

## Elaboration and characterization by XRD and SEM of the glass-ceramics in $\text{BaTiO}_3 - \text{NaPO}_3$ system

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There is a strong need for low cost glass-ceramic materials whose high chemical stability and dielectric properties can be engineered flexibly in bulk and fiber forms. Therefore we have manufactured transparent ferroelectric glass-ceramics consisting of barium titanate (BT) crystallites in a chain metaphosphate glass matrix. Several glass compositions, in the series  $(1-x) \text{NaPO}_3 - x \text{BaTiO}_3$  have been prepared by a conventional melt quenching method. The compositions have been selected on the basis of chemical stability. X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicate the formation of small particle size of  $\text{BaTiO}_3$  in the glass network when its amount is above 4 mol%.

### I. INTRODUCTION:

The traditional ionic glasses we are interested in here, are network glasses. They consist of network former  $\text{P}_2\text{O}_5$ , and of a network modifier  $\text{Na}_2\text{O}$ . The network modifier is important ingredient, since it open up the glass structure and lower the glass temperature. It has been known since the earliest times of glass making that the glassy state is obtained from the melt by cooling sufficiently rapidly. At the melting temperature  $T_m$ , the liquid does not reach the thermodynamically stable crystalline state, but is transformed to an undercooled liquid and then, at still lower temperatures, to a glass. During the cooling process the viscosity increases strongly. At the glass transition temperature the viscosity attains a value of  $10^{13}$  poise. Furthermore, the glass structure is very complex, certainly not long-ranged, but exhibits some short-to-medium range order. As has been suggested already by Zachariasen [1] and Warren et al. [2], the network former (as the name suggests) form some type of network, with bridging and non-bridging oxygens, and with the alkali ions in the free space in between. While the global structure is frozen in, the local structure, however, is arguably not frozen in, since the network-modifying ions are quite mobile also below the glass transition temperature. On the other hand,

Angell [3] regards the mobile cations as being effectively decoupled from the glass network.

Barium titanate  $\text{BaTiO}_3$ , is a crystal of the perovskite family and has been the object of many theoretical and practical investigations. This material exhibits a sequence of ferroelectric phase transitions. At high temperature,  $\text{BaTiO}_3$  is paraelectric with cubic structure. On cooling this material undergoes successive structural phase transitions [4]. All these phase transitions are strongly of first order

character and related to a large thermal hysteresis [5,6], a remarkable optical anisotropy [7] and a large spontaneous polarization [4].

Numerous glass-ceramics based on the association of silicate or vanadate and barium titanate have been reported [8]. This work intends to define a new group of phosphate glasses based on the  $\text{NaPO}_3$ - $\text{BaTiO}_3$  association. It was expected that barium titanate content would influence significantly chemical and thermal properties [9]. Especially, medium  $\text{BaTiO}_3$  concentrated vitreous samples would be very stable against devitrification and would present special properties observed in crystalline  $\text{BaTiO}_3$  such as optical anisotropy or large spontaneous polarization. The aim of this article is to elaborate multicomponent  $\text{NaPO}_3$ - $\text{BaTiO}_3$  glasses or ceramics with different  $\text{BaTiO}_3$  contents. The synthesis conditions allowing the

formation of micrometer grain size of BaTiO<sub>3</sub> incorporated in the glass matrix are precised.

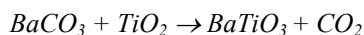
## II. EXPERIMENTAL.

Glass or glass-ceramic samples of ferroelectric BaTiO<sub>3</sub> doped sodium metaphosphate NaPO<sub>3</sub> have been prepared using reagent chemical grade having 99.9% purity of Na<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, and BaTiO<sub>3</sub> employing conventional melt quenching method [9]. After mixing and finely grinding appropriate ingredients, the mixtures are transferred in platinum crucible. The first heating was at 650K to remove volatile products then melting at 1000-1200K for few hours. The melts were then poured on a stainless steel plate preheated at 450K, and the vitreous samples obtained were annealed at T=650K to relieve residual internal stress, and slowly cooled at room temperature.

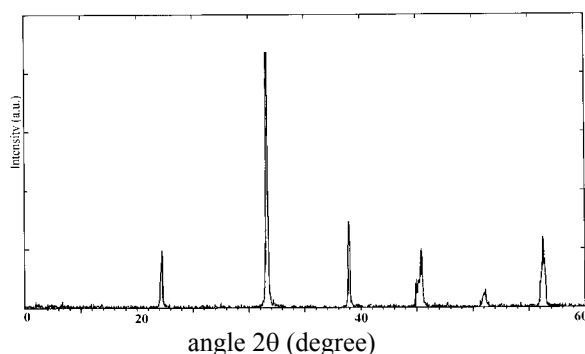
The characterization of the synthesized BaTiO<sub>3</sub> and the amorphous nature of the elaborated glass-ceramics were checked by XRD analysis, using a Seifert XRD 3000 diffractometer. The microstructure of the glass-ceramics is carried out by a JSM-5610LV scanning electron microscopy (SEM).

## III. RESULTS AND DISCUSSION

The BaTiO<sub>3</sub> composition used in the elaboration of the glass-ceramic samples is produced by solid state reaction route according to the equation:



The obtained white powder was characterized at room temperature by means of X-ray diffraction (XRD). Fig.1 shows the representative XRD pattern of the as-prepared BaTiO<sub>3</sub> powder.

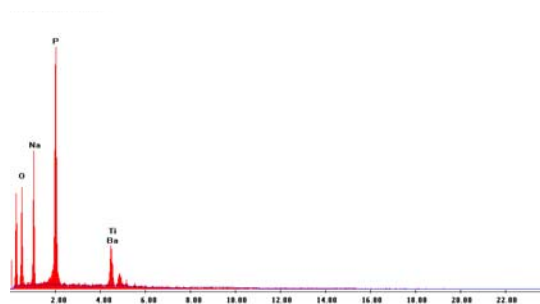


**FIG.1** : XRD of the synthesized BaTiO<sub>3</sub> powder.

One can see that all peaks are identified as from perovskite BaTiO<sub>3</sub> (BT). The peak sharpness and intensity indicate that BT is well crystallized. The particles were found to have a cubic phase.

Glass-ceramic samples of the ferroelectric BaTiO<sub>3</sub> containing NaPO<sub>3</sub>:

(1-x)NaPO<sub>3</sub>- x BaTiO<sub>3</sub> with 0 ≤ x ≤ 14 mol% have been prepared and characterized. To control their chemical composition, Energy Dispersive X-Ray Analysis (EDAX) which allows detailed qualitative and quantitative elemental analysis is used. Elemental analysis of the powders (Fig.2) has revealed the atomic ratio Na:Ba:P:Ti is in good consistence with that in the start compositions, indicating a good compositional control of our method. Also it confirms that the synthesis conditions (heating temperature, time of heating, ...etc) used in the experimental procedure are adequate. Up to 10 mol% of BaTiO<sub>3</sub> could results in vitreous phases. Only ceramics were obtained for high BaTiO<sub>3</sub> ratios.

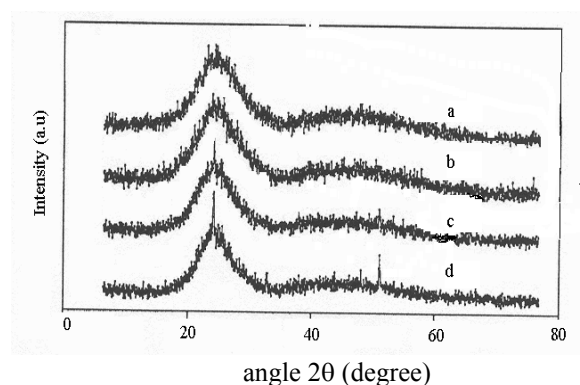


**FIG.2** : Elemental analysis of the glass (1-x)NaPO<sub>3</sub>-xBaTiO<sub>3</sub> (x = 1mol%)

This suggests that low contents of barium titanate could be incorporated in a metaphosphate glass. Even though the glass forming region is very narrow the stability against devitrification increases when the ferroelectric phase amounts goes up. This is exemplified by the value of the thermal stability range  $\Delta T = T_c - T_g$  (where  $T_c$  is the crystallization temperature and  $T_g$  the glass transition temperature) that increases from 50 to about 75 °C when BaTiO<sub>3</sub> concentration rises from 0 to 10 mol% [9]. The increase in  $T_g$  values up to 10 mol% of BaTiO<sub>3</sub> content indicates strengthening of the bond and hence, the compactness of the glass network structure. That increase of the glass transition temperature  $T_g$  could be explained as follow : addition of BaTiO<sub>3</sub> to the glass network transform some double bonds of metaphosphate groups into bridging bonds, which result in an increase in the cross linkages and thus, the rigidity of the network. The above result is in consistent with the linear increase of the density versus BaTiO<sub>3</sub> content. The previous evolutions of density and  $T_g$  versus barium titanate content are consistent with the larger atomic weight and bond strength of barium and titanium cations. Hence, one can supposed that up to 10 mol% of BaTiO<sub>3</sub> content, modification of the glass structure could be monotonic. A general

structural study of these glasses by vibrational spectroscopy is now in progress.

The observed XRD and SEM of all the glass samples studied in the present investigation show the amorphous nature for the glasses with  $x < 10$  mol% BaTiO<sub>3</sub>. This vitreous state of these materials could be ascribed to the incorporation of nanocrystalline BaTiO<sub>3</sub> phases in the glass network. However, the samples with  $x \geq 10$  mol% BaTiO<sub>3</sub> contain small particles/clusters of BaTiO<sub>3</sub> in the glass matrix as reported in XRD/SEM studies. A typical XRD results are shown in Fig.3.



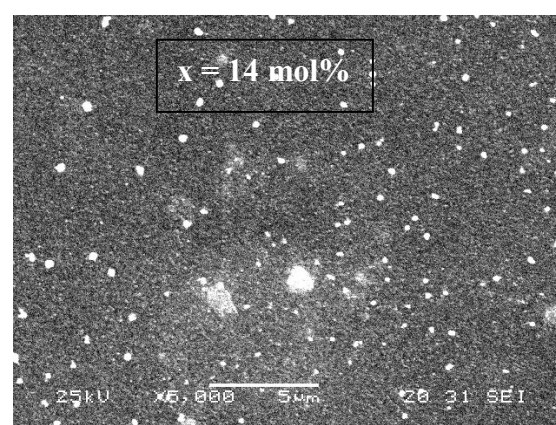
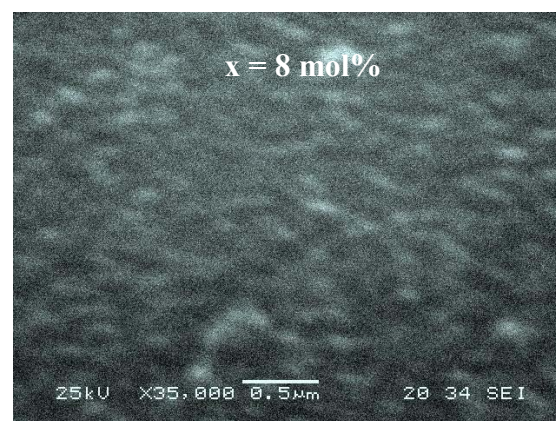
**FIG.3** : XRD pattern with Cu K $\alpha$  radiation of some glass-ceramic materials: (a)  $x = 0$ , (b)  $x = 4$ , (c)  $x = 10$  and (d)  $x = 14$  mol%.

The presence of small particles or clusters of microcrystalline BaTiO<sub>3</sub> embedded in the glass matrix at high BaTiO<sub>3</sub> content are evident from the observed Bragg's peaks in the XRD pattern (Fig.3). The same is evident from the SEM observation as shown in Fig.4. Similar results concerning the existence of fine clusters/particles of microcrystalline BaTiO<sub>3</sub> content in vanadate-phosphate glasses [10] is also confirmed by means of XRD and SEM studies. It is very known that the properties of small-sized structures differ from that of bulks due to their large surface-to-volume ratios [11,12]. Such size effect is not only observed in metallic nanostructures but also in many complex oxides, such as the perovskite ferroelectric materials [13,14]. Hence our success to elaborate small grain sizes in a vitreous matrix would open several issues as perspective of this present work. Mainly, our interest will be focused on the study of some physico-chemical properties in order to get more insight on the structure-property relationship in these materials.

#### IV. CONCLUSION:

Glasses and ceramics in the BaTiO<sub>3</sub>-NaPO<sub>3</sub> system were prepared by the conventional quenching method. They were characterized by means of XRD and SEM studies. The glasses with low BaTiO<sub>3</sub> content ( $< 10$  mol%) show amorphous nature. However, the vitreous materials with  $x \geq 10$

mol% of BaTiO<sub>3</sub> content contain small particles/clusters of microcrystalline BaTiO<sub>3</sub> embedded in the phosphate glass matrix. The above studies illustrate clearly the possibility of the incorporation of BaTiO<sub>3</sub> (for  $x \geq 10$  mol%) as microcrystalline grains in the metaphosphate chain network.



**FIG. 4** : SEM pattern of two typical glasses ( $x = 8$  mol%) showing amorphous nature and ( $x = 14$  mol%) showing small microcrystalline BaTiO<sub>3</sub> clusters/particles.

#### Acknowledgment

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