Microsc. Microanal. 18 (Suppl 5), 2012

doi:10.1017/S1431927612013104

Microscopy and the Solid Solubility Limit in $K_{1-x}Mn_xTaO_3$ Ceramics

Alexander Tkach*, Paula M. Vilarinho** and Abílio Almeida*

* IFIMUP and IN, Department of Physics and Astronomy, Faculty of Science of University of Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
** CICECO, Department of Ceramics and Glass Engineering, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

Multiferroic materials, combining at least two of three properties: ferromagnetism, ferroelectricity and ferroelasticity in the same phase, have been widely studied nowadays and have tremendous potential for multifunctional applications, although magnetoelectric multiferroics are difficult to obtain. Recently, dielectric and magnetic anomalies were found to be coupled in the incipient ferroelectrics $SrTiO_3$ and $KTaO_3$ doped with Mn on A-site of ABO_3 perovskite lattice [1].

Although the formation of the secondary phase was found to have insignificant influence on the dielectric response, the magnetic response of manganese oxide like Mn_3O_4, which exhibits a transition into a ferrimagnetic state at 42 K, can be very strong on the diamagnetic background of $KTaO_3$, making the question of solid solubility limit very important [2]. However, to the authors' best knowledge, no research on the solid solubility limit of Mn, microstructure and dielectric behaviour has been undertaken for $K_{1-x}Mn_xTaO_3$ ceramics. In this work the crystallographic structure of $K_{1-x}Mn_xTaO_3$ ceramics prepared by conventional mixed oxide method is analyzed by x-ray diffraction (XRD), while scanning electron microscopy (SEM) together with energy dispersive x-ray spectroscopy (EDS) is employed for microstructural and local chemical characterization.

Figure 1 presents the XRD patterns for the $K_{1-x}Mn_xTaO_3$ ceramics with $x \leq 0.03$, which reveal a single cubic perovskite phase. However, the lattice parameter calculated from XRD, after increasing from 3.9893(1) Å for $x = 0$ to 3.9901(1) Å for x = 0.015, remains independent on the Mn content with the value of 3.9901(1) Å for $x = 0.03$, as seen from inset of Figure 1. This implies a limitation of the incorporation of Mn into the perovskite lattice of $KTaO_3$ above $x = 0.015$.

Dense microstructures with an average grain size decreasing continuously with increasing Mn content from 6.5 μm for undoped $KTaO_3$ via 1.8 μm for $K_{0.985}Mn_{0.015}TaO_3$ to 1.3 μm for $K_{0.97}Mn_{0.03}TaO_3$, were observed by SEM, as shown in Figure 2. EDS within SEM shows homogeneous distribution of the chemical elements for $KTaO_3$ and $K_{0.985}Mn_{0.015}TaO_3$ ceramics (Figures 2a and 2b). However, for $K_{0.97}Mn_{0.03}TaO_3$ ceramics (Figure 2c), areas rich in Mn and poor in K could be detected, implying the formation of a secondary phase. The energy dispersive spectra of $K_{0.97}Mn_{0.03}TaO_3$ ceramics reveal a correspondence between the Mn amount and ceramics grain shape. High amounts of Mn are found in the elongated grains (see Figure 2d), while the small amounts of Mn are detected in the rounded grains, confirming the incorporation of Mn into the perovskite lattice of $KTaO_3$ as well (see Figure 2e). Thus, despite XRD analysis did not reveal any secondary phase for the studied samples, the solid solubility of Mn in $K_{1-x}Mn_xTaO_3$ looks to be limited to $0.015 < x < 0.03$.

References

1. W. Kleemann, S. Bedanta, P. Borisov, V.V. Shvartsman, S. Miga, J. Dec, A. Tkach, and P.M. Vilarinho, Eur. Phys. J. B 71: 407, 2009
2. V.V. Shvartsman, S. Bedanta, P. Borisov, W. Kleemann, A. Tkach, and P.M. Vilarinho, J. Appl. Phys. 107: 103926, 2001

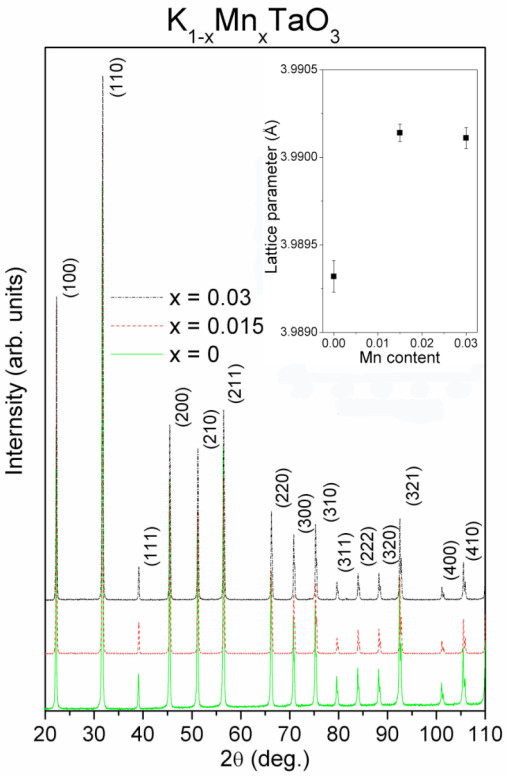

Figure 1. X-ray diffraction patterns of sintered KTaO3, K0.985Mn0.015TaO3, and K0.97Mn0.03TaO3 ceramics. Inset shows the lattice parameter as a function of Mn content.

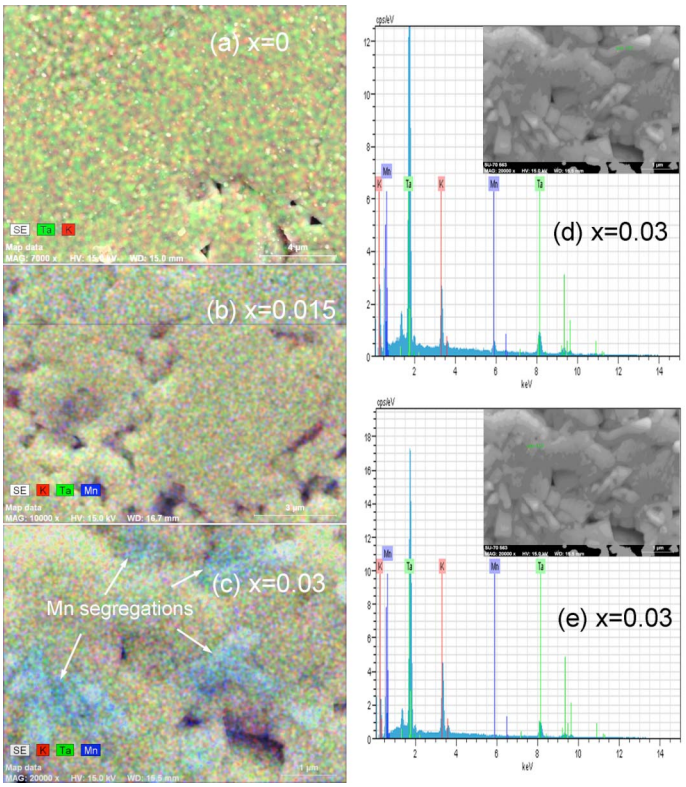

Figure 2. Elemental x-ray maps of K, Ta, and Mn in K1-xMnxTaO3 ceramics with x = 0 (a), 0.015 (b) and 0.03 (c) and local energy dispersive spectra of elongated (d) and rounded (e) grains of K0.97Mn0.03TaO3. Insets show the acquisition points.

https://doi.org/10.1017/S1431927612013104 Published online by Cambridge University Press