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Synthesis and structure of nanomaterials in the system K_2O-Nb_2O_5-SiO_2

Georgi Chernev[1], Bisserka Samuneva[1], Isabel M. Miranda Salvado[2], Paula Vilarinho[2], Aiying Wu[2]

[1]*University of Chemical Technology and Metallurgy 1756 Sofia, Bulgaria*
[2]*Department of Ceramic and Glass Technology, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*

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Abstract

The aim of the present work is synthesis of ferroelectric nanomaterials, in the K_2O-Nb_2O_5-SiO_2 system via sol-gel method and studying the processes of formation and structure of the synthesized ferroelectric nanomaterials. The structure of synthesized materials has been studied by means of the following methods: EDS, XRD, FT-IR, SEM and AFM. The results obtained showed that the structure of the investigated compositions does not depend on the niobium content and all the samples keep their amorphous nature at room temperature. The surface structure shows random distribution of different kinds of aggregates with dimensions about 200–500 nm. The presence of a hybrid nanostructure with well-defined nanounits having special geometry is clearly observed.

Keywords: *sol-gel synthesis, ferroelectric nanomaterials, K_2O-Nb_2O_5-SiO_2 system*

I. Introduction

The sol–gel preparation method [1,2] is being increasingly used to produce novel materials with interesting physical and chemical properties. Some of these materials are of great technological interest because they combine novel chemical properties with controllable porosity and large surface areas. Silica-based materials are some of the most important sol-gel formed materials, especially with the addition of secondary oxides (e.g. TiO_2, ZrO_2) which introduce different surface acid sites, making them ideal catalysts.

Niobium compounds and materials are now interesting and important catalysts for various reactions. Although there are few differences in electronegativity and ionic radius between Nb and its neighbours (V, Zr, Mo) in the periodic table of elements, it is intriguing that the catalytic behaviours of niobium compounds are quite different from those of the surrounding elements' compounds. Thus, the research and development on the catalytic application of niobium compounds have been very active for the last 20 years [3]. The development of studies within synthesis, characterization and application of Nb-containing catalysts was possible thanks to the great progress of the spectroscopic as well as the other physical techniques which allow the analysis of Nb state in the solids [4].

Properties of MO_x-SiO_2 binary materials are highly dependent on the structure and dispersion of the two oxides. Recently the relatively little studied Nb_2O_5-SiO_2 binary system has been generating significant interest for a range of chemical processes including potential for heterogeneous catalysis [5–7]. The use of this system includes methanol oxidation, ethanol dehydrogenation, partial methane oxidation, selective adsorption and use as a biosensor after immobilising mediator species. Despite the chemical interest in this system there is still relatively little known about the structural basis of these properties. For the Nb_2O_5-SiO_2 system it is still unclear as to whether catalytic properties are related to surface niobium atoms that are actually in the silica framework, or a separate surface dispersed phase, or a mixture of both of these effects.

Several reports on hydrothermal synthesis of $KNbO_3$ have been documented recently [8–12]. One issue addressed is the large variations in the amount of reaction products, whose structure phase and morphology are great-

* Corresponding author: tel: +359 2 8163 373
fax: +359 2 8685 488, e-mail: *georgi_chernev@yahoo.com*

ly different, using the same precursor reagents and equipment. The studies of the reactions between sodium and/or potassium carbonates and niobium oxide by diffusion couples between 500°C and 700°C have been published [13].

In the last years, some attempts have been made to produce transparent glass ceramics exhibiting second harmonic generation (SHG). More recently transparent glass ceramics with remarkable SHG efficiency were synthesized in the K_2O-Nb_2O_5-SiO_2 (KNS) system [14,15].

The aim of the present work is synthesis of ferroelectric nanomaterials, with composition K_2O-Nb_2O_5-SiO_2, via sol-gel method and studying the processes of formation and structure of the synthesized ferroelectric nanomaterials.

II. Experimental

The ferroelectric K_2O-Nb_2O_5-SiO_2 materials with different composition (Nb_2O_5 : SiO_2 ratio of 1:10 and 1:20) have been obtained using sol-gel method. The precursors used are as follows: tetraethylortosilicate, niobium (V) ethoxide and potassium ethoxide. A poly-step procedure has been applied at strictly controlled conditions in order to obtain the desired nanostructred materials. A small amount of 0.1 N HCl is added, to increase hydrolysis rate. No phase separation is observed before and after the gelation point. The main steps of the synthesis have been described and published previously [16].

The structure of the investigated materials has been studied using the following methods: X-ray diffraction (XRD) (Philips, PW1730/10), Furrier transforming-infrared (FT-IR) spectroscopy (MATSON 7000), Raman spectroscopy (Bruker RFS-100/S), scanning electron microscope (SEM) (Philips - 515), atomic force microscopy (AFM) (NanoScope Tapping ModeTM) and roughness analysis (RA).

III. Results and discussionxperimenta

XRD patterns of the prepared samples (Fig. 1) exhibit a diffuse maximum at about 2θ = 24°, which is typical for the amorphous silica. It should be emphasized that regardless of the niobium content all samples keep their amorphous nature at room temperature.

FTIR and Raman spectra of dried gel are shown in Figs. 2 and 3. As expected, the analysis of these data gives detailed information about the siloxane backbone structure and the distribution of hydroxyl groups, as well. The characteristic intensive band at ~1064 cm^{-1} is related to the presence of Si-O-Si. The shoulder at 950 cm^{-1} can be assigned to the Si-O(-Nb) bonds. For the T-Nb_2O_5 phase three different stretching modes should be expected: the collinear Nb-O-Nb (850 cm^{-1}), the Nb_3O (470 cm^{-1}) and the bridging Nb-O-Nb (650 cm^{-1}). The band at 1430 cm^{-1} is assigned to C-O-H vibrations. The characteristic bands at around 3450 cm^{-1} and at 1620 cm^{-1} assigned to H-O-H vibration can also be detected. The band at 807 cm^{-1} is related to symmetric vibration of two sili-

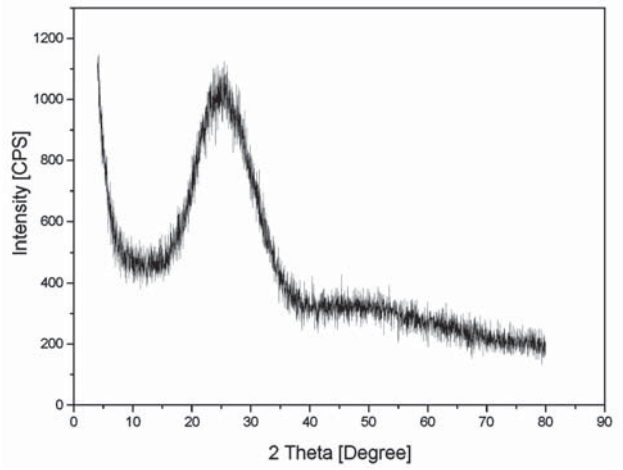

Figure 1. XRD pattern of the dried gel K_2O-Nb_2O_5-SiO_2 system (Nb_2O_5:SiO_2 ratio 1:10)

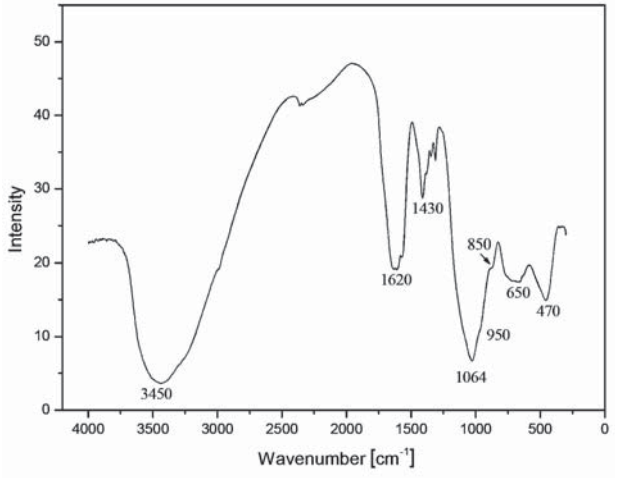

Figure 2. FT-IR spectra of the dried gel K_2O-Nb_2O_5-SiO_2 system (Nb_2O_5:SiO_2 ratio 1:10)

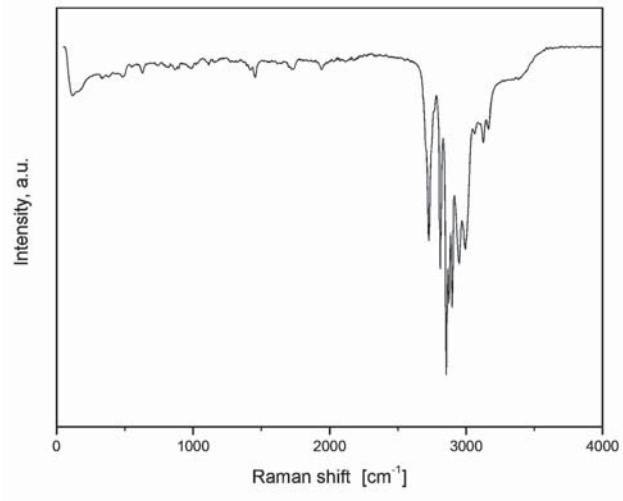

Figure 3. Raman spectra of the dried gel K_2O-Nb_2O_5-SiO_2 system (Nb_2O_5:SiO_2 ratio 1:10)

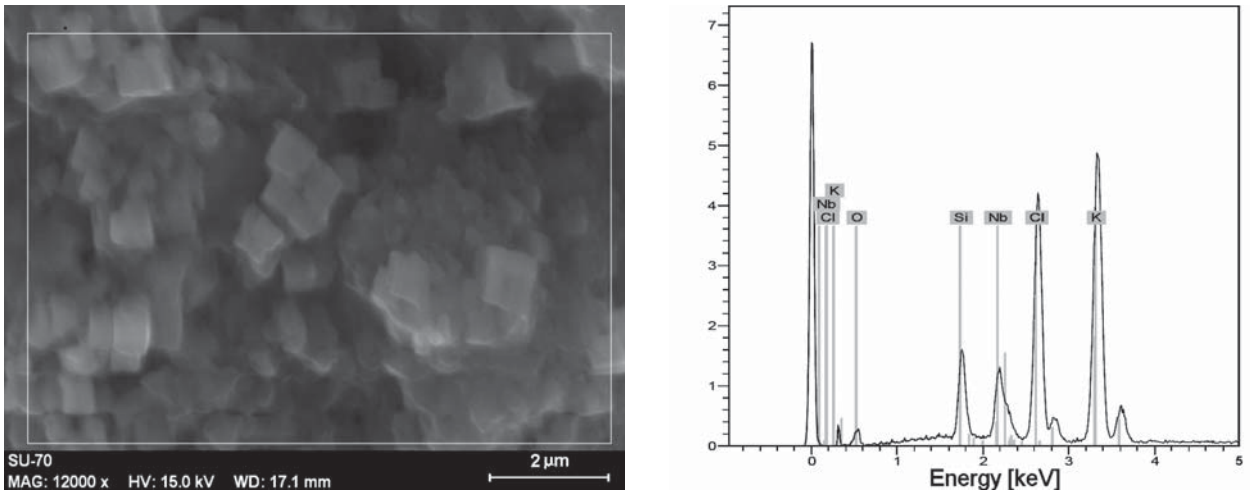

Figure 4. SEM image (a) and EDS analysis (b) of the ferroelectirc nanomaterial in the system K_2O-Nb_2O_5-SiO_2 (Nb_2O_5:SiO_2 ratio 1:10)

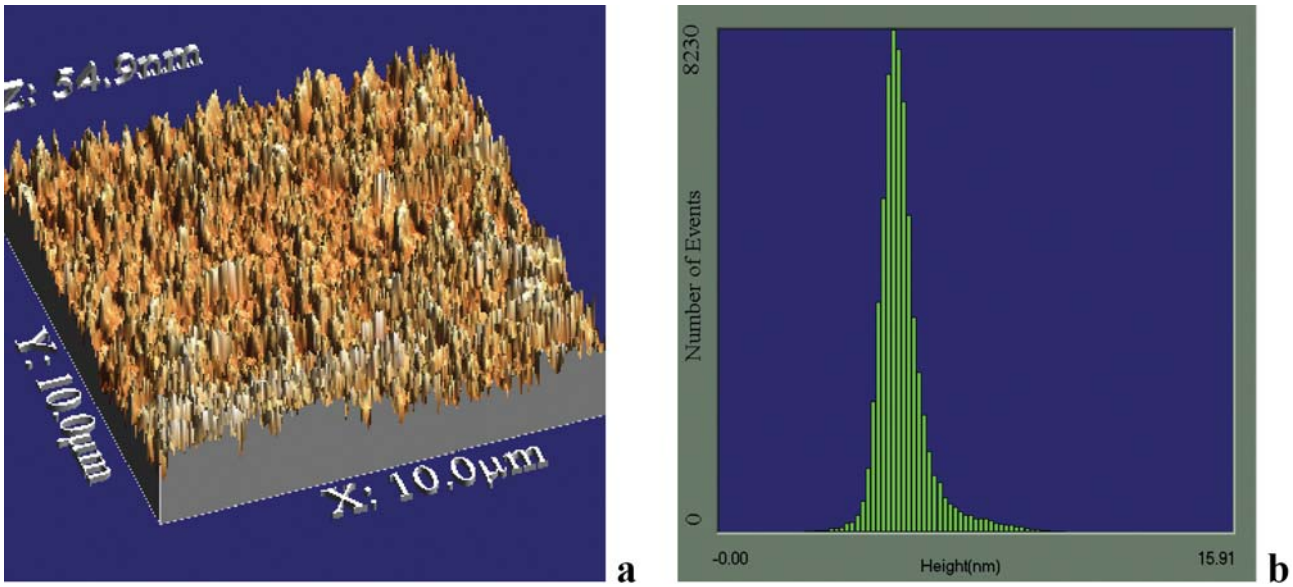

Figure 5. AFM images and RMS roughness of ferroelectirc nanomaterials in the systems K_2O-Nb_2O_5-SiO_2 (Nb_2O_5:SiO_2 ratio 1:10)

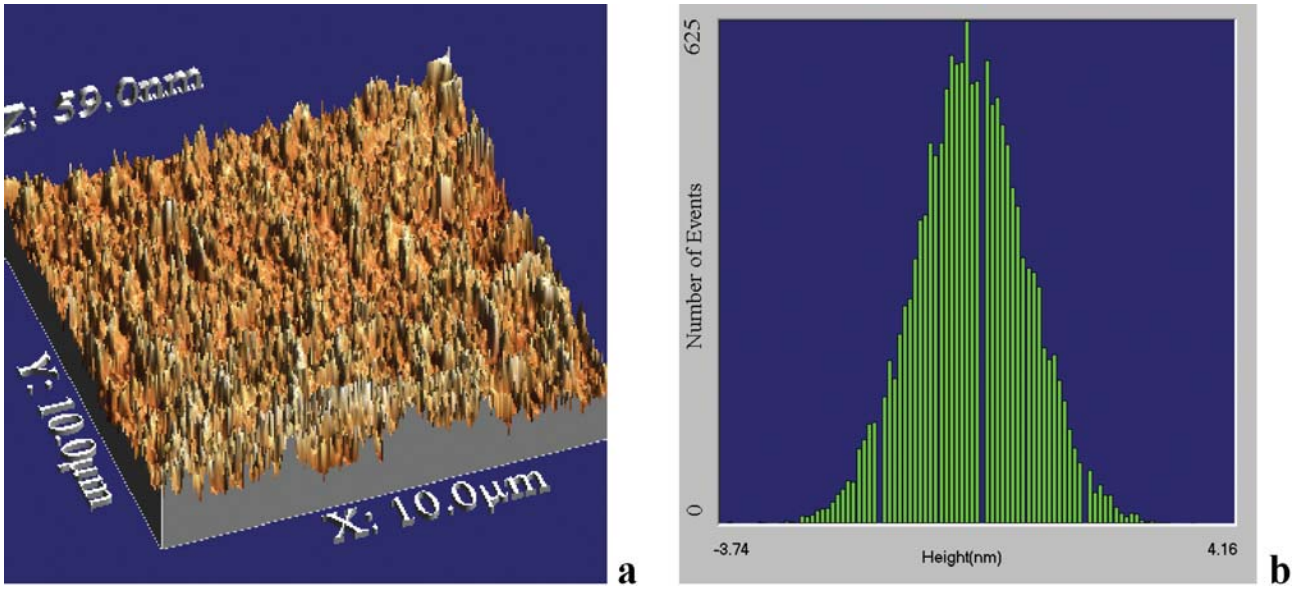

Figure 6. AFM images and RMS roughness of ferroelectirc nanomaterials in the systems K_2O-Nb_2O_5-SiO_2 (Nb_2O_5:SiO_2 ratio 1:20)

con atoms about their bridged oxygen. The bands at 815 cm^{-1} and 870 cm^{-1} can be related to the Nb–O stretching modes of distorted NbO_6 octahedra sharing a corner with SiO_4 tetrahedra. Particularly, they can be related to the Nb-O(-Nb) and Nb-O(-Si), respectively. Actually, the niobium is dispersed within the siloxane network mainly as NbO_4 tetrahedra (band at 770 cm^{-1}).

FTIR and Raman spectra of the niobium containing dried gels exhibit some differences depending on the niobium amount. The highest absorption band gradually shifts toward lower frequencies going from 1082 cm^{-1} to 1064 cm^{-1} suggesting that the portion of Si-O-Si is progressively influenced by the presence of niobium. In addition, as the Nb content increases, NbO_6 octahedra (bands at 815, 870 and 950 cm^{-1}) and cluster (band at 680 cm^{-1}) start to appear, while the tetrahedra disappear.

The surface structure of the ferroelectrics in the K_2O-Nb_2O_5-SiO_2 system observed by SEM is shown in Fig. 4a. The random distribution of different kinds of aggregates with dimensions about 200–500 nm have been observed. In all studied samples presence of Si, Nb and K cations are confirmed by EDS analysis (Fig. 4b).

The presence of a hybrid nanostructure with well-defined nanounits having special geometry and their aggregates, formed by self-organizing processes, is clearly observed by AFM studies (Figs. 5 and 6). The size of nanoparticles calculated from AFM images are about 12–21 nm (Figs. 5a and 6a). In the same figures the height distribution profiles of surfaces roughness were shown. The histograms of the surface height distribution profiles (Figs. 5b and 6b), obtained from AFM images, showed that all synthesized samples had surfaces with irregularities of quite small height.

IV. Conclusions

The XRD pattern of the dried gel shows that regardless of the niobium content all samples keep their amorphous nature at room temperature. FTIR and Raman spectra give detailed information about the siloxane backbone structure and the distribution of hydroxyl groups, as well. The presence of a hybrid nanostructure with well-defined nanounits having special geometry and their aggregates, formed by self-organizing processes, is clearly observed by AFM studies. The surface morphology and structure of nanobuilding blocks in each synthesized ferroelectric nanomaterials is different and depends on its chemical composition.

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