linear at 640°C and 700°C to sigmoid at higher temperatures. Lk is the most reactive material, because decomposition proceeds faster, whereas Mn is the least reactive carbonate. However the reaction rate for thermal decomposition of calcite is not controlled solely by grain size, because La with minimum calcite grain size displays isothermal curves comparable to Ma, which has considerably larger grain size (1.5 µm and 335 µm for Lk and Ma respectively). The role of porosity is also significant for the progress of decomposition reaction. The porosity of La is comparable to that of Ma and Mn. The firing properties affect lime reactivity as was shown by the specific surface area (SSA) and slaking temperature of the carbonate rocks [1].

[1] Triantafyllou, G., Christidis G.E., Markopoulos Th. In D.G Eliopoulos et al. (eds) *Mineral exploration and sustainable development*, Millpress Rotterdam 2003, 931.

#### MS41 P04

**Transmission electron microscopy studies on a tetrasilic mica** V.K. Kis<sup>a</sup>, I. Dódony<sup>b</sup>, J-L. Robert<sup>c</sup>

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**Keywords:** mica; crystal structure; electron microscopy

Tetrasilic magnesium mica crystals synthesized hydrothermally (500 C°, 1 kbar) were studied using transmission electron microscopy. The aim of this work is to characterize the distribution of magnesium over octahedral and interlayer sites.

The size of the mica crystals varies in the 200 nm and 2 µm range. Energy filtered [001] selected area electron diffraction (SAED) patterns around 0.8 Å resolutions were recorded and quantitatively evaluated. The thickness of the platelets, estimated from the SAED resolutions, varies between 60-90 Å, i.e. 6-9 mica layers. This small thickness value allows using kinematical approximation. Two types of SAED patterns were obtained: compared to the calculated SAED patterns of phlogopite the abundant ones show unusual intensity distribution with strong  $h = 2n$  reflections on the  $k = 6n$  rows, however crystals with phlogopite-like intensity distributions also occur. The energy filtered [001] high resolution (HR)TEM images showing components up to 1.7 Å<sup>-1</sup> on their Fourier transform, revealed characteristic heterogeneities at nanometre scale.

The results of analytical (A)TEM revealed two groups in crystal compositions. In the case of dominant group the Mg/Si ratio is larger than the expected 0.75 value for a trioctahedral tetrasilic mica, whereas the K/Si ratio is

smaller than the expectable 0.25 value. The magnesium excess is located into the interlayer space in the deduced formula;  $(K_{0.8}Mg_{0.2})Mg_3[Si_4O_{11.2}(OH)_{0.8}]$ . By its composition the dominant phase of the sample proved to be a trioctahedral tetrasilic oxy mica. No straightforward correlation between the different compositions and SAED patterns were observed.

The cation distributions over octahedral and interlayer sites are measured crystal by crystal in their [001] projected SAED patterns and corresponding HRTEM images.

#### MS41 P05

**Influence of the symmetry on the Raman spectra of isolated SbS<sub>3</sub> pyramids.** Sherif Kharbish<sup>a,b</sup>, Eugen Libowizky<sup>a</sup>, Anton Beran<sup>a</sup>. <sup>a</sup>*Institut für Mineralogie und Kristallographie, Geozentrum, Althanstraße 14, A-1090 Wien, Austria.* <sup>b</sup>*Geology Department, Faculty of Science, Zagazig University, Zagazig City, El-Sharkia, Egypt.*  
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**Keywords:** Raman spectroscopy, SbS<sub>3</sub> pyramids, vibration

The flat pyramidal four-atom SbS<sub>3</sub> group in tetrahedrite and pyrrargyrite with C<sub>3v</sub> symmetry and in stephanite and bournonite with C<sub>s</sub> symmetry has been investigated at room temperature by Raman spectroscopy. The fundamental stretching and bending vibrations of the pyramidal SbS<sub>3</sub> groups occur between 150 and 400 cm<sup>-1</sup>. In addition to a "lattice mode", four prominent peaks and shoulders occur in the spectra of tetrahedrite and pyrrargyrite, representing the symmetric and antisymmetric stretching ν<sub>1</sub> (A<sub>1</sub>) and ν<sub>3</sub> (E) and bending vibrations ν<sub>2</sub> (A<sub>1</sub>) and ν<sub>4</sub> (E). The bands at 362 and 350 cm<sup>-1</sup> in tetrahedrite and at 323 and 300 cm<sup>-1</sup> in pyrrargyrite were assigned to the ν<sub>1</sub> and ν<sub>3</sub> modes, respectively. The bands representing the ν<sub>2</sub> and ν<sub>4</sub> modes occur at 324 and 298 cm<sup>-1</sup> in tetrahedrite and at 274 and 252 cm<sup>-1</sup> in pyrrargyrite, respectively. In comparison with the spectra of tetrahedrite and pyrrargyrite, two to four additional bands occur in the spectra of stephanite and bournonite. Peak fitting of the stephanite and bournonite spectra give band maxima at 335, 319, 301, 233, 204 and 178 cm<sup>-1</sup> and at 335, 324, 293, 275, 227, 197, 168 and 110 cm<sup>-1</sup>, respectively. The increase of the number of the bands in stephanite and bournonite can be attributed to the splitting of the degenerate ν<sub>3</sub> (E) and ν<sub>4</sub> (E) modes due to lowering of the symmetry of the SbS<sub>3</sub> pyramids [1]. Comparison between the spectra of the C<sub>3v</sub> isolated pyramidal SbS<sub>3</sub> groups in tetrahedrite and pyrrargyrite and those of the C<sub>s</sub> isolated SbS<sub>3</sub> pyramids in stephanite and bournonite shows amazing similarities in the rough pattern of the spectra and the number of the strong bands. However, the band positions decrease continuously in wavenumber from tetrahedrite to bournonite, stephanite and pyrrargyrite. The similar band pattern of the investigated minerals may be attributed to the only small distortion of the SbS<sub>3</sub> pyramid in stephanite and bournonite. The shift of the positions of the bands in stephanite and bournonite to lower wavenumber regions relative to those in tetrahedrite can be attributed to the increasing Sb-S distances. The latter observation can also explain the shift of the band positions in the bournonite spectra to higher frequencies relative to those in pyrrargyrite with larger bond lengths. It has also been noticed that although the pyramidal SbS<sub>3</sub> groups in stephanite have larger bond lengths than those in

pyrargyrite, the band positions in stephanite spectra are shifted to higher vibrational regions than those in pyrargyrite. This may be attributed to the complex structure of the stephanite and the effect of the surrounding elements.

[1] Nakamoto K., *Wiley-Interscience* 5<sup>th</sup> ed., New York, 1997, 408p

#### MS41 P06

**C and/or C<sub>2</sub> in Reduced Rare Earth Carbide Halides**  
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**Keywords:** Rare Earth, Cluster, Endohedrals

The variety of compounds of Rare Earth metal carbide halides  $REX_nX_z$  ( $X=Cl, Br, I$ ) is unexpectedly large. As known from the structural chemistry of the metal-rich compounds of 4d and 5d elements frequently discrete or condensed metal clusters occur [1]. For many cluster topologies the  $M_6X_{12}$  with an octahedral core is dominating. For the electron-poor Rare Earth metals the clusters are nearly always stabilised by interstitial atoms [2]. In the case of carbon as endohedral (i) single C atoms, (ii) C<sub>2</sub> dimers are known as well as both C and C<sub>2</sub> entities simultaneously (iii). According to X-ray analysis the C atoms and the C<sub>2</sub> dumbbells are statistically disordered in the center of the RE octahedra for (iii). The C/C<sub>2</sub> disorder is accompanied by an elongation/contraction of the Rare Earth metal clusters. The occurrence of isolated C atoms or C<sub>2</sub> units is determined firstly by the size of the surrounding RE cage and secondly by the electron count for the compound. A simple ionic treatment in the Zintl-Klemm concept in connection with the qualitative molecular orbital scheme for a C<sub>2</sub> dimer can reasonably predict the expected length of the C-C-distance. In all known examples the maximum formal charge assigned to the C<sub>2</sub> units is -6 corresponding to an ethanide ion C<sub>2</sub><sup>6-</sup>. When the formal charge exceeds 6- the dimers are no longer stable with respect to dissociation into two C<sup>4-</sup> ions. On the other hand, when the surplus of electrons is consumed in metal metal bonds also C<sub>2</sub> dimers are possible. When the formal charge on C<sub>2</sub> becomes less than 6-, shorter C-C distances result as in the ethenide ions C<sub>2</sub><sup>4-</sup>. Our investigations on  $REX_nX_z$  compounds confirm these expectations.

[1] Simon, A., *Angew. Chem.* 1988, 100, 163, *Angew. Chem. Int. Ed. Engl.* 1988, 27, 159.

[2] Simon, A., Mattausch, H., Ryazanov, M., Kremer, R. K. Z. *Anorg. Allg. Chem.* 2006, 632, 919.

#### MS41 P07

**Structural disorder in natural pearceite-T2ac: A combined TEM and SCXREF study**

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**Keywords:** structural disorder, crystal structure, polytypism

Pearceite-T2ac is a member of the pearceite-polybasite group of minerals. These minerals - general formula  $[Ag,CuS_4]_n[(Ag,Cu)_6M_2S_7]$  with  $M = Sb, As$  - have been recently structurally characterized [1,2,3]. On the whole, the structure of the polytype pearceite-T2ac can be described as a regular succession of two module layers stacked along the *c* axis: a first module layer (labeled *A*), with general composition  $[(Ag,Cu)_6(As,Sb)_2S_7]^{2+}$ , and a second module layer (labeled *B*), with general composition  $[Ag_9CuS_4]^{2+}$ . In the structure, (As,Sb) forms isolated (As,Sb)S<sub>3</sub> pyramids typically occurring in sulfosalts, copper links two sulfur atoms in a linear coordination, and silver occupies sites with coordination ranging from quasi linear to almost tetrahedral. In the *B* layer the silver cations are found in various sites corresponding to the most pronounced probability density function locations of diffusion-like paths. The structure was solved and refined on a twinned crystal up to  $R = 4.34\%$  in the space group *P321*. It was anticipated that correlated local ordering of the relative positioning of the heavily disordered Ag cations within the *B* module layers might give rise to structured diffuse scattering. An electron diffraction study searching for this was therefore carried out on the same natural sample used for the structural investigation (sample AB6829, Naturhistorisches Museum of Vienna). The discovery of a highly structured, essentially continuous diffuse intensity distribution (particularly in the vicinity of the  $[1\bar{1}1]$  and  $[441]$  zone axis orientations) shows that the diffusion of neighbouring Ag ions must be highly correlated both within the *a-b* planes as well as from one such plane to the next. More detailed electron diffraction studies are underway to attempt to determine the detailed shape of the observed diffuse distribution and to model the real space Ag ion ordering presumed to be responsible.

[1] Bindi L., Evain M., Menchetti S., *Acta Cryst.*, 2006, B62, 212.

[2] Evain M., Bindi L., Menchetti S., *Acta Cryst.*, 2006, B62, 447.

[3] Bindi L., Evain M., Menchetti S., *Can. Miner.*, 2007, 45, in press.

#### MS41 P08

**Hybrid twinning in staurolite** M. Nespolo<sup>a</sup>, G. Ferraris<sup>b</sup>  
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**Keywords:** Effective twin index; Hybrid twinning; Staurolite

Staurolite gives two penetration twins, known as 90° or "Greek cross" twin 60° or "Saint Andrew" cross, with twin elements 4<sub>[100]</sub> or 2<sub>[013]</sub> for the former, and 3<sub>[102]</sub> or 2<sub>[313]</sub> for the latter [1,2]. The Greek cross twin has twin index 6, at the upper limit of Friedel's empirical limit for the occurrence of twinning, while the Saint Andrews twin has twin index 12, far too high to be more than an exceptional case. Despite this unusually high twin index, the Saint Andrews twin is the most frequent twin in staurolite and its occurrence frequency cannot be explained on the basis of the classical reticular theory of twinning.

The occurrence frequency of the Saint Andrews twin becomes less intriguing once it is explained as hybrid twin [3]. Hybrid twins are twins in which more than one concurrent sublattice exists, contributing to the overall lattice restoration, which is higher than what the classical twin index states. These concurrent sublattices occur when