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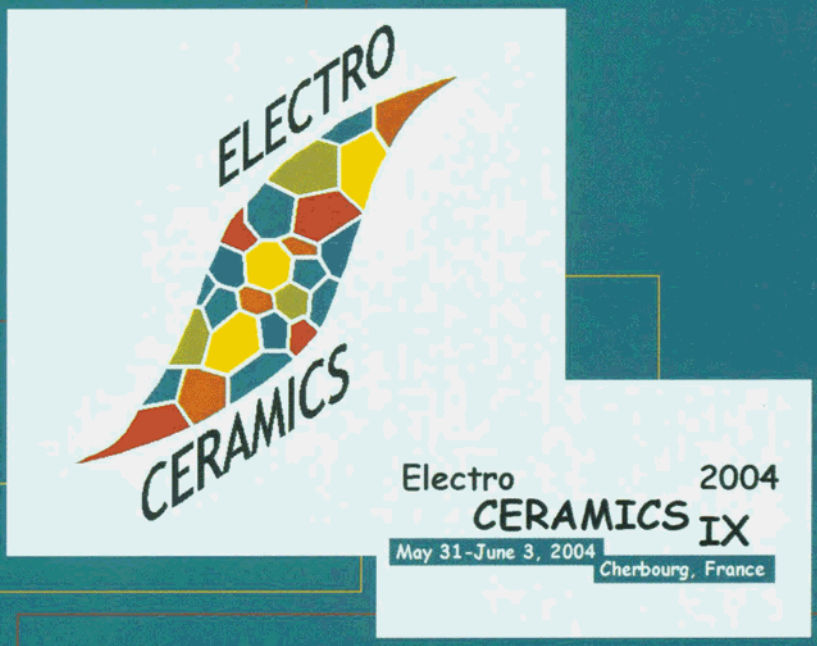

Programme & Abstracts

Organised by :

Raman study of $La_{0.5}Li_{0.5-x}Na_xTiO_3$ ($0 \leq x \leq 0.5$) compounds

M. A. Laguna[1], M. L. Sanjuán[1], O. V'yunov[2], A. Belous[2].

[1]Instituto de Ciencia de Materiales de Aragón (Universidad de Zaragoza-CSIC), Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain.

[2]Solid State Chemistry, Inst. Inorg. Chem., Ukrainian Academy of Sciences, 252680, Ukraine.

$La_{(2-x)/3}Li_xTiO_3$ (LLTO) compounds are excellent ionic conductors. To explain its high conductivity it has been proposed that Li ions are not located at A sites of the perovskite structure, but at square windows between A sites. So, the number of vacant sites is much higher than that expected from the formula. In support of this model, no ionic conductivity is found in $La_{0.5}Na_{0.5}TiO_3$, where Na ions are located at A sites. Along the series $La_{0.5}Li_{0.5-x}Na_xTiO_3$ (LLNTO) ($0 \leq x \leq 0.5$) the transport properties vary drastically from the lithium-only end, where ionic conductivity is high, to the sodium-only case, where no ionic conductivity is found. A percolation mechanism for Li diffusion has been proposed to explain the sharp decrease of conductivity for $x \geq 0.2$.

In this work Raman spectra of LLNTO compounds have been measured as a function of Na content and temperature. In our previous work on LLTO, a high-frequency band (around 560 cm^{-1}) was found to be sensitive to Li dynamics, its intensity decreasing above 280 K with an activation energy of 0.2 eV. We have now applied the same type of analysis to LLNTO, with the following results:

The intensity of the 560 cm^{-1} band decreases when Na content increases, which supports its attribution to lithium-oxygen vibration. In all cases the band intensity decreases with increasing temperature, denoting lithium mobility, even in compositions beyond the percolation limit where no long-range lithium conductivity occurs. The onset temperature and activation energy for this process are the same as for the LLTO compounds, indicating that the local structure and energies are very similar in both systems. These results suggest that Raman spectrum is showing the effect of short-range lithium dynamics, to a scale of several unit cells, even in compositions with lithium concentration below percolation limit.