EXAFS study of sol-gel prepared $Bi_{12}SiO_{20}$ thin films

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Recent advances in mobile telecommunication and satellite broadcasting have created the need for new frequency channels. Lower frequency bands are heavily occupied and therefore a move to higher frequencies is necessary. This fact stimulates the progress in microwave integrated-circuit technology. We have focused our research to sillenites $Bi_{12}MO_{20}$ (M = Si, Ge, Ti, Pb, Mn, $B^{1/2}P^{1/2}$) for their potentially interesting microwave dielectric properties. They crystallize in I23 space group with body centered cubic cell. The framework of the structure is formed by Bi-O polyhedral, where Bi ions are coordinated with oxygen ions which together with the stereochemically active $6s^2$ lone electron pair of Bi^{3+} forms an octahedral arrangement. The Bi-O polyhedral network connects to the geometrically regular MO_4 tetrahedra formed by four oxygen anions with the M cation occupying the tetrahedral interstice. For M = Si the sillenite $Bi_{12}SiO_{20}$ is stoichiometric with fully occupied oxygen sublattice. It exhibits piezoelectric, electro-optic, photo-refractive and optical activity which, together with its good dielectric properties, a low sintering temperature and chemical compatibility with Ag electrode and other functional ceramics, makes it a promising material in low temperature cofired ceramics technology.

In this work, the structure of intermediates of sol-gel prepared $Bi_{12}SiO_{20}$ thin films is studied by EXAFS. The sols are prepared from $Bi(NO_3)_3.5H_2O$ and $Si(OC_2H_5)_4$ as precursors, 2-ethoxyethanol, acetic acid or ethanol as the solvent, and formamid as the drying additive. Structures resulting from three synthesis routes using different solvents are compared at two stages of heat treatment: as prepared xerogels and pyrolysed at 220 ºC for 2 min.

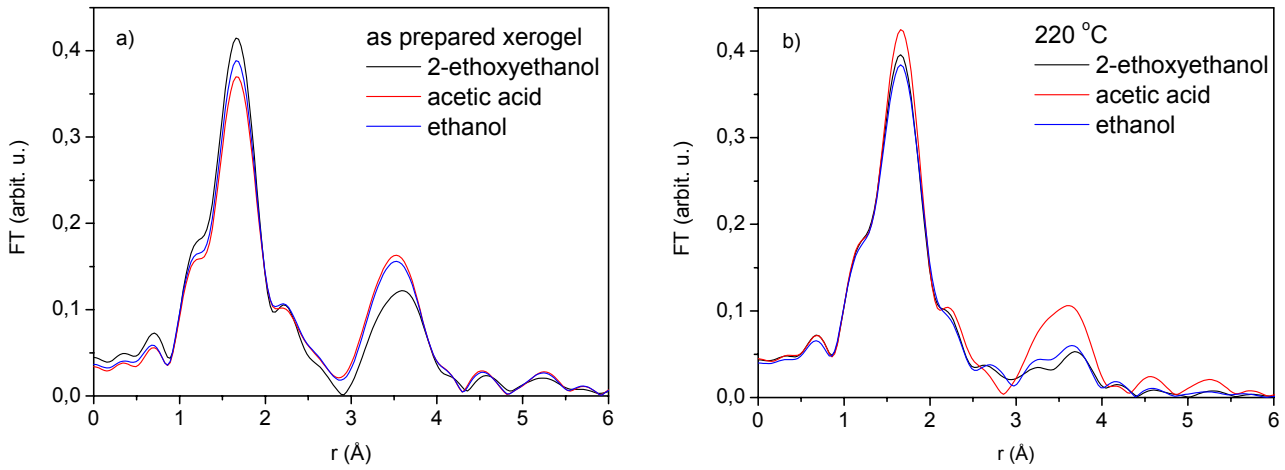

Figure 1: Fourier transforms of k^2 weighing spectra (k = 4 – 13 Å^{-1}), Hanning window, dk = 1 Å^{-1}.
a) as prepared xerogels, b) pyrolysed at 220 ºC.

Standard Bi L_3 edge (13419 eV) EXAFS spectra are recorded at beamline C of Hasylab equipped with two-crystal Si 111 monochromator with energy resolution of 1.5 eV at 13 keV. Feedback control is used for slight detuning of the monochromator crystals to suppress higher beam

harmonics. Ionization cells are filled with 360 mbar Ar, 1000 mbar Kr, and 1000 mbar Kr. Absorption of a Bi foil between the second and the third ionization chamber is measured simultaneously for energy calibration.

For the purpose, thin films with thickness of ~700 nm are prepared on aluminium foil to reduce absorption in the supporting material. A stack of 12 films yields an absorption jump of ~0.6 with good signal/noise ratio. The spectra are analysed with IFEFFIT program package [1,2].

Two peaks are resolved in Fourier transforms (Fig. 1) of the measured data. They can be identified with two shells of neighbours, oxygen and Bi atoms. Among model EXAFS signals of numerous possible Bi-oxide structures, no exact match to the measured spectra has been found. An *ad hoc* model comprising only two scattering paths describes the two peaks rather well. It gives 2,16 Å as an average Bi-O distance and 3,66 Å as Bi-Bi distance for all samples. Small variations in the height of the first (oxygen) peak between the spectra can be attributed to variation in the Debye-Waller factor. The second (bismuth) peak is very weak in comparison to the data of fully crystallized samples and its height is lower in pyrolysed films.

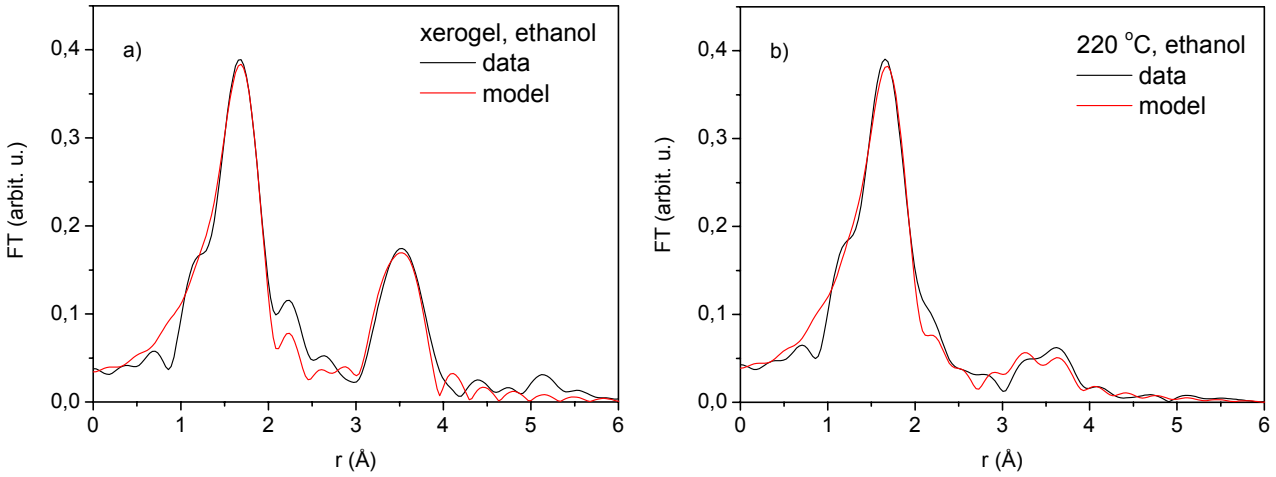

Figure 2: Example of model to data fit, with ethanol as solvent a) as prepared xerogel, b) pyrolysed at 220 ºC. k = 4-13 Å-1, r = 1-4 Å, Hanning window, k weighing values 1, 2 and 3 used simultaneously in fit.

From the basic EXAFS model, it can be concluded that the first shell of oxygen neighbours is built already in as prepared xerogels and it does not change appreciably with heat treatment. Beyond the first neighbourhood the films exhibit low degree of order which even decreases with heat treatment. The effect can be explained as a decomposition of the starting structure prior to the growth of the high temperature $Bi_{12}SiO_{20}$ phase. The degree of the decomposition depends on the type of the precursor: it is stronger in samples with 2-ethoxyethanol or ethanol as solvent.

Acknowledgment

This work was supported by the Slovenian Research Agency research programme P1-0112, by DESY, and the European Community under the FP6 Programme "Structuring the European Research Area" contract RII3-CT-2004-506008 (IA-SFS). Access to synchrotron radiation facilities of HASYLAB (project II-04-065) is acknowledged. We would like to thank Edmund Welter of HASYLAB for expert advice on beamline operation.

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