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Lead-free relaxor ferroelectrics with ‘TTB’ structure

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Abstract – Preparation and dielectric characterisations of a great number of TTB-type ceramics have allowed us to show that some of them present relaxor behaviour, due to the occupation of the same crystallographic site by two different cations or anions. One of the cation in the octahedral site has to be ferroelectrically active. The relaxor effect is correlated to either cationic distribution disorder in the same site or dilution of the ferroelectric character. *To cite this article: J. Ravez, A. Simon, C. R. Chimie 5 (2002) 143–148* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

relaxor ferroelectrics / TTB structure / lead-free

Résumé – La préparation et la caractérisation diélectrique d’un grand nombre de céramiques de type BQT nous ont permis de montrer que certains d’entre eux présentent un comportement relaxeur, imputable à l’occupation d’un même site cristallographique par deux anions ou cations différents. L’un des cations dans le site octaédrique doit être ferroélectriquement actif. L’effet relaxeur est corrélé, soit au désordre de la distribution cationique sur le même site, soit à la dilution du caractère ferroélectrique. *Pour citer cet article : J. Ravez, A. Simon, C. R. Chimie 5 (2002) 143–148* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

relaxeurs ferroélectriques / structure TTB / sans plomb

1. Introduction

Ferroelectric materials may be divided into two classes: classical or relaxor ferroelectrics [1]. Typically, relaxors have at least one crystallographic site that is occupied by two or more ions. In addition to the usual applications for classical ferroelectrics, relaxors are of great interest for dielectrics in capacitors and actuators. Most used relaxors are lead-based perovskite ceramics such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) and derived compounds [2]. However, these compositions have the obvious disadvantages associated with the volatility and toxicity of PbO . Therefore, much current research is directed towards more environmentally friendly Pb-free relaxor materials. In this way, a large number of relaxor lead-free BaTiO_3 derived

ceramics with perovskite structure was recently prepared and characterised [3].

Likewise lead-free relaxor compositions belonging to tetragonal tungsten bronze (TTB) could be also of interest. Fig. 1 shows a schematic representation of the TTB structure projection along a 001 direction. For a general formulation $\text{A}_2\text{BC}_2\text{M}_5\text{X}_{15}$ ($\text{X} = \text{O}, \text{F}$), large cations (e.g. Na^+ , K^+ , Sr^{2+} , Ba^{2+} , Pb^{2+} , La^{3+} , Bi^{3+} ...) occupy the 15 CN (A) and the 12 CN (B) sites, small cations like Li^+ are in the 9 CN (C) sites and small and highly charged cations (e.g. Nb^{5+} , Ta^{5+} ...) are in the octahedral (M) site.

Previous authors had announced the solid-state solution $\text{Sr}_{2.5(1-x)}\text{Ba}_{2.5x}\text{Nb}_5\text{O}_{15}$ to be relaxor [4–9]. The present work is devoted to other lead-free relaxor compositions selected among a great number of TTB-type compositions.

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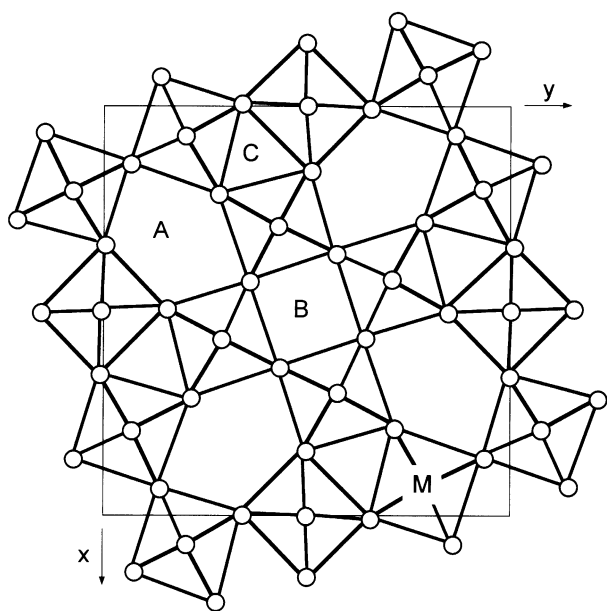


Fig. 1. Schematic projection of the anionic TTB structure along the 4-fold c axis (A, B and C correspond to cationic sites with 15, 12 and 9 coordination number).

2. Experimental

The oxides and the oxyfluorides were prepared by solid state reaction at temperatures between 900 and 1100 °C for 15 h from intimate and ground mixings of starting oxides, fluorides and carbonates in stoichiometric amounts. After new intimate and ground mix-

ings, powders obtained were pressed under 100 MPa into disks of 8 mm diameter and about 1 mm thickness. Depending on the compositions, heat treatments were then performed at temperatures between 1150 and 1450 °C in air for the oxides and in platinum sealed tube under dry oxygen for the oxyfluorides, in order to avoid hydrolysis at high temperature.

Room temperature powder X-ray diffraction patterns were recorded on a Philips diffractometer, using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), in the angular range $5 \leq 2\theta \leq 60^\circ$. This made it possible to verify that the samples were single phase. The diameter shrinkages $\Delta\Phi/\Phi$ were systematically determined as $(\Phi_{\text{init}} - \Phi_{\text{fin}})/\Phi_{\text{init}}$. Their values were in the range 0.13–0.17.

Dielectric measurements were performed on the ceramic disks after deposition of gold or platinum electrodes on the circular faces. The real ϵ'_r and imaginary ϵ''_r relative permittivities were determined under helium as a function of both temperature (77–900 K) and frequency (10^2 – 2×10^5 Hz) using a Wayne–Kerr 6425 component analyser.

3. Results

In addition to barium–strontium niobates, a relaxor behaviour was recently demonstrated in various other TTB compositions including niobates, tantalates, niobo-tantalates and niobo-titanates (Table 1). As an example, Fig. 2 shows the typical temperature dependence of ϵ'_r for a relaxor ceramic with composition

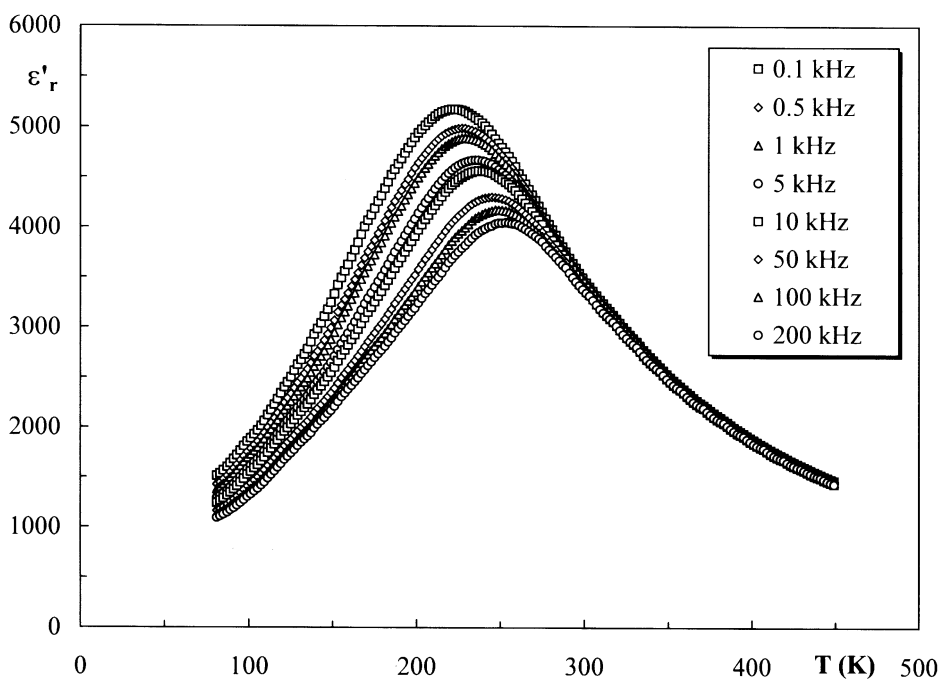


Fig. 2. Temperature dependence of ϵ'_r , the real part of the permittivity, for a ceramic with composition $\text{Sr}_2\text{K}(\text{Nb}_{0.775}\text{Ta}_{0.225})\text{O}_{15}$.

Table 1. Lead-free TTB relaxor compositions.

Relaxor compositions	T_m (± 10 K) at 10^3 Hz	ΔT_m (K)
$K_2LaNb_5O_{15}$	165	22
$K_2BiNb_5O_{15}$	220	80
$BaLa\Box Nb_5O_{15}$	203	55
$BaBi\Box Nb_5O_{15}$	319	73
$BaLa_{2/3}\Box_{1/3}NaNb_5O_{15}$	210	34
$BaLaNa(Nb_4Ti)O_{15}$	171	41
$BaLaK(Nb_4Ti)O_{15}$	146	13
$Ba_2Bi(Nb_3Ti_2)O_{15}$	270	25
$Sr_2NaTa_5O_{15}$	120	25
$Sr_2KTa_5O_{15}$	< 80	*
$Ba_2NaTa_5O_{15}$	< 80	*
$Ba_2KTa_5O_{15}$	< 80	*
$K_3LiNb_5O_{14}F$	210	40
$Ba_{2.25}\Box_{0.75}Nb_5O_{14.5}F_{0.5}$	175	30
$SrK_2Nb_5O_{14}F$	112	16
$BaNa_2Nb_5O_{14}F$	140	17
$Sr_2Na(Nb_{1-x}Ta_x)_5O_{15}$ ($0.40 \leq x \leq 1$)	$222 \geq T_m \geq 120$	20 (0.40) to 25 (1)
$Sr_2K(Nb_{1-x}Ta_x)_5O_{15}$ ($0.16 \leq x \leq 1$)	$263 \geq T_m \geq 80$	21 (0.16) to * (1)
$Ba_2Na(Nb_{1-x}Ta_x)_5O_{15}$ ($0.65 \leq x \leq 1$)	$260 \geq T_m \geq 80$	6 (0.65) to * (1)
$Ba_{2-x}Na_{1+x}Nb_5O_{15-x}F_x$ ($0.31 \leq x \leq 1$)	$250 \geq T_m \geq 140$	40 (0.31) to 17 (1)
$Ba_2Na(Nb_{5-x}Ti_x)O_{15-x}F_x$ ($0.31 \leq x \leq 0.50$)	$265 \geq T_m \geq 168$	15 (0.31) to 30 (0.50)
$Sr_{2-x}K_{1+x}Nb_5O_{15-x}F_x$ ($0.20 \leq x \leq 1$)	$290 \geq T_m \geq 112$	15 (0.20) to 16 (1)
$Sr_{2.5(1-x)}Ba_{2.5x}\Box_{0.5}Nb_5O_{15}$ **	**	**

$\Delta T_m = T_m(10^5 \text{ Hz}) - T_m(10^3 \text{ Hz})$. In the case of solid solutions, the given values of T_m correspond to the x limit values. *: Unknown values due to the experimental low temperature limitation of our dielectric measurements. **: A relaxor behaviour was also announced by previous authors; due to some disagreements between them, the values of x , T_m and ΔT_m are not given here.

$Sr_2K(Nb_{0.775}Ta_{0.225})O_{15}$: the temperature T_m of ϵ'_r maximum is shifted towards higher values for increasing frequencies.

Of all the lead-free compounds studied, it is with one of the compositions containing Bi^{3+} , another $6(sp)^2$ lone pair cation, that the highest value of T_m was obtained: $T_m(BaBiNb_5O_{15}) = 319$ K at 10^3 Hz. In addition, independently of the value of T_m , the bismuth compositions allow the highest values of ΔT_m : $\Delta T_m = 80$ and 73 K for the potassium and barium niobates respectively. Such a result is in good agreement with that obtained for lead-free compositions derived from $BaTiO_3$ [10].

Some solid solutions situated between classical ferroelectric and relaxor ones have also been studied. Such is the case with $A_2B(Nb_{1-x}Ta_x)_5O_{15}$. The relaxor behaviour occurs for the highest values of x . Fig. 3 shows, as an example, the variations of T_C

($0 \leq x < 0.16$) and T_m ($0.16 \leq x \leq 1$) for ceramics with composition $Sr_2K(Nb_{1-x}Ta_x)_5O_{15}$. Both values decrease when the tantalum rate increases.

This is also the case with the $Sr_2KNb_5O_{15}/SrK_2Nb_5O_{14}F$ and $Ba_2NaNb_5O_{15}/BaNa_2Nb_5O_{14}F$ systems; for the compositions close to the oxide, the behaviour is ferroelectric, while it becomes relaxor when the fluorine rate and thus the sodium or potassium rate are sufficiently high. Fig. 4 shows as an example the variations of T_C ($0 \leq x \leq 0.25$) and T_m ($0.20 \leq x \leq 1$) for the barium/sodium system. It is interesting to notice that both relaxor and classical ferroelectric phases coexist for compositions ($0.20 \leq x \leq 0.25$) giving thus the transition sequence: relaxor–classical ferroelectric–paraelectric, on heating. Here also both values of T_C and T_m decrease when x increases. The frequency dependence of the permittivi-

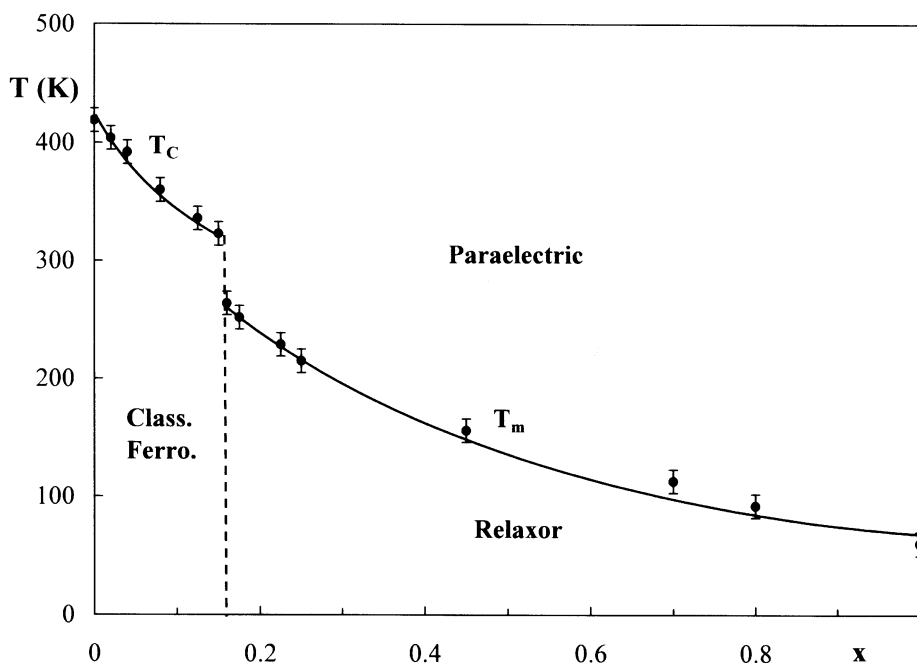


Fig. 3. Variation of transition temperatures with x for ceramics with composition $\text{Sr}_2\text{K}(\text{Nb}_{1-x}\text{Ta}_x)\text{O}_{15}$.

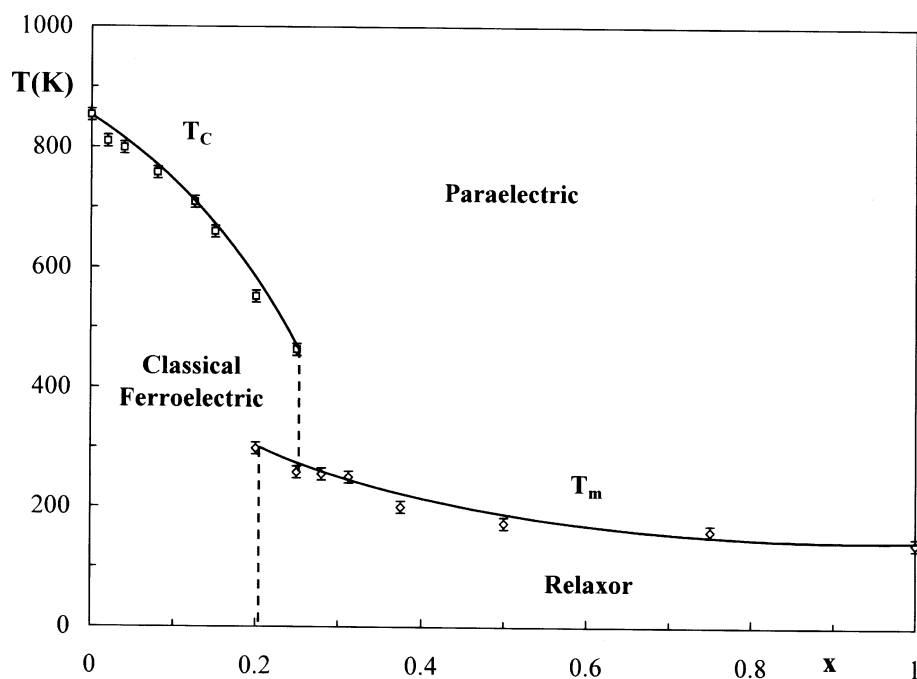


Fig. 4. Variation of transition temperatures with x for ceramics with composition $\text{Ba}_{2-x}\text{Na}_{1+x}\text{Nb}_5\text{O}_{15-x}\text{F}_x$.

ties of a ceramic with a composition $\text{BaNa}_2\text{Nb}_5\text{O}_{14}\text{F}$ clearly displays a frequency relaxation at 77 K, while it disappears at 300 K, i.e. for $T > T_m$ ($T_m = 140$ K at 10^3 Hz) (Fig. 5).

4. Discussion

Some compositions had been previously prepared and characterised. They had been announced to be

ferroelectric, measurements having been realised only at one frequency (10^3 Hz) and not at various frequencies as it has to be the case for relaxor property studies. It is the automation of dielectric measurements performed with an impedance analyser that allows us to obtain such actual results.

As for the perovskites, the relaxor effect appears in many TTB-type compounds when at least two ions occupy the same crystallographic site. The co-

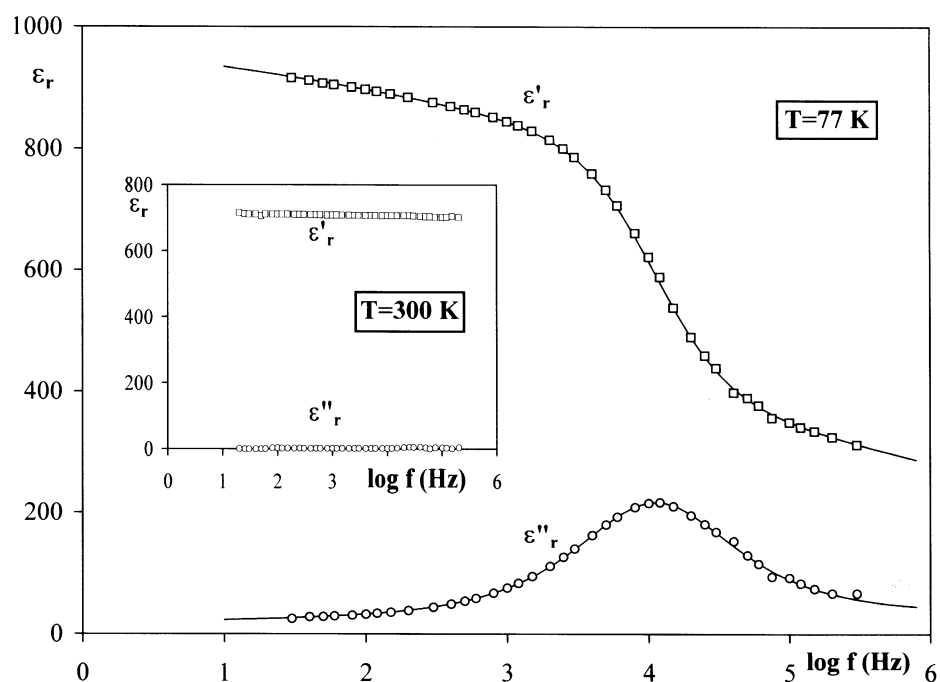


Fig. 5. Frequency dependencies of the permittivities ϵ'_r and ϵ''_r for a ceramic with composition $\text{BaNa}_2\text{Nb}_5\text{O}_{14}\text{F}$.

existence of cations seems as favourable in the A site as in the M site. In addition, at least one cation ferroelectrically active (Ti^{4+} , Nb^{5+} , Ta^{5+}) must be present in the octahedral site.

The relaxor effect can be due to a cationic disorder in the A site, whatever the coupled substitution ensuring the electrical neutrality; this is the case with $\text{BaLaNb}_5\text{O}_{15}$, when Ba^{2+} and La^{3+} occupy only the A site. $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, in which the same two Ba^{2+} cations occupy the A site, is a classical ferroelectric; on the contrary, $\text{BaNa}_2\text{Nb}_5\text{O}_{14}\text{F}$ is a relaxor one. The crystal structure determination of this last compound is in good agreement with the dielectric properties, i.e. the A-site is statistically occupied by equal quantities of Ba^{2+} and Na^+ , thereby giving a cationic disorder in this A-site while the B-site is filled by Na^+ cations [11]. In addition, there is here coexistence of F^- and O^{2-} in the anionic sites.

Concerning the Ta–Nb substitution, the replacement of Nb^{5+} , highly polarisable, by Ta^{5+} transforms the macroscopic polarisation into a local one. This results in a relaxor state as the long-range order is not induced by a local dipolar order. The higher the associated cationic order in the A and B sites, the higher the Ta–Nb substitution rate leading to relaxor behaviour (Table 1); e.g. $x = 0.16$ for $\text{Sr}_2\text{K}(\text{Nb}_{1-x}\text{Ta}_x)_5\text{O}_{15}$ and $x = 0.65$ for $\text{Ba}_2\text{Na}(\text{Nb}_{1-x}\text{Ta}_x)_5\text{O}_{15}$. In fact, there is no ambiguity regarding the disordered distribution of the two small Sr^{2+} cations and the single large K^+ one, nor regarding the ordered distribution of the two large Ba^{2+} cations and the single small Na^+ ones,

since both occur in two large A sites and in one smaller B one.

For oxyfluorides, F^- – O^{2-} substitution is coupled with a cationic one in order to ensure the electric neutrality. The origin of the relaxor effect comes from cationic or/and anionic substitutions when there are two different cations in the same crystallographic site, e.g. $\text{Ba}_{2-x}\text{Na}_{1+x}\text{Nb}_5\text{O}_{15-x}\text{F}_x$, the A site being filled by both Ba^{2+} and Na^+ for $x > 0$. However, it seems that it can be attributed to the only anionic F^- – O^{2-} substitution in the lack of different cations in the same site, e.g. $\text{K}_3\text{LiNb}_5\text{O}_{14}\text{F}$: due to their very different sizes, the K^+ and the Li^+ cations occupy only the (A + B) sites and C site respectively. It is also the case of $\text{Ba}_{2.25}\text{K}_{0.75}\text{Nb}_5\text{O}_{14.5}\text{F}_{0.5}$, where A and B sites are occupied by only Ba^{2+} . In these two compositions, the relaxor effect is induced by a dilution of the oxygen network, leading to a local polarisation that breaks the long-range order usually at the origin of classical ferroelectric properties.

5. Conclusion

In TTB-type compositions, the relaxor behaviour appears when at least two ions occupy the same crystallographic site. The M^{n+} cations in the octahedral site have to be ferroelectrically active (e.g. Ti^{4+} , Nb^{5+} or Ta^{5+}). In any case, local polarisation leads to a relaxor effect; on the contrary a macroscopic one gives a classical ferroelectric behaviour. The relaxor

effect is due to either a cationic or an anionic disorder in the A or B sites, or to a dilution of the ferroelectric character by cationic or anionic substitutions. Some of

these materials could prove valuable (dielectrics for capacitors and actuators), because they are environment-friendly.

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