Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 545–549

www.elsevier.com/locate/jeurceramsoc

Luminescence and structural study of $Bi_{4-x}Eu_xTi_3O_{12}$ solid solution

M.E. Villafuerte-Castrejón[a,*], F. Camacho-Alanís[a], F. González[a], A. Ibarra-Palos[a], G. González[a], L. Fuentes[b], L. Bucio[c]

[a] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Cd. Universitaria A.P. 70-360, CP 04510 México D.F., México
[b] Centro de Investigación en Materiales Avanzados (CIMAV), Complejo Industrial Chihuahua, M. Cervantes 120, Chihuahua 31109, México
[c] Instituto de Física, Universidad Nacional Autónoma de México, A.P. 20-364, CP 01000, México D.F., México

Abstract

The $Bi_4Ti_3O_{12}$ (BIT) is a well known ferroelectric ceramic within the family of so called Aurivillius phases. The present work shows that when bismuth (Bi^{3+}, $r = 0.96$ Å) is substituted by trivalent europium ($r = 0.95$ Å), a solid solution, $Bi_{4-x}Eu_xTi_3O_{12}$ (BIET), is formed. This solid solution was obtained by coprecipitation and characterized by X-ray diffraction, electron microscopy and density measurements. The solubility limit x was determined, and the variation of the lattice parameters was measured through profile fitting of the whole pattern. In order to establish the europium substitution site, we studied the luminescent properties of the material. The excitation spectra, at room temperature, show a broad band associated with a charge transfer state and with the intrinsic absorption of Bi^{3+}. We found at least two Eu^{3+} sites, selectively excited. The Eu^{3+} emission spectra reveal a significant rising of the point symmetry at the rare earth site with respect to the Bi C_1, deduced from the crystallographic analysis.

Keywords: Powders-chemical preparation; Electron microscopy; X-ray methods; Optical properties

1. Introduction

The ever-increasing demand for nonvolatile memories[1,2] has led to the search for a new material with large spontaneous polarization and fatigue-resistant features. Among ferroelectrics, $Bi_{4-x}La_xTi_3O_{12}$ (BLT) is currently regarded as one of the most promising materials[2] for nonvolatile ferroelectric random access memories (NoFRAM). BLT consists of a layered structure of $(Bi_2O_2)^{2+}$ and $(Bi_{2-x}La_xTi_3O_{10})^{2-}$ pseudo-perovskite layers stacked along the c-axis direction. Recent works report this structure has been modified by the lanthanide substitution by Bi in the pseudo-perovskite layer, thus enhancing the ferroelectricity.[3] This property of lanthanum naturally suggests further studies on the substitution of Bi by other rare earth ions. On the other hand, some ferroelectric materials show excellent optical properties. Thus, given these characteristics, it is interesting to investigate the doping effect of Eu^{3+}, known as activator ion in phosphors. In fact, the Eu^{3+} has a double advantage; it is a structural probe and a structural modifier. Finally, the crystal structure determination of a ferroelectric material leads to a better understanding of electrical properties.

In the present paper, $Bi_{4-x}Eu_xTi_3O_{12}$ (BIET) solid solution was prepared by coprecipitation and characterized by X-ray diffraction and photoluminescence spectroscopy.

2. Experimental

The BIET samples were obtained by coprecipitation, starting from a solution consisting of a mixture of bismuth nitrate, europium oxide (dissolved in nitric acid solution at 50% (v/v)) and titanium isopropoxide (dissolved in a nitric acid and isopropanol (20/80) mixture), the precipitation was produced increasing the pH with NH_4OH. The precipitate was filtered and washed with isopropanol until reach neutral pH. The powder was dried at 80 °C overnight. After grinding in attrition milling, the powders were pressed into pellets, which were synthesized and sinterized at 1000 °C for 2 h.

X-ray analysis was performed in a D8 Advance, Bruker Instruments diffractometer, with Cu Kα radiation at 40 kV and 35 mA. For phase identification, the angle step and the counting time were 0.05° (2θ) and 1 s respectively; the acquisition conditions for profile fitting were: step 0.02° (2θ) and counting time of 9 s. Densities were measured in a specific gravity bottle using CCl_4 as displacement liquid.

The photoluminescence spectra were acquired using a FLUOROLOG (SPEX) spectrofluorometer FL111, equipped with

---

[*] Corresponding author. Tel.: +52 55 56 22 46 46; fax: +52 55 56 16 13 71.
E-mail address: mevc@servidor.unam.mx (M.E. Villafuerte-Castrejón).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.04.092

a 450 W Xenon lamp. The time resolved spectra and the lifetime measurements were acquired with the same apparatus, but attaching the phosphorimeter 1934 D and a pulse Xenon lamp, with 40 μs pulse width pulses. The excitation and emission wavelengths were selected by two 0.34 m SPEX spectrometer. The signal detection was performed with a R928 Hamamatsu PMT.

Samples were observed in a Scanning Electron Microscopy Leica Cambridge Stereo Scan 440 with accelerating 20 kV and 500 pA of beam current.

3. Results and discussion

3.1. Analysis by X-ray diffraction

The powder X-ray diffraction patterns exhibit the characteristic Bragg reflections corresponding to the $Bi_4Ti_3O_{12}$ over the solid solution range $Bi_{4-x}Eu_xTi_3O_{12}$ ($0 \leq x \leq 1.2$) and a little amount of $Bi_2Ti_2O_7$ is presented in all the diffractograms due to the Bi deficiency in the samples, produced by the annealing treatment.

$Bi_4Ti_3O_{12}$ crystallizes in the monoclinic system[4] whose deviation to orthorhombic symmetry is too small to be detectable with neutron diffraction data.[5] If the amount of Eu^{3+} is increased, the *a* and *b* parameters become similar, being practically equal in the solubility limit composition, $x = 1.2$, at this composition a tetragonal distortion is probably presented. Fig. 1 shows the increasing overlap of the 2 0 0 and 0 2 0 reflections for different amounts of Eu–Bi substitution (*x*).

Fig. 2 is a plot of the unit cell parameters obtained from profile fitting analysis of the whole pattern as a function of the Eu^{3+} content parameter *x*. The substitution of Bi^{3+} ($r_i = 0.96$ Å) by Eu^{3+}($r_i = 0.95$ Å)[6] is accompanied by a decrease of the *a* and *b* parameters (more pronounced for *a*), and a decreasing tendency of *c*. Although both ions radius are very similar, the Bi environment will be more asymmetric than Eu, because Bi^{3+} ion has a lone pair $6s^2$.

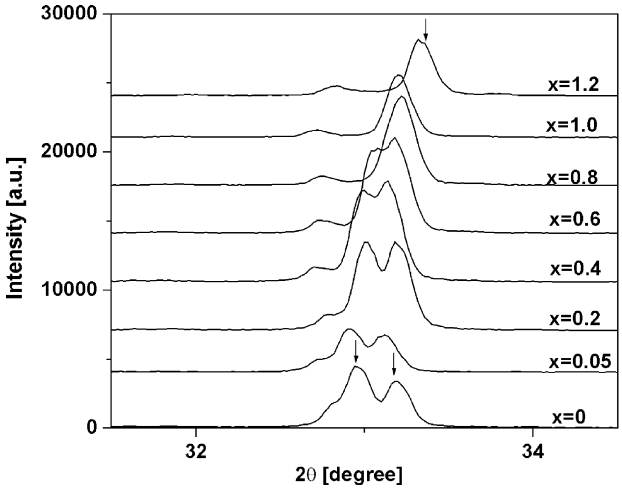

Fig. 1. Overlapping behavior of 2 0 0 and 0 2 0 Bragg reflections in $Bi_{4-x}Eu_xTi_3O_{12}$.

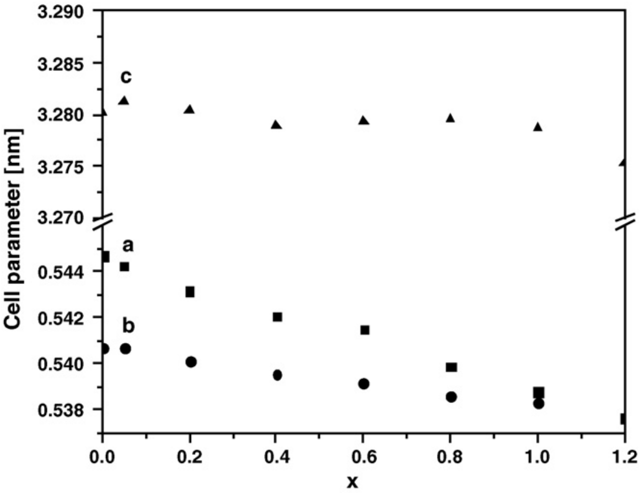

Fig. 2. Variation of the unit cell parameters *a*, b and *c* vs. *x* for the solid solution $Bi_{4-x}Eu_xTi_3O_{12}$.

The solid solution formation mechanism was confirmed by density measurements. The density variation of the solid solution specimens was measured within the range of compositions of the solid solution. The results obtained are given in Fig. 3. In the same figure the calculated values of ρ using the solid solution substitution mechanism $Bi^{3+} \leftrightarrow Eu^{3+}$, in which the total number of cations is constrained to remain constant, are also included for comparison purposes. The reasonable agreement between the experimental and calculated ρ confirms the mechanism of solid solution formation in which Bi^{3+} ions is substituted by Eu^{3+} ions.

3.2. Microstructure: SEM images and density measurements

Fig. 4 shows SEM micrographs of the sintered $Bi_{4-x}Eu_xTi_3O_{12}$ for $x = 0.05$, 1.0 and 1.2. The grain size increases with the Eu content and sintering temperature, the plaque shape mor-

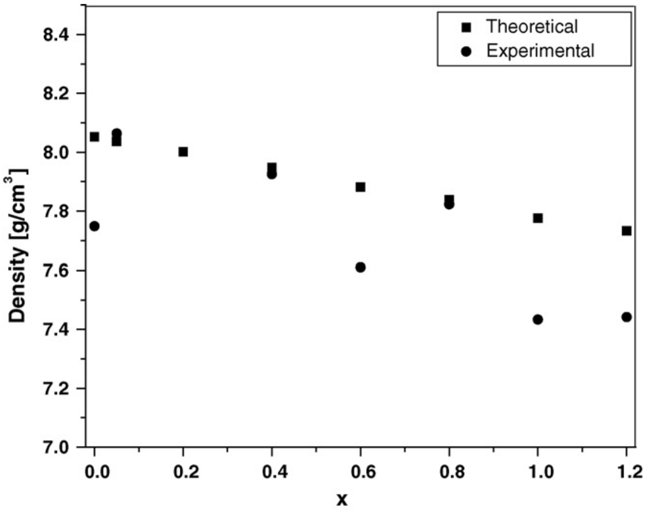

Fig. 3. Experimental and calculated densities of the $Bi_{4-x}Eu_xTi_3O_{12}$ solid solution.

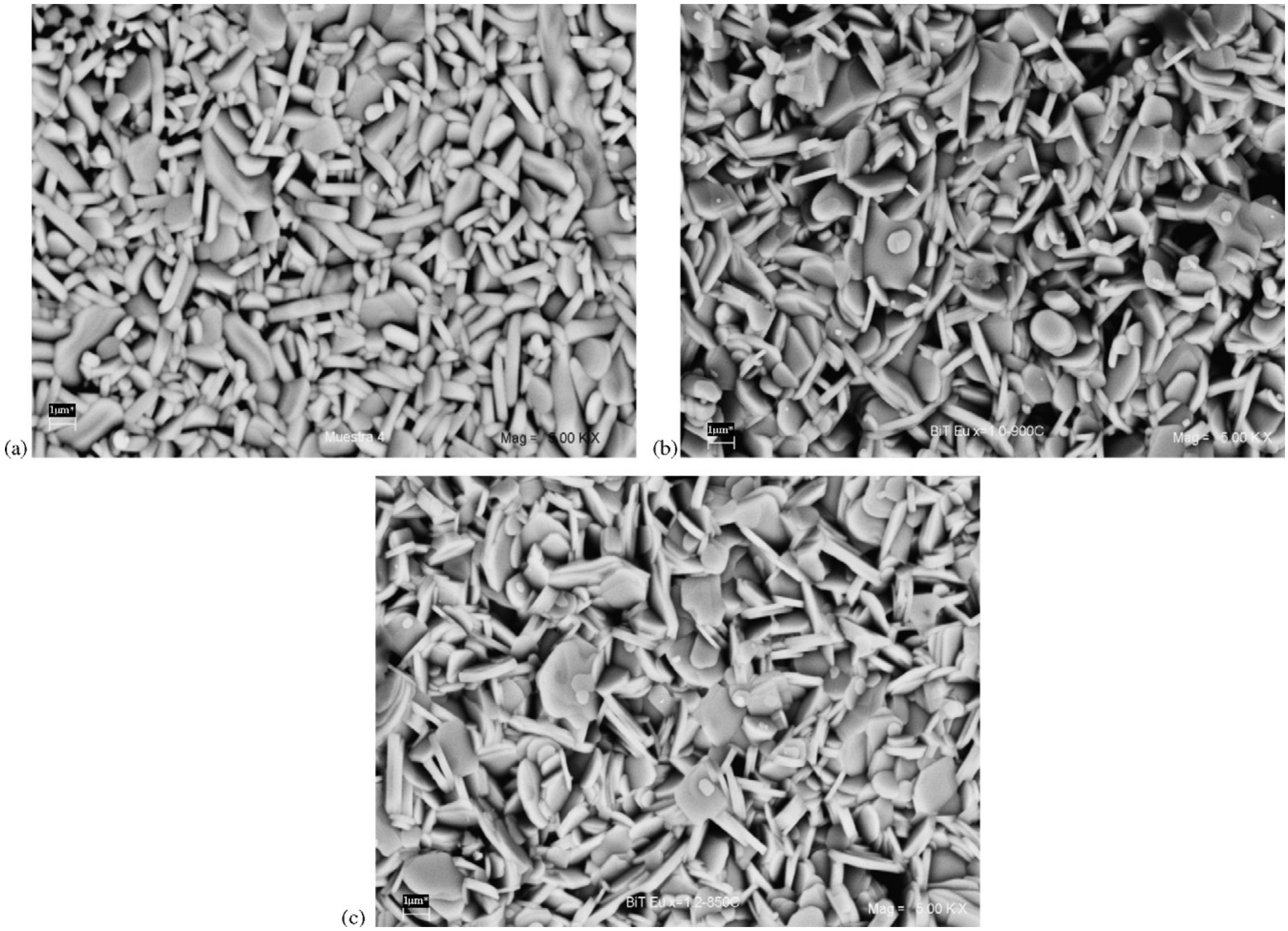

Fig. 4. SEM images at 5k× of sintered $Bi_{4-x}Eu_xTi_3O_{12}$ samples for: (a) $x = 0.4$ (1000 C), (b) $x = 1$ (900 C) and (c) $x = 1.2$ (850 C).

phology is compatible with a texture revealed also by the XRD patterns.

3.3. Optical spectroscopy

Fig. 5 displays the RT excitation spectra of $Bi_{4-x}Eu_xTi_3O_{12}$ pellets. The spectra were taken for the $^5D_0$–$^7F_2$ Eu-emission peak at 615 nm, and consist of several lines associated with transitions from the ground state $^7F_0$ to the excited state components of the $4f^6$ configuration of the Eu^{3+}. In addition to the absorption lines, a broad band is observed in the region of 200–425 nm. This band might be associated with both, the Eu–O charge transfer transition[7] and the absorption of Bi^{3+}.

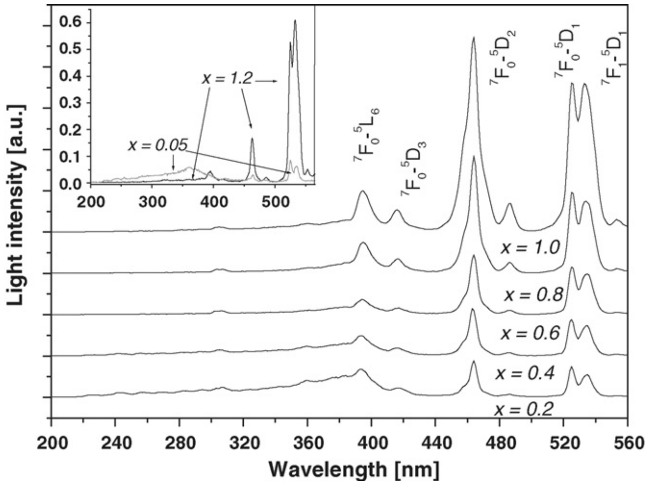

Fig. 5. Excitation spectra of the $^5D_0$–$^7F^2$ Eu^{3+} emission transition peaking at 615 nm.

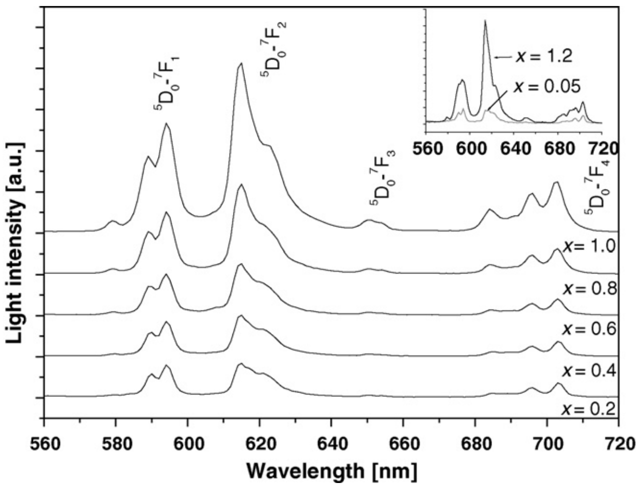

Fig. 6. Emission spectra under continuous excitation at 525 nm ($^7F_0$–$^5D_1$).

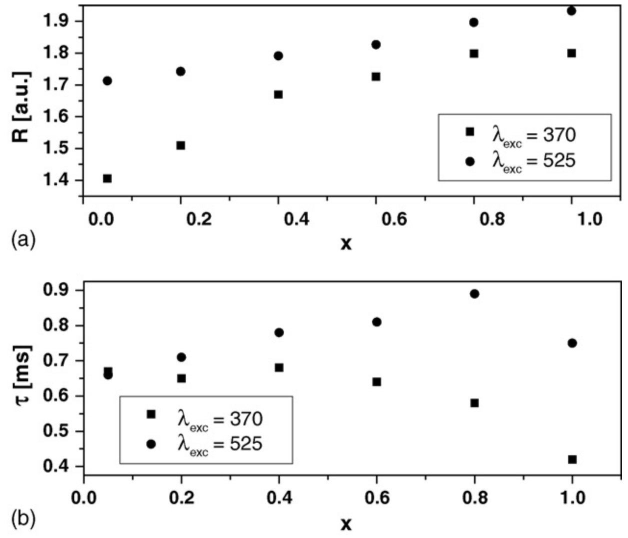

Fig. 7. Intensity ratio *R* (a) and lifetimes (b) of $Bi_{4-x}Eu_xTi_3O_{12}$ pellets.

Fig. 6 portrays the RT emission spectra of $Bi_{4-x}Eu_xTi_3O_{12}$ pellets, under continuous excitation at 525 nm ($^7F_0$–$^5D_1$). In the range of 570–720 nm the strongest bands correspond to radiative transitions from the $^5D_0$ to the ^7F_j ($j = 0$–4) levels of the Eu^{3+}. The spectra shape is explained considering that. Whenever the Eu ions occupy sites with low symmetry, their emission spectrum may include dipole-electric lines such as the $^5D_0$–$^7F_{0,2,4}$. The fluorescence intensity of the $^5D_0$–$^7F_2$ transition is determined only by the $\Omega_2\langle\|U^{(2)}\|\rangle$ in the expression for the strength of transition in Judd–Ofelt theory.[8] Where Ω_2 is one phenomenological parameter and $\langle\|U^{(2)}\|\rangle$ is one of the reduced tensor operators in Judd–Ofelt theory.[9,10] The $^5D_0$–$^7F_2$ transition is very sensitive to the variation of environment of Eu^{3+} ions.[11,12] And their relative intensity gives the asymmetry degree of Eu^{3+} ion environment.[13] The $^5D_0$–$^7F_1$ transition, which is a magnetic dipole, is always observed and its intensity is almost independent of the symmetry site. Therefore, it is generally admitted that the fluorescence intensity ratio $R = I(^5D_0–^7F_2)/I(^5D_0–^7F_1)$ indicates the degree of asymmetry in the vicinity of europium ions. However, it must be underlined that the covalence degree of Eu–O bond brings its own contribution to the $^5D_0$–$^7F_2$ transition intensity by modulating the admixture of the $4f^65d$ odd states in the $4f^6$ states.[13] Values for *R* in $Bi_{4-x}Eu_xTi_3O_{12}$ pellets are shown in Fig. 7(a). The fluorescence intensity ratio (*R*) gives information on the $Bi_{4-x}Eu_xTi_3O_{12}$ structure, and its variation is related to the structural changes in the vicinity of the Eu ions. Specifically it is possible to use the Eu^{3+} ion as a probe of the crystalline structure average as a function of *x*. Then, our spectroscopic data shown in Fig. 7(a) seem to reveal that the Eu^{3+} ions occupy different crystallographic sites in the $Bi_{4-x}Eu_xTi_3O_{12}$ series. Lifetime measurements performed in $Bi_{4-x}Eu_xTi_3O_{12}$ pellets, revealed that Eu^{3+} luminescence decay was purely exponential. The results obtained are shown in Fig. 7(b). From the data presented in this figure, we observed that the value, for the characteristic decay time τ, reaches its maximum excitation at $x = 0.8$ via the $^7F_0$–$^5D_1$ transition (525 nm). Also, the europium ions are located in sites selectively excited at 370 and 525 nm with different lifetimes (Fig. 7(b)). Moreover, as expected, each site has a different environment as the *R* ratio suggests in Fig. 7(a), i.e. the difference in lifetime for each *x* ($x > 0.05$), confirms the existence of different crystallographic sites for the Eu^{3+}, probably these different sites correspond to the substitution at both Bi^{3+} sites: the $(Bi_2O_2)^{2+}$ and the $(Bi_2Ti_3O_{10})^{2-}$ pseudo-perovskite layers.

Currently, time resolved spectroscopy experiments are being conducted in our laboratory in order to get a better understanding on the crystallographic Eu^{3+} substitution sites. Time resolved spectra give information on the energy transfer process between ions. It is, then possible, to determine the first order environment of Eu. We expect that each site will have a specific environment and thus assign univocally each of them to specific positions in the crystalline structure of the $Bi_{4-x}Eu_xTi_3O_{12}$.

4. Conclusions

A solid solution with formula $Bi_{4-x}Eu_xTi_3O_{12}$ ($0 \leq x \leq 1.2$) was synthesized by coprecipitation route, lattice parameters *a* and *b* become similar as the Eu^{3+} content increases in the solid solution, being practically equal in the solubility limit composition at $x = 1.2$.

An exponential behavior of the Eu^{3+} luminescence decay was observed in the lifetime measurements performed in $Bi_{4-x}Eu_xTi_3O_{12}$ pellets. This fact corresponds to a non-energy transfer decay process.

The lifetime behavior and the *R* factor suggest that the Eu^{3+} ions occupy at least two crystallographic sites with different point symmetry in the $Bi_{4-x}Eu_xTi_3O_{12}$ series, generating an important global change in the structure of the solid solution from $x = 0.6$. Further high resolution spectroscopy work should been done in order to know which sites are occupied by Eu^{3+} in the structure.

Acknowledgements

We thank for the financial support extended by DGAPA, UNAM, PAPIIT No. IN103603, CONACYT-SEP-2004-CO1-47541 and CYTED PI.VIII-13 PROALERTA Project.

References

1. Scott, J. F. and Paz de Araujo, C. A., Ferroelectric memories. *Science*, 1989, **246**, 1400–1405.
2. Kingon, A., Device physics: memories are made of . . .. *Nature*, 1999, **401**, 658–659.
3. Noguchi, Y., Miyayama, M. and Kudo, T., Direct evidence of A-site strontium bismuth tantalate and its enhanced ferroelectric properties, *Phys. Rev. B*, 2001, **63**, 214102, 1–5.
4. Yong-Il, K., Mi Ku, J. and Seong Ihl, W., Structural study of $Ba_4Ti_3O_{12}$ using neutron diffraction study. *J. Mater. Sci. Lett.*, 2003, **22**, 1655–1657.
5. Hervoches, C. H. and Lightfoot, P., A variable-temperature powder neutron diffraction study of ferroelectric $Bi_4Ti_3O_{12}$. *Chem. Mater.*, 1999, **11**, 3359–3364.
6. Shannon, R. D., Revised effective ionic radii and systematic of interatomic distances in halides and chalcogenides. *Acta Crystllogr. A*, 1976, **A32**, 751–761.

7. Boulon, G., Moine, B. and Bourcet, J.-C., Spectroscopic properties of $^3P_1$ and $^3P_0$ excited states of Bi^{3+} ions in germanate glass. *Phys. Rev. B*, 1980, **22**, 1163–1169.
8. Wever, M. J., In *Optical Properties of Ion in Crystal*, ed. H. M. Crosswhite and H. M. Moos. Interscience, New York, 1967, p. 467.
9. Judd, B. R., Optical absorption intensities of rare-earth ions. *Phys. Rev.*, 1962, **127**, 750–761.
10. Ofelt, G. S., Intensities of crystals spectra of RE ions. *J. Chem. Phys.*, 1962, **37**, 511–520.
11. Oomen, E. W. J. L. and van Dongen, A. M. A., Europium (III) in oxide glasses: dependence of the emission spectrum upon glass composition. *J. Non-Cryst. Solids*, 1989, **111**, 205–213.
12. Nageno, Y., Takebe, H., Morinaga, K. and Izumitani, T., Effect of modifier ions on fluorescence and absorption of Eu^{3+} in alkali and alkaline earth silicate glasses. *J. Non-Cryst. Solids*, 1994, **169**, 288–294.
13. Zahir, M., Olazcuaga, R., Parent, C., Le Flem, G. and Hagenmuller, P., A structural interpretation of the Pb^{2+}, Eu^{3+} and Nd^{3+} optical spectra in doped sodium borate glasses. *J. Non-Cryst. Solids*, 1985, **69**, 221–229.