

Ferroelectric Relaxor Behaviour in Some Lead-Free Compositions and their Potential Applications as Photocatalyst to Hydrogen Production

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Abstract—New lead-free ferroelectric relaxor ceramics were prepared by conventional solid-state synthesis in the BaTiO₃-Bi₂O₃-Y₂O₃ systems. Some of these ceramics present a ferroelectric relaxor with transition temperature close to room temperature. These new materials are very interesting for applications and can replace lead-based ceramic to prevent the toxic pollutions during the preparation state. In the other hand, the energy band diagram shows the potentiality of these compounds for the solar energy conversion. Thus, some compositions have been tested successfully for H₂ production upon visible light. The best activity occurs in alkaline media with a rate evolution of about 0.15 mL g⁻¹ mn⁻¹ and a quantum yield of 1% under polychromatic light.

Keywords—Ferroelectric, Hydrogen production, Lead-free, Photocatalysis.

I. INTRODUCTION

A large compound of perovskite materials exhibits a ferroelectric behaviour. Much attention has been given to the complex perovskite compounds with disorder cations which lead to a new kind of ferroelectric materials called relaxor ferroelectric. The latter's are of great interest both for device application and in the fundamental understanding of ferroic systems [1, 2]. In complex perovskites (AA'BB'O₃), the relaxor ferroelectric materials present a large range of interesting properties related to their complex order/disorder nanostructures. These types of materials are characterized by a diffuse phase transition, a strong frequency dispersion, large dielectric constant and wide space charge region. These characteristics could be interesting for solar applications and especially in photocatalytic hydrogen production. In fact, perovskite-related compounds have shown very interesting abilities as photocatalysts [3]. The usual ferroelectric relaxor materials are lead-based ceramics and derived compounds which present a disadvantage due to the volatility and the toxicity of PbO. Actually, many actions have been managed in order to protect the environment. To respect this important objective, research of new components is oriented toward more environmental friendly materials. In this way, several

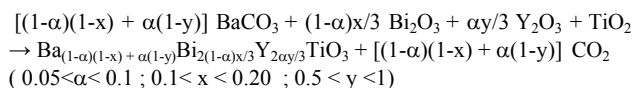
lead-free compositions derived from BaTiO₃ were investigated by homovalent and/or heterovalent substitution [4-6].

On the other hand, photocatalytic hydrogen production represents a very promising contribution to a clean and renewable energy system. Furthermore, current interest in alkaline earth perovskites (AA'BB'O₃) as photo electrochemical (PEC) functional materials is based in part on aspects like water splitting and environmental protection [7-9].

In our contribution, we present the ferroelectric properties of some lead-free compositions belonging to BaTiO₃-Bi₂O₃-Y₂O₃ systems and their behaviour as photocatalyst for hydrogen production.

II. EXPERIMENTAL

Materials with compositions Ba_{(1-α)(1-x) + α(1-y)}Bi_{2(1-α)x/3}Y_{2αy/3}TiO₃ (BaBiYTio₃) were prepared by the conventional mixed oxide method. They were obtained by solid state synthesis from BaCO₃ (Merck 99,9%), Bi₂O₃, Y₂O₃ and TiO₂ (Aldrich 99,9%) according to the following reactions



Weighed ingredients were wet mixed for 2 hours and calcined at 850°C for 12 hours under oxygen. After new intimate and ground mixings, calcined powder obtained were pressed under 100 MPa into disk of 8 mm diameter and about 1 mm thickness. Disk shaped ceramic were then sintered under oxygen atmosphere for 2 hours at 1100 °C. Loss weight systematically determined, before and after heat treatment, is less than 1%. The diameter shrinkage $\Delta\Phi/\Phi$ ($\Phi_{\text{init}} - \Phi_{\text{final}}/\Phi_{\text{init}}$) and the compactness (experimental density /theoretical density) were respectively 0.14 and 0.94. Room temperature powder X-ray diffraction patterns were recorded on a Philips diffractometer using CuKα radiation ($\lambda = 1.5406 \text{ \AA}$) in the angular range $5 < 2\theta < 80^\circ$, in order to verify that the samples were single phases and of perovskite structure. For the dielectric measurements, samples (into disk forms) were polished and gold electrodes were sputtered on both sides. The real and imaginary relative permittivities ϵ'_r and ϵ''_r were determined under helium atmosphere, as a function of both temperature (77–500 K) and frequency (10^2 – 10^5 Hz), using Agilent 4263B LCR Meter.

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Photocatalytic characterizations were done in a standard three electrode cell. Electrical contacts of less than $10\ \Omega$ resistances were established by soldering copper wires onto the back pellets with conductive silver paint. The working electrode was encapsulated in a glass holder and isolated by epoxy resin. The auxiliary electrode was a Pt foil ($1\ \text{cm}^2$, Tacussel), all the potentials were referenced against a saturated calomel electrode (SCE) and monitored with a Voltalab PGZ301 potentiostat (Radiometer). The electrolyte KOH (0.5 M), used to maintain high electro conductivity, was continually flushed with nitrogen. The electrode was irradiated through a flat window with a 650 W halogen lamp (Dyr, General Electric). The interfacial capacitance was measured as a function of the potential with a rate of $10\ \text{mV step}^{-1}$. The complex impedance data, recorded at the open circuit potential (OCP), were acquired using small amplitude wave signals through a frequency response analyser in the frequency range (10^{-3} - $10^5\ \text{s}^{-1}$). The solutions have been prepared from reagents of analytical quality and doubly distilled water. The procedure and apparatus for H_2 -evolution have been described in details elsewhere [10].

III. RESULTS AND DISCUSSION

3.1 ferroelectric properties

In the investigated domain, the X-ray spectra at room temperature are characteristics of cubic symmetry and the dielectric measurements show only one broad peak. Dielectric measurements show only one broad peak in the range of x and α investigated. For example, Fig. 1 and Fig. 2 give the temperature dependence of ϵ'_r and ϵ''_r at various frequencies for a ceramic with composition $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$. The temperature T_m of ϵ'_r maximum was shifted to higher values at greater frequencies. A frequency dispersion took place for $T < T_m$, the value of ϵ'_r decreasing when the frequency increased. The temperature and frequency variations of the imaginary part ϵ''_r of the permittivity were also specific: the temperature T_m of ϵ''_r maximum was shifted to higher values at greater frequencies, but unlike the evolution of ϵ'_r , the frequency dispersion was here characterized by an increase in ϵ''_r when frequency increased. In addition, there was a small deviation from the Curie-Weiss law (Fig. 3). The value of the Curie-Weiss temperature T_0 was greater than that of T_m . A strong dielectric dispersion appeared leading to a Vögel-Fulcher (VF) relationship [11-12]. All these dielectric characteristics are typical of relaxor character.

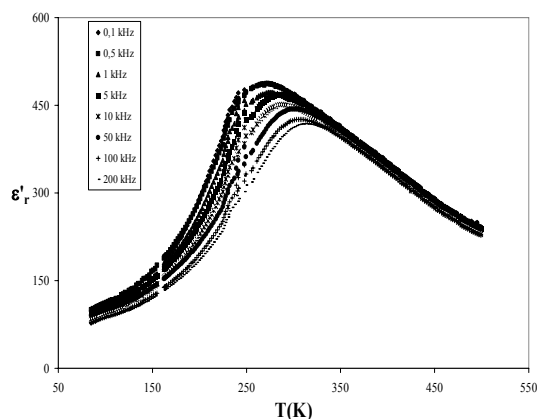


Fig. 1 Thermal variation of ϵ'_r for a $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$ composition

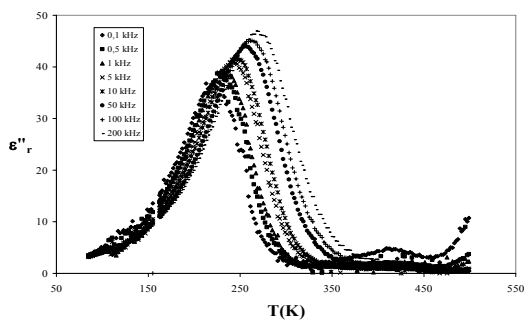


Fig. 2 Thermal variation of ϵ''_r for a $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$ composition

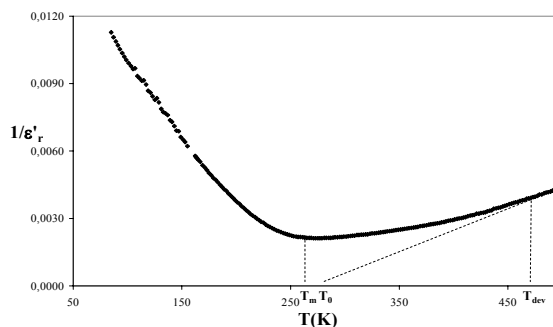


Fig. 3 Thermal variation of $1/\epsilon'_r$ for a $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$ composition

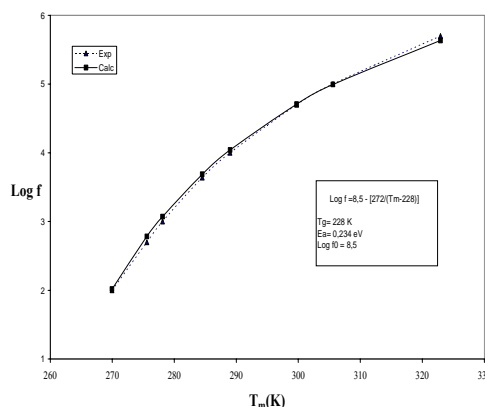


Fig. 4 Variation of $\log f$ with T_m for a $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$ composition

Table 1 shows some characteristics of the BaBiYTiO_3 compositions. According to these results, the dual introduction of Bi^{3+} and Y^{3+} in the network of BaTiO_3 leads to the following remarks:

*For $[\text{Bi}]/[\text{Ba}]$ ratio values lower than 10%, BaBiYTiO_3 solid solutions exhibit three phase transitions as for the case for a normal ferroelectric BaTiO_3 .

*For the weak value of $[\text{Bi}]/[\text{Ba}]$ ratio, close to 10% ($0.107 \leq [\text{Bi}]/[\text{Ba}] \leq 0.110$), there is only one dielectric peak without frequency dependence. The phase transition is diffuse but there is no yet relaxor behaviour

*For [Bi]/[Ba] ratio values greater than 10% ($0.148 \leq [\text{Bi}]/[\text{Ba}] \leq 0.164$), there is only one broad peak of ϵ'' , occurring at T_m , which is accompanied by a frequency dispersion for $T < T_m$ and a shift of T_m with frequency, showing a relaxor behaviour for these compositions. The relaxor behaviour is not dependent of [Y]/[Bi] ratio.

The value of the frequency dispersion $\Delta\epsilon''/\epsilon''_r$ at a normalized temperature $T = T_m - 60$ K is about 225 K. there is a good fit of the data $\log f$ vs T_m (Fig. 4) with a Vögel-Fulcher law leading to the value $T_{VF} = 228 \pm 10$ K and activation energy about 0.234 e.V.

All these dielectric characteristics are typical of relaxor behavior [1]. In our case, the relaxor effect is certainly due to a cationic disorder in the A site. In fact the substitution of Ba^{2+} by respectively Bi^{3+} and Y^{3+} give rise to a non stoichiometric compositions and a composition heterogeneity which promote the relaxor effect. In structural viewpoint, the relaxor behavior is generated par the presence of polar nanodomains with electric charge unbalance which leads to the presence of local polarization responsible of frequency dispersion.

3.2 Photoelectrochemical characterization

The study was achieved on $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$ composition. The oxide exhibits an excellent chemical stability over the entire pH range. The electro kinetic parameters i.e. the exchange current density ($4.9 \mu\text{A cm}^{-2}$) and the corrosion potential (+0.65 V) were determined from the semi logarithmic plot (Fig. 5, Insert). The voltammogram recorded in the dark in alkaline electrolyte (NaOH 0.5 M, pH~ 13) shows a small current density over a large potential range (Fig. 5). Additional support of the electrons localization is brought by the existence of the peak O (0.56 V) corresponding, to the electrochemical couple $\text{Ti}^{3+/4+}$. By contrast, there is no anodic current indicating a low electrocatalytic oxygen evolution. On the reverse scan, the peak R (-0.79 V) is attributed to the reversible reduction of Ti^{4+} .

3.3 Photocatalytic hydrogen production

The above results are relevant of potential applications for the solar energy conversion. The spontaneous polarization in relaxor ferroelectric materials is an attractive property for the water photo splitting. The presence of domains favours the separation of electron/hole (e^-/h^+) pairs. The charges carriers migrate in opposite directions under the electric field of the polar nanoregions and eventuate in photoredox reactions. However as mentioned above, this composition is known to be good photo catalyst but does not match the sunlight adequately. The ionization of the substituted atoms introduces extra electrons into the lattice, the consequence being a decrease of the space charge region. Therefore, in order to limit the electrons concentration the substitution onto the A sublattice must be compensated by the cations vacancies. With a gap of 2.5 eV, most of the sun spectrum is sub band gap and therefore weakly converted on $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$ although its beneficial features like the chemical stability, the non toxicity and the cathodic potential V_{fb} . Therefore it is necessary to find a suitable activator in order to improve the photoactivity. The best performance for H_2 formation is achieved on $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$ in neutral electrolyte (NaOH, 0.1 M) with an evolution rate of $0.15 \text{ mL g}^{-1} \text{ min}^{-1}$ and a quantum yield of 1% under polychromatic light (Fig. 6).

TABLE I SOME CHARACTERISTICS IN THE $\text{BaTiO}_3\text{-Bi}_2\text{O}_3\text{-Y}_2\text{O}_3$ SYSTEMS

Compositions			$\epsilon''_{r(\text{max})}$ (at 1 kHz)	T_m (K)	ΔT_m (K)	$\Delta\epsilon''_r / \epsilon''_r$
[Y]/[Bi]	[Bi]/[Ba]	[Y]/[Ba]				
0.144	0.107	0.015	443	387	2	0.09
0.222	0.108	0.024	449	395	2	0.07
0.300	0.109	0.033	599	387	2	0.10
0.366	0.110	0.040	516	392	2	0.08
0.056	0.148	0.008	583	275	55	0.24
0.108	0.150	0.016	500	283	46	0.22
0.275	0.156	0.043	472	276	52	0.21
0.500	0.164	0.082	443	288	45	0.15

$$\Delta\epsilon''_r / \epsilon''_r = \epsilon''_r(10)^2 \cdot \epsilon''_r(10)^5 / \epsilon''_r(10)^2$$

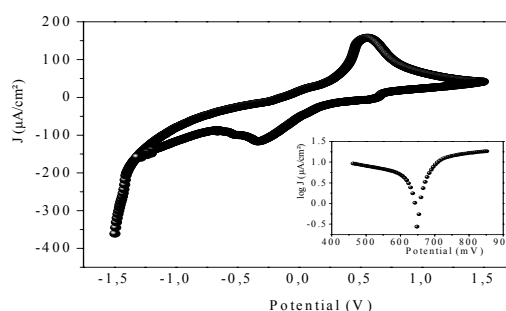


Fig. 5 Cyclic voltammetry in KOH 0.5 M (inset: Tafel plot) for a $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$ composition

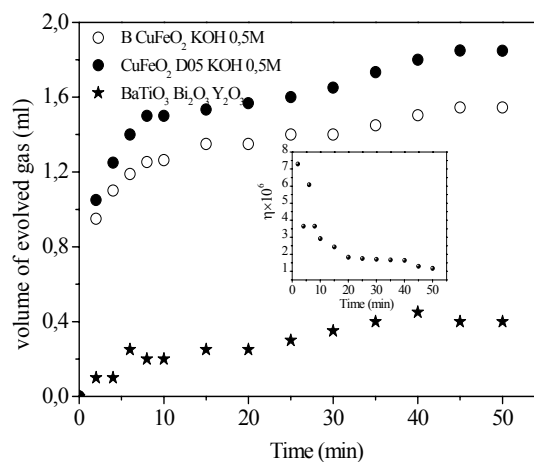


Fig. 6 H_2 evolution Vs illumination time for a $\text{Ba}_{0.725}\text{Bi}_{0.120}\text{Y}_{0.033}\text{TiO}_3$ composition

IV. CONCLUSION

According to the dielectric investigations, the introduction of Bi^{3+} and Y^{3+} in the BaTiO_3 lattice leads to a new ferroelectric relaxor materials. The value of T_m , near to room temperature, allows the use of relaxor properties in normal conditions. These new materials are very interesting for ferroelectric applications and can replace lead-based ferroelectric ceramics to prevent the environmental pollutions during the preparation step. The oxide emerged as having a great promise as photo electrode. Its conjunction with a narrow band gap SC extends the spectral sensitivity toward the visible region and the system has been tested successfully for the hydrogen formation under visible light.

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