o.m13.p5 **Infrared Spectroscopy of $Li_2B_4O_7$.** N.D. Zhigadlo [1,2], M. Zhang [1], E.K.H. Salje [1], [1] *Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK,* [2] *Institute of Solid State and Semiconductors Physics, P. Brovki 17, 220072 Minsk, Belarus*
Keywords: $Li_2B_4O_7$; infrared; Li disordering

Infrared active phonons have been studied in $Li_2B_4O_7$ in the spectral region of 50-1600 cm^{-1} at temperatures between 20 K and 680 K. In the contrast to the sharp B-O bands, the Li-related bands in the region between 300-510 cm^{-1} are rather broad even at 20 K. With increasing temperature the bands between 300-510 cm^{-1} show stronger thermal response those bands in the higher frequency region: the bands at 350 cm^{-1} and 420 cm^{-1} shift significantly in frequencies and become very broad above 500 K and 508 cm^{-1} appear to split into two individual. The broadening of Li-related bands is probably due to the thermally induced Li disorder. No evidence for structural phase transitions was found based on the observed temperature evolution of infrared spectra.

o.m13.p6 **Phase transitions and structures of the Ag_8TiS_6 ionic conductor.** F. Duc, M. Dusek, P. Pattison, M. Onoda*, G. Chapuis, *Institut de Cristallographie, Université de Lausanne, BSP Dorigny, 1015 Lausanne, Switzerland*, **National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan.*
Keywords: superionic conductor, phase transition, anharmonic refinement.

Discovered several years ago[1], the Ag_8MX_6 compounds (M = Si, Ge, Sn or Ti and X = S, Se, or Te) are still investigated owing to their manifold structural and physical properties. They belong to the more general argyrodite family, which is characterized by the presence of tetrahedrally close-packed structures[1]. More particularly, the Cu- and Ag-containing materials are of great interest due to their high ionic conductivity at high temperature[1,4]. Moreover, vacant sites on the cationic network give rise to order-disorder phenomena and phase transitions at lower temperatures. These transitions are attributed to the ordering of the Ag^+ cations within the MX_6 matrix.

Despite their interesting properties, few Ag_8MX_6 phases have been fully structurally characterized. One reason for this lack of structural information is probably related to the lack of efficient description of the Ag electron density in the high-temperature ionic conductor γ forms. To this purpose, a non harmonic model based upon a development of the atomic displacement factor seems the most appropriate approach[2-3].

To get more information on the new Ag_8TiS_6[4] argyrodite compound, we have undertaken the study of its structural phase transitions by means of differential scanning calorimetry, single crystal X-ray and synchrotron diffraction methods.

Both calorimetric and synchrotron x-ray diffraction measurements revealed two reversible phase transitions at low temperature, one occurring at T_{c1} ~ 286 K and the other at T_{c2} ~ 205 K.

The structure of the high-temperature ionic conductor γ form (*F-43m*, *a* = 10.658(1) Å, Z = 4), which is stable at room temperature, has been refined including anisotropic and anharmonic atomic displacement parameters for silver atoms. These refinements lead to a reliability factor of R = 0.0586 for 190 independent reflections and 38 variables.

The first evaluation of the data collected below the 1st and 2nd phase transitions seems to indicate that the phase transitions induce twinning phenomena. The structure resolution of the low temperature phases is still in progress.

[1] Kuhs W.F., Nitsche R. and Scheunemann K. "The Argyrodites-A new family of tetrahedrally close-packed structures", Mater. Res. Bull., (1979), 14 : 241-248.

[2] Boucher F., Evain M. and Brec R. "Single-Crystal Structure Determination of γ-Ag_8SiTe_6 and Powder X-ray Study of Low-Temperature α and β Phases", J. Solid State Chem., (1992), 100 : 341-355.

[3] Boucher F., Evain M. and Brec R. "Distribution and Ionic Diffusion Path of Silver in γ-Ag_8GeTe_6 : A Temperature Dependent Anharmonic Single Crystal Structure Study", J. Solid State Chem., (1993), 107 : 332-346.

[4] Wada H., Ishii M., Onoda M., Tansho M., Sato A. "Preparation, crystal structure and silver ionic conductivity of the new compound Ag_8TiS_6", Solid State Ionics, (1996), 86-88 :159-163.