

# Effect of transition metal ions on the development of nanocrystalline phase and optical properties in the BaO–B<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> system

S.A.M. Abdel-Hameed, M.A. Azooz \*

*Glass Research Department, National Research Center, Dokki, Cairo, Egypt*

Received 5 September 2007; received in revised form 15 October 2007; accepted 25 January 2008

Available online 23 April 2008

## Abstract

Transparent glass–ceramics were prepared from the BaO–B<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> system doped with definite amounts of different transition metals. X-ray diffraction analysis revealed the crystallization of BaB<sub>8</sub>O<sub>13</sub> and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> phases according to the transition metal added. It was found that Mn ions enhance the crystallization of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> while other transition metals ions enhance BaB<sub>8</sub>O<sub>13</sub>. SEM revealed nanocrystalline phases in uniform texture. Absorption and transmission spectra were measured for glasses and the corresponding transparent glass–ceramics.

© 2008 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

**Keywords:** C. Optical properties; Transparent; Nanophase glass–ceramics; Transition metals

## 1. Introduction

Transparent glass–ceramics have a wide spectrum of applications including active and passive optical applications that related to the possibility of doping these materials with transition metal or rare-earth ions. Such applications include solar collectors, upconversion devices, laser active and passive media [1–4]. Also the knowledge of spectroscopic properties of transition metal or rare-earth ions in different glass–ceramic matrices is very important for their applications in optics [5]. Among materials used, BaB<sub>8</sub>O<sub>13</sub> which is expected to be a suitable host for the luminescence of divalent lanthanide ions [6].

Recently microwave dielectric materials have been extensively investigated because of their growing potential for applications in mobile communication systems as well as in satellite broadcasting system [7–11]. The desirable characteristics of the microwave materials include low dielectric loss, high quality factor, high dielectric constant and small temperature coefficient of resonant frequency [12,13].

Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> was one of the most common high-Q dielectric materials used in the microwave range. It has been first

reported by Jonker and Kwestroo [14] and investigated as microwave materials by O'Bryan and Plourde et al. in the 1970s [15–18]. It possesses superior dielectric properties for microwave resonator applications [16,17]. It has a good quality factor (8000 at a frequency of 4 GHz), a high dielectric constant (39.8), and a low temperature coefficient ( $T_f = 2 \text{ ppm } ^\circ\text{C}^{-1}$ ) [19]. So it could eventually work as a kind of superior resonator material.

It is well known that the formation of the single phase of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> is very difficult; it can only be formed within a very narrow range of Ba/Ti ratio close to 2:9 [20].

Most all the previous work studied the effect of inducing rare-earth elements in optical properties of BaB<sub>8</sub>O<sub>13</sub>. Here, we try to study the effect of adding different transition metals on the crystallization and optical properties of the BaO–B<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> system to obtain the desired BaB<sub>8</sub>O<sub>13</sub> and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> phases.

## 2. Experimental

For this study we have chosen glasses of the composition 37.41BaO–54.22B<sub>2</sub>O<sub>3</sub>–8.31TiO<sub>2</sub> (mol%). 0.0025 mol% of NiO, CuO, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, CoO and Cr<sub>2</sub>O<sub>3</sub> were introduced above the total of 100%. The raw materials were of reagent grade quality. Batches for producing 100 g of glass were melted in a platinum crucible in a laboratory electric

\* Corresponding author.

E-mail address: [moenis9@yahoo.com](mailto:moenis9@yahoo.com) (M.A. Azooz).

furnace at 1350 °C for 2 h with stirring. The glass was poured onto a metal plate and annealed at 450 °C. One-stage heat treatment at 595 °C for 30 h with heating rate 5 °C/min was carried out [21] for well polished samples. Glass–ceramics samples prepared according to this procedure described before were transparent, and the crystallized phases on their surfaces were identified by X-ray diffraction analysis using Cu-tube diffractometer (Phillips, PW1390).

The surfaces of glass–ceramics samples were examined with a scanning electron microscope (SEM), type JEOL-840A electron probe microanalyzer after coating with 5- $\mu$ m thickness gold layers sputtered over the surfaces.

Optical transmission in the UV–vis region was analyzed using a JASCO V350 spectrophotometer.

### 3. Results and discussion

The XRD study of all the investigated glass–ceramics Fig. 1 shows the crystallization of  $\text{BaB}_8\text{O}_{13}$  in the base glass. The amount of this crystalline phase decreases (where the peak intensity become lower) by adding 0.0025 mol% of CoO.  $\text{Cr}_2\text{O}_3$  addition enhances the crystallization process of  $\text{BaB}_8\text{O}_{13}$  more than CoO but it is still lower than in the base glass. Addition of CuO or NiO leads to better development of the crystalline phase, where more identified sharp peaks are observed (the effect of NiO is slightly higher than CuO).  $\text{Fe}_2\text{O}_3$  has a superior effect on the amount and development of the crystallization of the  $\text{BaB}_8\text{O}_{13}$ .

While all the above transition metals enhance the crystallization of  $\text{BaB}_8\text{O}_{13}$ , adding  $\text{MnO}_2$  is observed to enhance the crystallization of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ , and  $\text{V}_2\text{O}_5$  depresses the crystallization process, where only a hump appears in the crystallization region in X-ray analysis (Fig. 1).

The ability of  $\text{MnO}_2$  to crystallize  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  more than  $\text{BaB}_8\text{O}_{13}$ , may be due to the similarity in cell parameter between  $\text{MnO}_2$  ( $c = 14.62$ ) and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  ( $a = 14.81$ ).

It is noticed that all the transition metals are still in their valence states as they were added and did not converted to the

higher valence states. This may be due to the fact that, the  $\text{BaB}_8\text{O}_{13}$  structure is built up of two separate interlocking three-dimensional infinite networks as triborate and pentaborate groups from triangles  $\text{BO}_3$  and  $\text{BO}_4$  tetrahedral units [22]. This structure is considered to be a rigid framework that can prevent the divalent ions from being easily attacked by oxygen even when they are heated at high temperature in air [23].

SEM images of selected samples of glass–ceramics Fig. 2 shows, in general, homogenous, ultrafine grain microstructure. It is noticed that the grain sizes of all crystals are very small and ranged between 150 and 300 nm.

The crystal size in glass–ceramic containing  $\text{Co}^{2+}$  is very small, about 150 nm; it increases in the sample containing  $\text{Cr}^{3+}$  to about 300 nm, while the crystallinity is largely increased and becomes overlapped and interlocked by adding  $\text{Fe}^{+3}$  with grain size of about 150 nm.

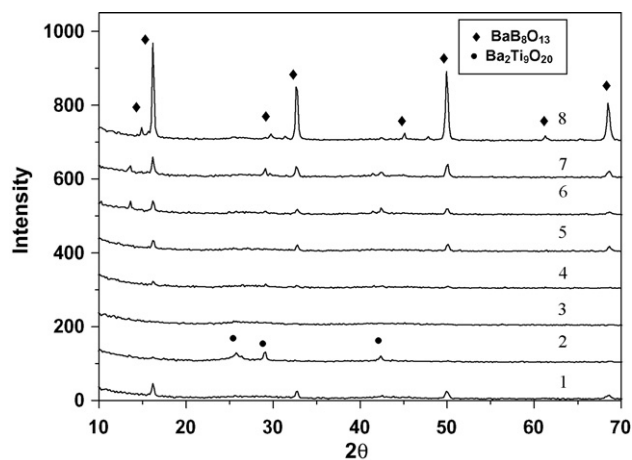


Fig. 1. XRD patterns of the samples heat-treated at 595 °C/30 h: (1) base, (2) with  $\text{MnO}_2$ , (3) with  $\text{V}_2\text{O}_5$ , (4) with CoO, (5) with  $\text{Cr}_2\text{O}_3$ , (6) with CuO, (7) with NiO and (8) with  $\text{Fe}_2\text{O}_3$ .

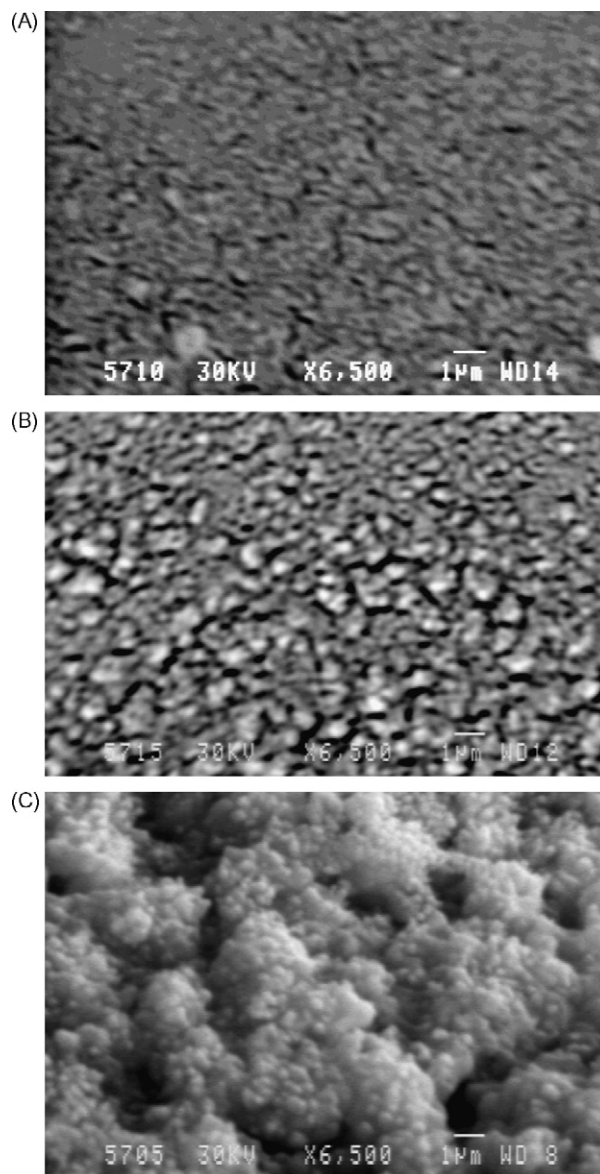


Fig. 2. SEM of samples heat-treated at 595 °C/30 h: (A) with CoO, (B) with  $\text{Cr}_2\text{O}_3$  and (C) with  $\text{Fe}_2\text{O}_3$ .

It is known that the glass–ceramics materials may transmit visible light if either are of the following conditions are operative: (i) the crystallites of all species are much smaller than the wavelength of visible light, or (ii) the optical anisotropy (birefringence) within the crystals and refractive index difference between crystals and glass are very small [24]. Here the crystal size is smaller than 300 nm.

### Optical properties

The optical UV–vis absorption spectra of the undoped and the various transition metal ions-doped  $\text{BaO–B}_2\text{O}_3\text{–TiO}_2$  glasses and their corresponding transparent glass–ceramics are shown in Fig. 3. From the figure it can be seen that:

- For the undoped glass and its transparent glass–ceramic derivative, there is an ultraviolet cutoff at about 330 nm and there are no obvious bands in the visible region.
- For glass containing 0.0025 mol%  $\text{CoO}$ , the ultraviolet cutoff remains at 330 nm as observed in the parent glass but there are three visible bands at about 520, 590 and 640 nm. The spectrum of the glass–ceramic derivative reveals a slight shift in the ultraviolet cutoff to longer wavelength (340 nm) and the intensities of all the absorption bands in the visible region slightly increase. These visible bands are due to  $\text{Co(II)}$  in octahedral and tetrahedral coordination, where cobalt is known to be normally existing in glass as divalent  $\text{Co}^{2+}$  ions in two coordination states  $\text{CoO}_4$  and  $\text{CoO}_6$  [25].
- For glass containing 0.0025 mol%  $\text{Fe}_2\text{O}_3$ , the ultraviolet cutoff shifts to longer wavelength (400 nm) and no obvious peaks are seen in the visible region. Its glass–ceramic derivative shows the same spectral feature as the original parent glass. The Fe-doped glass reveals before heat treatment strong characteristics in the UV and near-visible spectrum characteristic for iron species, namely  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.
- For glass containing 0.0025 mol%  $\text{V}_2\text{O}_5$ , the UV-cutoff is located at about 360 nm, and there are two weak visible bands at about 425 and 625 nm. For its glass–ceramic derivative, there are no obvious changes along the spectrum from 200 to 1000 nm. It is generally accepted that vanadium can exist in most glasses under atmospheric conditions in three possible valences, the  $\text{V}^{3+}$ ,  $\text{V}^{4+}$  and  $\text{V}^{5+}$  states. The trivalent vanadium ions seem to exist as highly distorted octahedral coordination with oxygen ions and usually show two characteristic visible bands at 425 and 625 nm and a third possible band in the ultraviolet region. The pentavalent ( $\text{V}^{5+}$ ) corresponds to the  $d^0$  configuration and will not give rise to d–d transitions but rather a charge transfer band in the UV region [26].
- For glass containing 0.0025 mol%  $\text{CuO}$ , the UV-cutoff is observed at about 360 nm, and a very broad visible band centered at about 760 nm could be identified, while the glass–ceramic spectrum is overlapped on the spectrum of its glass. The single absorption band at 760 nm can be assigned to cupric ions in octahedral state of symmetry and

corresponding to the transition  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ . It is noted that this band is broad and asymmetric, i.e., it consists of several overlapping symmetric bands due to the tetragonal distortion caused by Jahn–Teller effect [27].

- For glass containing 0.0025 mol%  $\text{Cr}_2\text{O}_3$ , the UV-cutoff shifts to longer wavelength at about 440 nm, and a very broad visible band centered at about 650 nm is also observed. The glass–ceramic spectrum is very close and completely overlaps its glass spectrum. The chromium ions can exist in glass in two forms  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$ , the  $\text{Cr}^{3+}$  ions are surrounded by six ligands of oxygen arranged in octahedral symmetry and show the two absorption bands in the visible region at 420 and 650 nm [28]. The  $\text{Cr}^{6+}$  ions form  $\text{CrO}_4^{2-}$  groups with a possibility of polymerization as polychromates and give two absorption bands in the UV at about 270 and 370 nm [28].
- For glass containing 0.0025 mol%  $\text{MnO}_2$ , the UV-cutoff at about 340 nm, and there is a broad band in the visible region centered at about 480 nm, while its glass–ceramic spectrum shows the same as the glass spectrum. Manganese is known to exist mostly as divalent and trivalent ions in glasses.  $\text{Mn}^{3+}$  ions usually give a single broad band under atmospheric or oxidizing conditions at about 450–490 nm and is attributed to the spin allowed transition  ${}^5\text{T}_5(\text{D}) \rightarrow {}^5\text{T}_3(\text{D})$  [29].
- For glass containing 0.0025 mol%  $\text{NiO}$ , the UV-cutoff is observed at about 340 nm and there are two visible bands, a sharp one at about 435 nm and a broad band at about 850 nm, and for its glass–ceramic derivative the UV-cutoff is shifted to longer wavelength and reaches to 360 nm with no obvious changes in the two other bands. Nickel exists in glass only as divalent ions. With respect to this divalent metal ion in glass, it produces various colors when introduced into different base glasses. These colors are caused mainly by the occurrence of two different coordination states namely  $\text{NiO}_4$  and  $\text{NiO}_6$  which are in mutual equilibrium [30]. The absorption band at about 430 nm is due to the transition  ${}^3\text{T}_2(\text{F}) \rightarrow {}^3\text{T}_4(\text{P})$  of nickel ion in the octahedral coordination [30].

Fig. 4 shows the transmittance (%) spectra of the undoped and various transition metal ions doped— $\text{BaO–B}_2\text{O}_3\text{–TiO}_2$  glasses and their derivative glass–ceramics. It is seen that the UV-cutoff for all samples shows the same cutoff as the optical absorption spectra.

The transmittance percent for the parent glass–ceramic is slightly lower than the parent glass. The same behavior is shown in all the transition metal-doped glass–ceramic derivatives except in the case of V-doped sample where, the transmittance percent of glass is about 60% in the region from 450 to 1000 nm, while the transmittance of its glass–ceramic reaches to about 80% in the same wavelength range.

From the spectral results it is obvious that the sample containing vanadium has higher transmittance values than the other transition metals-doped samples when the V-sample is

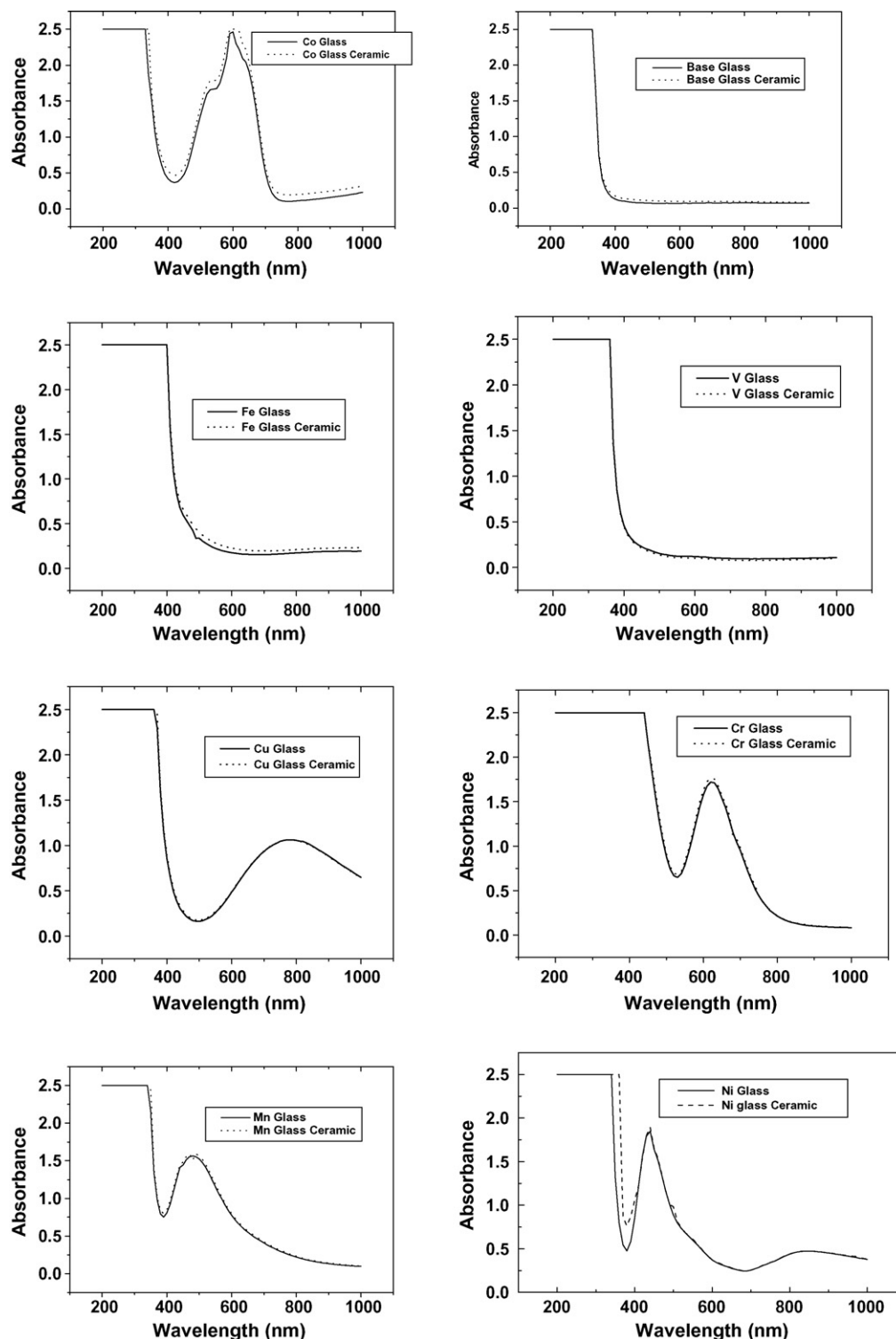


Fig. 3. The optical absorption spectra of the studied glass and its glass–ceramic containing different transition metal ions.

converted to glass–ceramic. The undoped transition metal sample still shows higher transmittance than all-doped samples after converting to glass–ceramics. The reason for this disparity is that Rayleigh scattering only applies to systems in which the scattering centers are non-interacting and interference between

scattered photons is not significant. This is not the case for most transparent glass–ceramics, or phase-separated glasses in which the scattering centers are spaced of the order of 10–50 nm or 10 times smaller than the wavelength of visible light [31].

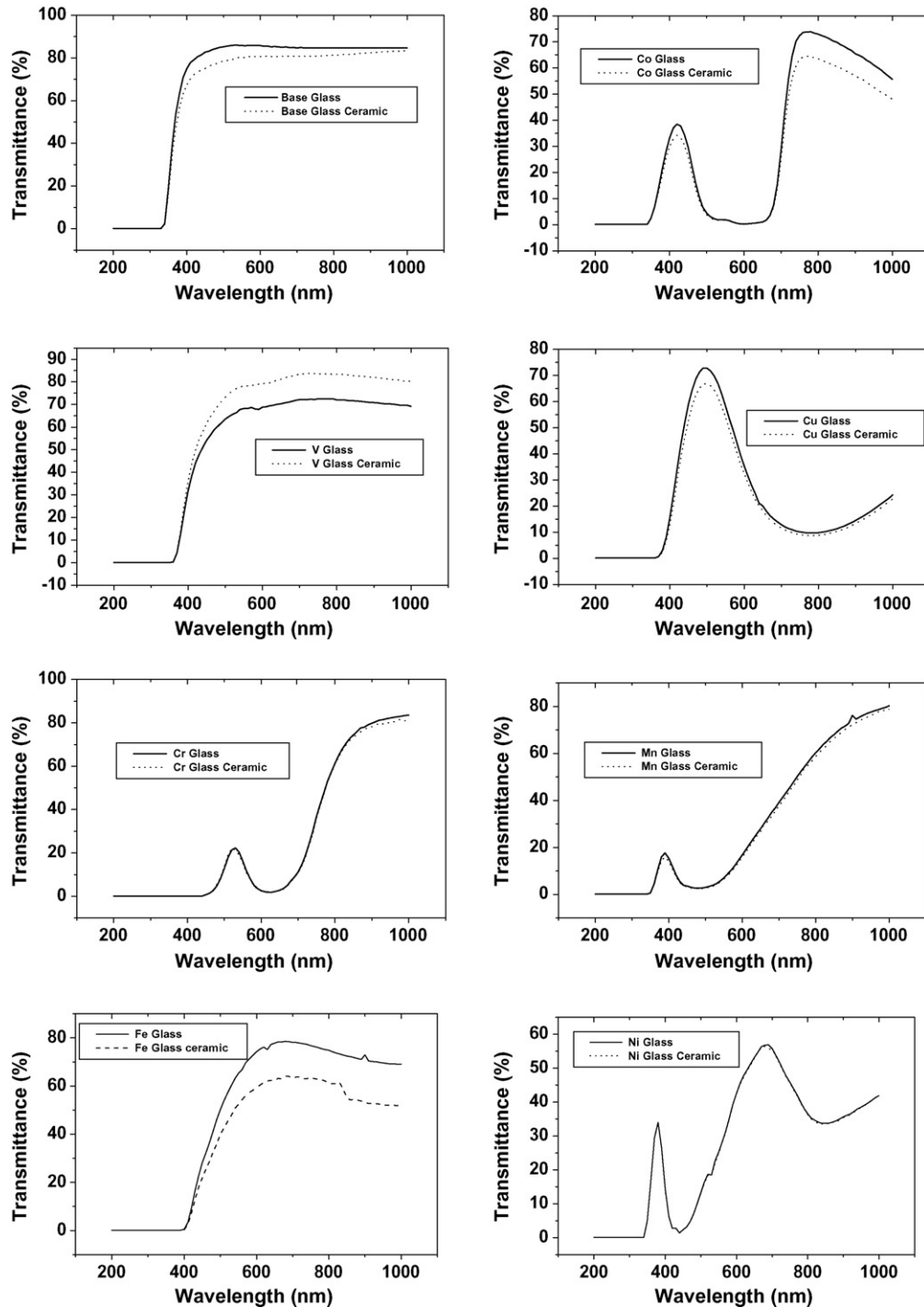


Fig. 4. The transmittance spectra of the studied glass and its glass–ceramic containing different transition metal ions.

#### 4. Conclusion

Transparent nanocrystalline glass–ceramics were prepared from the  $\text{BaO-B}_2\text{O}_3\text{-TiO}_2$  system doped with definite amount of different transition metals. Nanocrystals of  $\text{BaB}_8\text{O}_{13}$  and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  with uniform texture were crystallized according to the transition metal added. It was found that  $\text{Mn}^{2+}$  enhances the crystallization of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  while other transition metals

enhance  $\text{BaB}_8\text{O}_{13}$ .  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  enhance the crystallization process, respectively. Absorption and transmittance spectra were measured for glasses and the corresponding transparent glass–ceramics. The base has the highest transmittance than the transition metal ions-doped samples in both glass and glass–ceramic and the vanadium-doped glass–ceramic has the higher value of transmittance than other transition metal ion-doped glass–ceramic.

## References

- [1] K. Tanaka, T. Mukai, T. Ishihara, K. Hirao, N. Soga, S. Sogo, M. Ashida, R. Kato, *J. Am. Ceram. Soc.* 76 (1993) 2839.
- [2] G.H. Beall, L.R. Pinckney, *J. Am. Ceram. Soc.* 82 (1999) 5.
- [3] I. Shoji, S. Kurimura, Y. Sato, J. Saikawa, T. Taira, A. Ikesue, K. Yoshida, Advanced solid-state lasers, in: OSA Technical Digest, Optical Society of America, Washington, DC, 2000, pp. 174.
- [4] R. Boiko, A. Okhrimchuk, A. Shestakov, OSA trends in optics and photonics, in: W.R. Bosenberg, M.M. Fejer (Eds.), *Advanced Solid Absorption State Lasers*, vol. 19, Optical Society of America, Washington, DC, 1998, p. pp. 185.
- [5] A.M. Malyarevich, I.A. Denisov, Y.V. Volk, K.V. Yumashev, O.S. Dymshits, A.A. Zhilin, Nanosized glass–ceramics doped with transition metal ions: nonlinear spectroscopy and possible laser applications, *J. Alloys Compd.* 341 (2002) 247.
- [6] Q. Zeng, Z. Pei, Q. Su, S. Lu, Luminescence properties of  $\text{Sm}^{2+}$  in barium octaborates ( $\text{BaB}_8\text{O}_{13} \cdot \text{Sm}^{2+}$ ), *J. Lumin.* 82 (1999) 241.
- [7] H. Sreemoolanadhan, M.T. Sebastian, P.M. Phanan, *Brit. Ceram. Trans.* 95 (1996) 79.
- [8] K. Wakino, T. Nishikawa, Y. Ishikawa, *Brit. Ceram. Trans.* 89 (1990) 39.
- [9] X.M. Chen, J.S. Yang, *J. Eur. Ceram. Soc.* 19 (1999) 139.
- [10] J.P. Mercurio, M. Manier, *B. Frit. Mater. Lett.* 8 (1989) 112.
- [11] A. Silva, F. Azough, R. Freer, C. Leach, *J. Eur. Ceram. Soc.* 20 (2000) 2727.
- [12] D. Kajfez, P. Guillon, *Dielectric Resonators*, Artech House, Norwood, MA, 1986.
- [13] E.A. Nenasheva, N.F. Kartenko, *J. Eur. Ceram. Soc.* 21 (2001) 2697.
- [14] G.H. Jonker, W. Kwestroo, *J. Am. Ceram. Soc.* 41 (1958) 390.
- [15] H.M. O'Bryan Jr., J. Thomson Jr., *J. Am. Ceram. Soc.* 57 (1974) 522.
- [16] H.M. O'Bryan Jr., J. Thomson Jr., J.K. Plourde, *J. Am. Ceram. Soc.* 57 (1974) 450.
- [17] J.K. Plourde, D.F. Linn, H.M. O'Bryan Jr., J. Thomson Jr., *J. Am. Ceram. Soc.* 58 (1975) 418.
- [18] H.M. O'Bryan Jr., J. Thomson Jr., *J. Am. Ceram. Soc.* 66 (1983) 66–68.
- [19] W. Sea-Fue, C. Chuang-Chung, W. Chai-Hui, Effects of  $\text{B}_2\text{O}_3$  on the phase formation of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  ceramic, *Mater. Chem. Phys.* 79 (2003) 256.
- [20] W. Shunhua, W. Guoqing, Z. Yushuang, H. Su,  $\text{BaO-TiO}_2$  microwave ceramics, *Eur. Ceram. Soc.* 23 (2003) 2565.
- [21] F.H. Margha, M.Sc. Thesis, Ain Shams University, 2004.
- [22] J. Krogh-Moe, *Acta Crystallogr.* B25 (1969) 2153.
- [23] Q. Zeng, Z. Pei, S. Wang, Q. Su, S. Lu, Luminescence of rare earth<sup>2+</sup> (RE = Sm, Yb) in barium octoborate, *Mater. Res. Bull.* 34 (Nos. 12/13) (1999) 1837.
- [24] G.H. Beall, L.R. Pinckney, Nanophase glass–ceramics, *J. Am. Ceram. Soc.* 82 (1) (1999) 5.
- [25] F.H. ElBatal, M.S. Selim, M.A. Azoz, S.Y. Marzouk, *Phys. B* 398 (2007) 126.
- [26] S.Y. Marzouk, F.H. ElBatal, *Nucl. Instrum. Method Phys. Res. B* 248 (2006) 90.
- [27] A.A. Ahmed, G.M. Ashour, in: A. Bishay (Ed.), *Recent Advances in the Science and Technology of Materials*, vol. 2, Plenum Press, NY, 1974 p. 83.
- [28] G.H. Sigel Jr., in: M. Tomozawa, R.H. Doremus (Eds.), *Treatise on Materials Science and Technology*, vol. 12, Academic Press, NY, USA, 1977, pp. 35–89.
- [29] F.H. El Batal, M.A. Azoz, S.Y. Marzouk, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B* 47 (2006) 588.
- [30] W.A. Weyl, *Coloured Glasses Monograph* Reprinted by Dawson's of Pall Mall, London, 1959.
- [31] S.A.M. Abdel-Hameed, N.A. Ghoniem, E.A. Saad, F.H. Margha, Effect of fluoride ions on the preparation of transparent glass–ceramics based on crystallization of barium borates, *Ceram. Int.* 31 (2005) 499–505.