Available online at www.sciencedirect.com

SCIENCE DIRECT®

Solid State Communications 130 (2004) 777–781

solid
state
communications

www.elsevier.com/locate/ssc

Study of new rare earth family $Pb_{1.6}K_{1.2}R_{0.2}Nb_5O_{15}$ (R = La, Nd, Sm, Eu and Gd) of tetragonal tungsten bronze-type ferroelectrics

M. Oualla[a], M. Elaatmani[a], M. Daoud[a], D. Mezzane[b], I. Luk'yanchuk[c,*], A. Zegzouti[a]

[a]*Laboratory of Mineral Solid State Chemistry, Faculty of Sciences, University Cadi Ayyad, Bd. My Abdallah, BP 2390 Marrakech, Morocco*
[b]*Faculty of Sciences and Technics, University Cadi Ayyad, BP 549, Marrakech, Morocco*
[c]*University of Picardy Jules Verne, Laboratory of Condensed Matter Physics, 33 rue Saint Leu, 80039 Amiens Cedex 01, France*

Received 15 March 2004; accepted 14 April 2004 by P. Wachter

Abstract

A new ferroelectric rare earth family $Pb_{1.6}K_{1.2}R_{0.2}Nb_5O_{15}$ with R = La, Nd, Sm, Eu and Gd (PKRN) of tetragonal tungsten bronze type ferroelectrics was synthesized. The ferroelectric transition with nonuniform distribution of critical temperature over a ceramic sample was found from dielectric measurements. According to X-ray diffraction measurements, the ferroelectric phase has an orthorhombic symmetry. The transition temperature was shown to decrease weakly with increasing radius of the rare earth ion R.

PACS: 77.84. − s; 77.80. − e; 61.43.Gt

Keywords: A. Ferroelectrics; A. Oxides; B. Solid-state reaction; C. X-ray diffraction

1. Introduction

Compounds of 'Tetragonal Tungsten Bronze' (TTB) structure with general formula unit $A_xB_yC_zNb_5O_{15}$ form one of the greatest families of ferroelectric oxides. Their crystal structure may be described as a network of slightly distorted oxygen octahedra NbO_6 linked by the corner oxygen atoms [1]. The metallic ions A, B and C fill the pentagonal, quadratic and triangular cavities (with coordination numbers 15, 12 and 9) that exist in between the MO_6 octahedra. Juxtaposed in the *z* direction, these cavities form tunnels with chains of metallic ions inside. A-type cavities accept generally monovalent anions of quite large ionic radius like Rb or Tl, the divalent ions may be inserted in the B-type cavities whereas the C cavities accept ions with small radius like Li. The great variety of TTB-type compounds is provided by the different choices of the inserted anions.

The lead-containing oxide $PbNb_2O_6$ was the first compound of TTB family in which the ferroelectric phase transition at $T_c = 575$ °C was found [2]. Since that, different TTB-type ferroelectrics were discovered ([3] and references therein). The principal motivation of study of these compounds is their important electro-optical, pyroelectric and piezoelectric properties [4–7].

Although the prototype paraelectric phase of the whole family of $A_xB_yC_zNb_5O_{15}$ compounds has a tetragonal symmetry (4/*mmm*), the ferroelectric phase can be either of the tetragonal or of the orthorhombic symmetry. The tetragonal symmetry of ferroelectric phase when polarization *P* is directed along the 4th-fold symmetry axis *z* occurs mostly in the lead-free TTB-type compounds such as $K_3Li_2Nb_5O_{15}$ ($T_c = 430$ °C) [8]. The lead-containing compounds such as $Pb_2KNb_5O_{15}$ ($T_c = 450$ °C) [9–11] present generally an orthorhombic distortion in the ferroelectric phase provided by the strong polarizability of the Pb^{2+} ion that involves a structural anisotropy and distortion of oxygen octahedra [12]. Polarization in this case is perpendicular to the *z*-direction. Note, however, the special case of compound $PbK_2LiNb_5O_{15}$ ($T_c = 366$ °C) [13], in

---

[*] Corresponding author. Tel.: +33-3-22-82-78-83; fax: +33-3-22-82-78-9.
E-mail address: lukyanc@ferrorix.net (I. Luk'yanchuk).

0038-1098/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2004.04.017

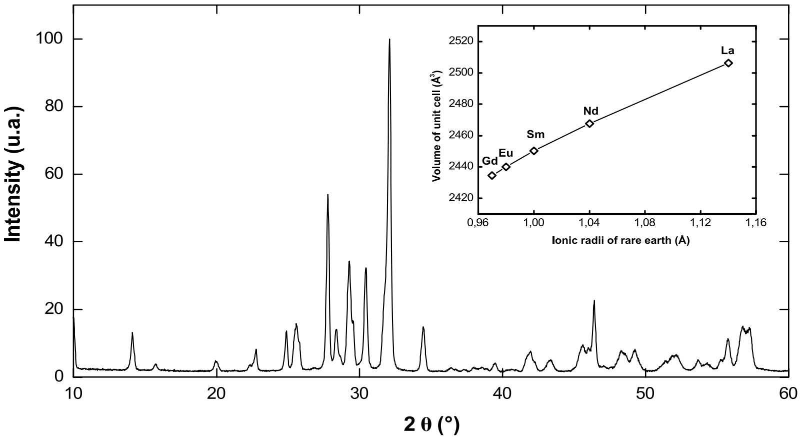

Fig. 1. X-ray diffractogram of the compound $Pb_{1.6}K_{1.2}Eu_{0.2}Nb_5O_{15}$. Inset shows the variation of the unit cell volume versus radius of rare earth ion R for the family PKRN.

which the ferroelectric phase is orthorhombic whereas the polarization P is directed along z.

Quite a few studies of TTB-type ferroelectrics were devoted to the compounds in which one of the metallic ions is the trivalent rare-earth anion R^{3+}. To our best knowledge, only the lead-free materials $K_2RNb_5O_{15}$ ($R = La$, Pr, Nd, Gd, Sm, Tb, Dy, Ho and Y) were synthesized and characterized [14,15]. The tetragonal ferroelectric phase that is characteristic for the lead-free TTB ferroelectrics was observed in these compounds.

In this paper, we explore the new family of rare-earth ferroelectric compounds of TTB type: $Pb_{1.6}R_{0.2}K_{1.2}Nb_5O_{15}$ with $R = La$, Nd, Sm, Eu or Gd that is called further as PKRN. This family contains an important amount of lead and therefore, similar to $Pb_2KNb_5O_{15}$, the occurrence of ferroelectric phase is expected. In the present study, we confirm this symmetry by X-ray diffraction measurements and investigate the ferroelectric transition by dielectric measurements. The role of the size of the rare earth ions in the crystallochimic and dielectric properties of the PKRN ceramic are also examined.

2. Sample preparation

The compounds of PKRN were prepared by solid reaction starting from oxides PbO, Ln_2O_3, Nb_2O_5 and carbonate K_2CO_3. The finely crushed mixtures undergone pre-heating at 650 °C during 6 h, and then they were carried at 1100 °C during 20 h. These two heat treatments are intersected with crushing to obtain the well homogenized mixtures.

The powders were initially compacted with a pressure of 2 ton/m^2 to obtain samples in the form of cylindrical pastilles of approximately 13 mm in diameter and of 1 mm in thickness. Then pastilles underwent a 2 h sintering at 1150 °C.

The obtained ceramics have a compactness of about 90%. The characteristic values of the diameter shrinkages $\Delta\Phi/\Phi$ were systematically determined as $(\Phi_{\text{initial}} - \Phi_{\text{final}})/\Phi_{\text{final}}$ and were in the range between 8 and 10% depending on the rare earth ions.

3. X-ray analysis

The X-ray diffractograms were obtained at room temperature using a Phillips diffractometer PW3040/00 X′ PERT MPD. The refinement of the lattice parameters was carried out using program LAPOD based on the least square method.

Presented in Fig. 1 is the room temperature X-ray diffractogram of compound $Pb_{1.6}K_{1.2}Eu_{0.2}Nb_5O_{15}$, which shows that this ceramic is pure and crystallizes with the structure of TTB. The same quality was also achieved for all the other studied compounds.

All the compositions of PKRN crystallize at room temperature with an orthorhombic symmetry showing a small distortion of the quadratic cell ~2% that is provided by the discussed above ferroelectric polarization of Pb^{2+} in the x or y direction. The volume of the elementary cell of PKRN increases with increasing of the size of rare earth ion R as shown in inset of Fig. 1.

4. Dielectric measurements

Measurements of dielectric constant as a function of the temperature and the frequency were carried out using the LCR-meter HP 4284A having a sensitivity of 0.05% that allows to measure the capacity and the loss factor of the sample in the frequency range from 10^2 to 10^6 Hz. This device permits to vary the ac potential from 5 mV to 2 V and current from 5 to 20 mA. The LCR-meter includes also a

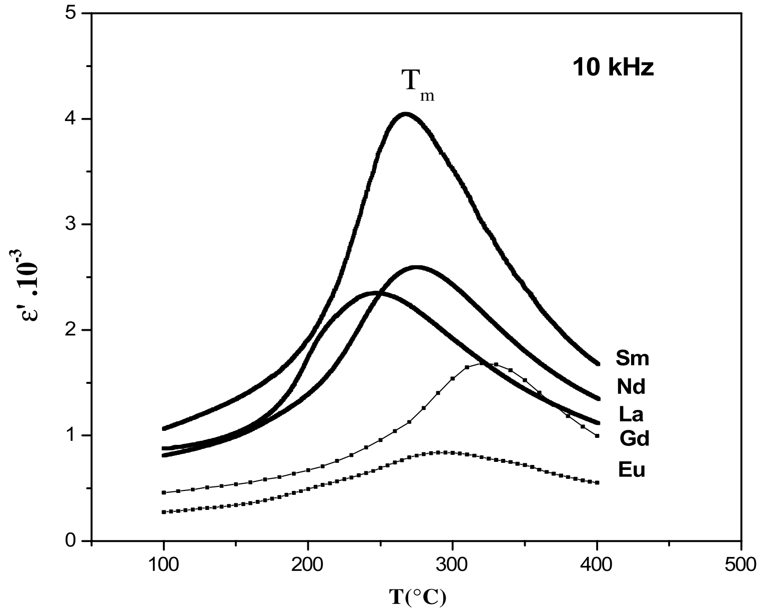

Fig. 2. Temperature dependence of the real part of dielectric constants ε' for compounds of PKRN family (R = Gd,Eu,Sm,Nd and La) at 10 kHz.

multimeter HP-34401A for measuring of the temperature using a chromel–alumel thermocouple with an accuracy of 0.2.

Ferroelectric transition is clearly seen for all the studied compounds of the PKRN family as peak in the temperature dependence of the presented in Fig. 2 real part of dielectric constants $\varepsilon'(T)$. The evolution of the characteristic transition temperature T_m (defined from max $\varepsilon'(T)$) with increasing of the radius of the rare earth ion R is shown in Fig. 3 both for the family PKRN and for the previously studied rare earth lead-free family $K_2RNb_5O_{15}$ [14]. The gradual decrease in the value of T_m is explained by the decrease in the rare earth ion polarizability due to restriction of its mobility in the cavity; the transition in the family $Pb_{1.6}K_{1.2}R_{0.2}Nb_5O_{15}$ being less sensitive to the choice of the rare earth ion R then in the $K_2RNb_5O_{15}$ family. Meanwhile, transition temperature strongly increases with increasing of lead concentration, for example, from − 91 °C in $K_2LaNb_5O_{15}$ to 243 °C in $Pb_{1.6}K_{1.2}La_{0.2}Nb_5O_{15}$ and then to 450 °C in $Pb_2KNb_5O_{15}$.

Fig. 4 shows the temperature hysteresis of the dielectric constant observed on the left ferroelectric side of the peak in $Pb_{1.6}K_{1.2}Nd_{0.2}Nb_5O_{15}$ after cooling–heating cycle. The

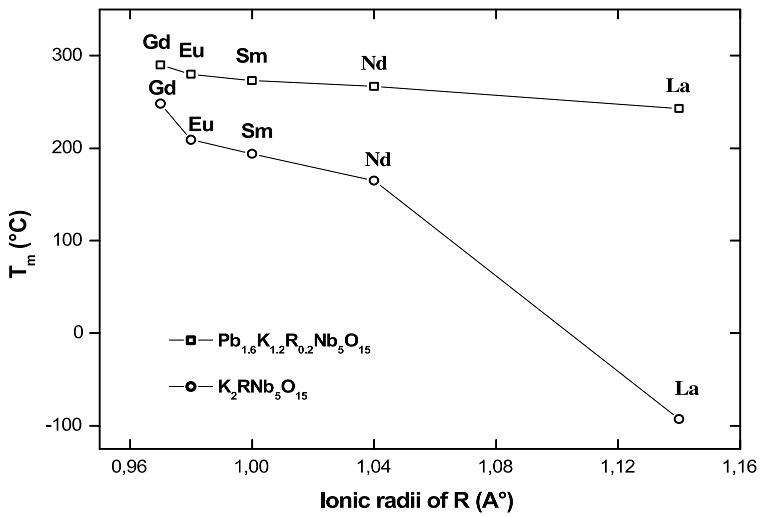

Fig. 3. Variation of the transition temperature T_m versus radius of rare earth ion R (R = Gd, Eu, Sm, Nd and La) for the lead containing PKRN family (our measurements) and for lead-free $K_2RNb_5O_{15}$ family (data from Ref. [14]).

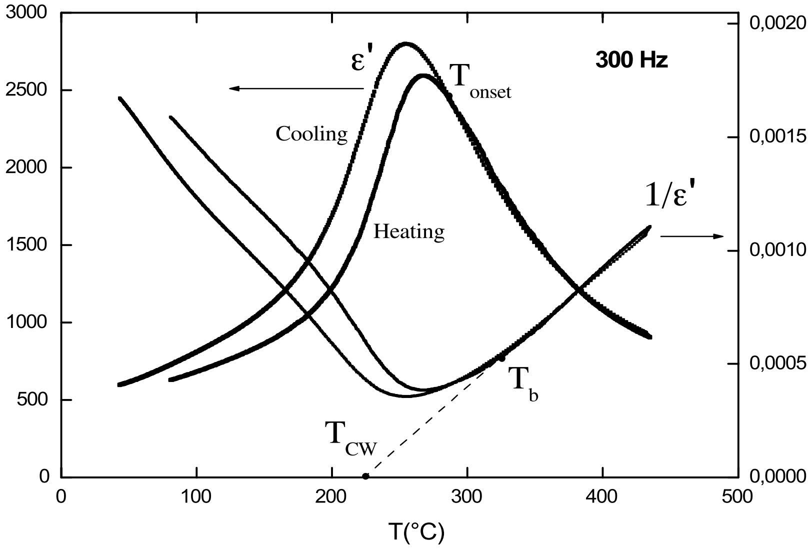

Fig. 4. Temperature dependence of the dielectric constant ε' and of the inverse dielectric constant $1/\varepsilon'$ (Curie behavior) for $Pb_{1.6}K_{1.2}Nd_{0.2}Nb_5O_{15}$ at 300 Hz on cooling and on heating

same type of hysteresis of the width 15–20 °C was observed for all the PKRN family. We attribute this hysteresis to the first-order phase transition. Absence of discontinuity in $\varepsilon'(T)$ and spreading of the hysteresis along all the left shoulder of the peak could signify the nonuniform distribution of transition temperatures in the ceramics. In this case the ferroelectric phase firstly appears at the temperature of hysteresis onset $T_{onset} = 280$ °C, that is, ~20 °C above the position of max $\varepsilon'(T)$. The more careful study of transition in the single-crystal of $Pb_{1.6}K_{1.2}Nd_{0.2}Nb_5O_{15}$ is required to confirm the nature of hysteresis.

The plot of the inverse susceptibility $1/\varepsilon'(T)$, shown in Fig. 4, demonstrates the linear Curie–Weiss behavior in the paraelectric phase above $T_b = 320$ °C: $\varepsilon'(T) = C/(T - T_{CW})$ with Curie–Weiss constant $C = 1.9 \times 10^5$ K and temperature $T_{CW} = 220$ °C. The large value of C indicates that transition is mostly of displacive type. The deviation of $\varepsilon'(T)$ from Curie–Weiss behavior below T_b could be due to nonuniform distribution of the critical temperatures in the ceramic sample. The small value of T_{CW} with respect to characteristic transition temperature T_m is the characteristic property of the first-order ferroelectric phase transition.

Frequency-dependent measurements demonstrate a dispersion of the dielectric constant with regular decreasing of the peak in $\varepsilon'(T)$ when frequency increases. The position of the peak was found to be independent of the frequency that excludes the relaxor-type behavior.

5. Conclusion

New ferroelectric compounds of TTB structure: $Pb_{1.6}K_{1.2}R_{0.2}Nb_5O_{15}$ with R = La, Nd, Sm, Eu or Gd (PKRN) that contain simultaneously lead and a rare earth ions were synthesized. All the phases are prepared by solid state reaction and are characterized by diffraction of X-rays and dielectric measurements.

Dielectric measurements show the existence of a maximum in the temperature dependence of $\varepsilon'(T)$ for the whole family PKRN that corresponds to the ferroelectric phase transition of the predominantly displacive type. The temperature hysteresis of $\varepsilon'(T)$ indicates that the transition is of first-order, with nonuniform distribution of critical temperatures inside ceramics. The transition temperature is not very sensitive to the choice of the rare earth ion R and decreases weakly with increasing ionic radius of R. According to the X-ray diffraction studies, the ferroelectric phase has an orthorhombic symmetry.

This study anticipates our future investigation of rare earth ferroelectric TTB family: $Pb_{2(1-x)}K_{1+x}R_xNb_5O_{15}$ in which the participation of Pb changes from 0 ($x = 1$, lead-free $K_2RNb_5O_{15}$) to 2 ($x = 0$, $Pb_2KNb_5O_{15}$) that will allow us to study the transition between tetragonal and orthorhombic ferroelectric phases, like it was earlier done for $Pb_{2(1-x)}K_{1+x}Gd_xNb_5O_{15}$ compounds [16].

Acknowledgements

This work was supported by NATO collaborative linkage grant PST.CLG.980055.

References

[1] M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Clarendon Press, Oxford, 1977.

[2] G. Goodman, J. Am. Ceram. Soc. 36 (1953) 368.

[3] Landolt-Börnstein, Ferroelectrics and Related Substances; Oxides, Numerical Data and Functional Relationships in Science and Technology, New Series. Group III, vol. 16a, Springer, Berlin, 1981.

[4] S. Nomura, H. Kojima, Y. Hattori, H. Hotsuka, Jpn. J. Appl. Phys. 13 (1974) 118.

[5] J.B. Thaxter, Appl. Phys. Lett. 15 (1969) 210.

[6] P. Gunter, Phys. Rep. 93 (1982) 201.

[7] E.J. Sharp, W.W. Clark III, M.J. Miller, G.L. Wood, B.D. Monson, G.J. Salamo, R.R. Neurgaonkar, Appl. Opt. 29 (1990) 743.

[8] L.G. Van Uitert, S. Singh, H.J. Levinstein, et al., Appl. Phys. Lett. 11 (1967) 161.

[9] J. Nakano, T. Yamada, J. Appl. Phys. 46 (1975) 2361.

[10] H. Yamauchi, Appl. Phys.Lett. 32 (1978) 599.

[11] J. Ravez, A. Simon, P. Hagenmuller, Ann. Chim. I (1976) 251.

[12] Ph. Sciau, G. Calvarain, J. Ravez, Acta Crystallogr. B55 (1999) 429.

[13] Y. Gagou, D. Mezzane, N. Aliouane, et al., Ferroelectrics 254 (2001) 197.

[14] B.A. Scott, E.A. Giess, G. Burns, D.F. O'Kane, Mater. Res. Bull. 3 (1968) 831.

[15] R.R. Neurgaonkar, J.G. Nelson, J.R. Oliver, L.E. Cross, Mater. Res. Bull. 25 (1990) 959.

[16] M. Oualla, A. Zegzouti, M. Elaatmani, M. Daoud, D. Mezzane, Y. Gagou, P. SaintGrégoire, Ferroelectrics 291 (2003) 133.