Journal of Alloys and Compounds 495 (2010) 288–291

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Preparation of Mn doped $Li_2B_4O_7$ nanoparticles by glass quenching

S. Kar, Sunil Verma, K.S. Bartwal*

Laser Materials Development & Devices Division, Raja Ramanna Centre for Advanced Technology, Indore 452013, MP, India

ARTICLE INFO

Article history:
Received 8 January 2010
Received in revised form 1 February 2010
Accepted 6 February 2010
Available online 13 February 2010

PACS:
81.10.Fq
81.10.h

Keywords:
Lithium tetraborate
Glass transition
XRD
Electron diffraction
Transmittance

ABSTRACT

Lithium tetraborate, $Li_2B_4O_7$ (LTB) glass samples doped with 1 mol% Mn were prepared by glass quenching technique. The prepared Mn:LTB glass samples were annealed at different temperatures. These samples remain amorphous up to the temperature of 470 °C and starts transforming into crystalline state above this temperature. Powder X-ray diffraction of the sample carried out after each annealing experiment exhibits the structural change with respect to the temperature. Differential thermal analysis also suggests that the crystallization was complete at 550 °C. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results confirm crystallization in the samples on annealing. The average size of the nanoparticles was found in the range of ~20–30 nm.

1. Introduction

Lithium tetraborate (LTB) glass and glass ceramics have wide potential interests for the advantages over their crystalline counterpart. LTB glass ceramics are considered as one of the materials for solid-state battery application with fast ion conduction [1]. Therefore, LTB in the form of crystal and glass is an active area of research as a functional material. Recently, the interests have focused on understanding and developing techniques for fabricating materials with sizes in the nanometer range. The electrical and the mechanical properties of the nanocrystalline materials are much different from those of large grain materials. Lithium tetraborate ($Li_2B_4O_7$) crystal is also an important material for nonlinear applications [2–4]. It is extensively used for frequency conversion in the ultraviolet region, piezoelectric actuator and surface acoustic wave (SAW) substrate [5,6]. It has been reported that the tetraborate materials doped by rare-earth ions are promising quantum electronic materials [7,8]. $Li_2B_4O_7$ single crystals can be used as pyroelectric temperature sensors [9]. It is a non-ferroelectric and piezoelectric material and belongs to a tetragonal symmetry 4 mm with a polar axis along the crystallographic *c*-axis. The preparation of LTB glass by quenching method is quite simple and highly efficient. The crystallite sizes could be controlled by controlling the process parameters, e.g. annealing temperature and the quenching speed during crystallization [10]. Specifically, when the main glassy phase of micron-size glass particles transforms into the nanocrystalline phase by the external heat energy, the surface energy of the particles, the heat conductivity of materials and the directional anisotropy of nucleation and growth can be different and affect the crystallization mechanism. LTB can also be used as thermoluminescent dosimetry of X-ray, gamma, and neutron radiations [11,12]. LTB contains Li and B, which possess large neutron capture cross-section. Effective atomic number for lithium tetraborate is 7.23 which is close to the value for soft tissue (7.22) composition $C_5H_{14}O_{18}N$ [13]. Mn:$Li_2B_4O_7$ have high thermoluminescence (TL) efficiency and can be used for low dose measurement [14].

In this paper we report the preparation of Mn doped LTB nanoparticles by glass quenching technique. The prepared nanoparticles were characterized by powder XRD, scanning electron microscopy and transmission electron microscopy. The transmittance in visible range was also monitored.

2. Experimental details

Lithium tetraborate ($Li_2B_4O_7$) is congruently melting composition with a melting point of 917 °C. High purity chemicals Li_2CO_3, B_2O_3 and MnO_2 (Aldrich make) were used for the synthesis of Mn doped $Li_2B_4O_7$ glass. The stoichiometric composition ($Li_2B_4O_7$) was weighted and thoroughly mixed in a ball mill. The mixed powder was then kept for solid-state reaction at 800 °C for 24 h in a platinum crucible. The charge kept in a platinum crucible covered with a lid was placed in a resistive heated furnace controlled by Eurotherm PID temperature controller (902 P) for melting. The melt was overheated to 1150 °C to remove traces of water and carbon dioxide present in the melt. Due to high evaporation rate of B_2O_3, 1 mol%

* Corresponding author. Tel.: +91 731 248 8656; fax: +91 731 248 8650.
E-mail address: bartwalks@yahoo.co.in (K.S. Bartwal).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.02.039

excess B_2O_3 was added in the starting composition. Homogenized melt was than poured into preheated stainless steel plate and pressed by another steel plate. The flat glass plates of dimensions 20–25 mm and 1–2 mm thicknesses were obtained. The quenched glass samples were polished properly by alumina powder for various studies. The crushed powder was taken to investigate the phase, crystalline structure and particle size using powder X-ray diffraction (XRD) with Cu Kα radiation at 1.5426 Å. The evolution of the crystalline structure of the LTB glass samples during the annealing process was recorded by taking powder XRD from these samples. Differential thermal analysis (DTA) was carried out to monitor the crystallization temperature. A small portion of the glass sample has been crushed properly for DTA analysis. The instrument SETARAM TG-92 thermal analyser was used for this study. Transmission spectra of the polished glass plates were taken using UV–VIS PC spectrophotometer. Scanning electron microscopy and transmission electron microscopy in high-resolution (HRTEM) mode were done to investigate the morphology, particle size and microstructure of the prepared nanoparticles. The sample for TEM observation was prepared by suspending the particles in ethanol by ultrasonification and drying a drop of the suspension on a carbon-coated copper grid. HRTEM was carried out employing Philips Tecnai G^2-20 (FEI) electron microscope operating at 200 kV.

3. Results and discussion

$Li_2B_4O_7$ (Mn:LTB) glass samples doped with 1 mol% Mn were prepared by quenching technique. The glass samples were annealed at various temperatures. The evolution of the crystalline structure of the Mn:LTB glass samples during the annealing process was recorded using powder X-ray diffraction (XRD). The diffraction patterns were taken for 2θ scan from 20 to 70 with a step of 0.02. Fig. 1 shows the XRD patterns taken for Mn:LTB samples recorded at various annealing temperatures. It is clear from the XRD patterns that the as quenched sample and the sample annealed at up to 470 °C are amorphous. After this temperature it has started showing the faint peaks for crystalline phase. Patterns taken at higher temperatures show the crystalline structure with single phase. However the grain size started increasing with higher annealing temperature as was expected. The well-resolved peaks are perfectly matching with JCPDS data for $Li_2B_4O_7$. There is no trace for the presence of any secondary phase in the sample. From powder X-ray diffraction pattern the effective crystallite size was calculated using full width half maxima (FWHM) approach on line broadening of XRD peaks. In a single line analysis the apparent crystallite size D was calculated from the relation $t = \lambda/B\cos\theta_B$. Crystallite size was found in the range of ~20–30 nm.

Differential thermal analysis (DTA) was employed to confirm the glassy nature of the as quenched samples and to find out the glass transition (T_g) and crystallization (T_c). The sample was heated up to 600 °C at a heating rate of 4 °C/min. Fig. 2 shows the DTA curve for as prepared Mn:LTB glass sample. The temperature assigned here as glass transition temperature (T_g) and crystallization temperature (T_c) is 491 °C and 545 °C respectively. The temperature difference between T_c and T_g represents the thermal stability in super cooled liquid region. This temperature difference between T_c and T_g is particle size dependant.

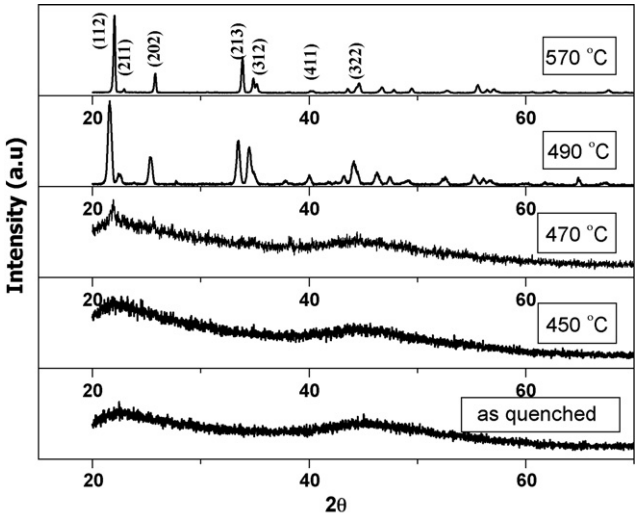

Fig. 1. XRD pattern for Mn:LTB glass samples annealed at various temperatures.

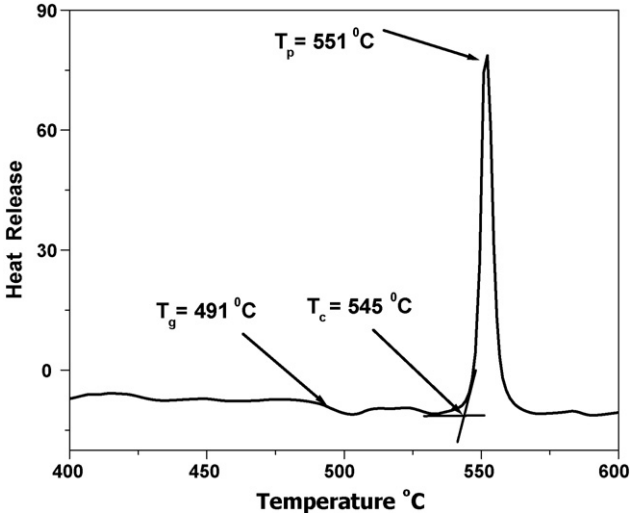

Fig. 2. Representative DTA curve for as prepared Mn:LTB sample.

Scanning electron microscopy (SEM) was done on the glass samples to monitor the glassy surface and the crystallite sizes of the samples. Fig. 3 shows the SEM micrographs taken from Mn:LTB samples annealed at 450 °C and 570 °C respectively. Fig. 3(a), the

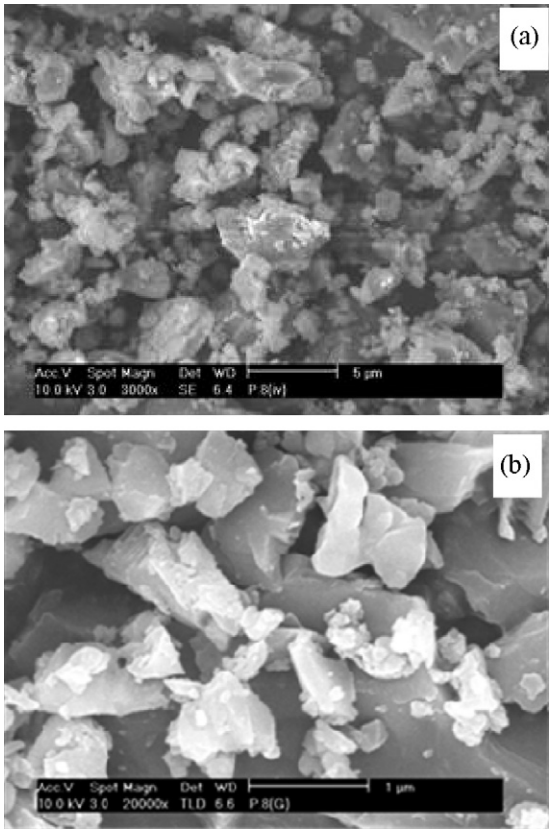

Fig. 3. Representative SEM images for Mn:LTB samples annealed at (a) 450 °C and (b) 570 °C.

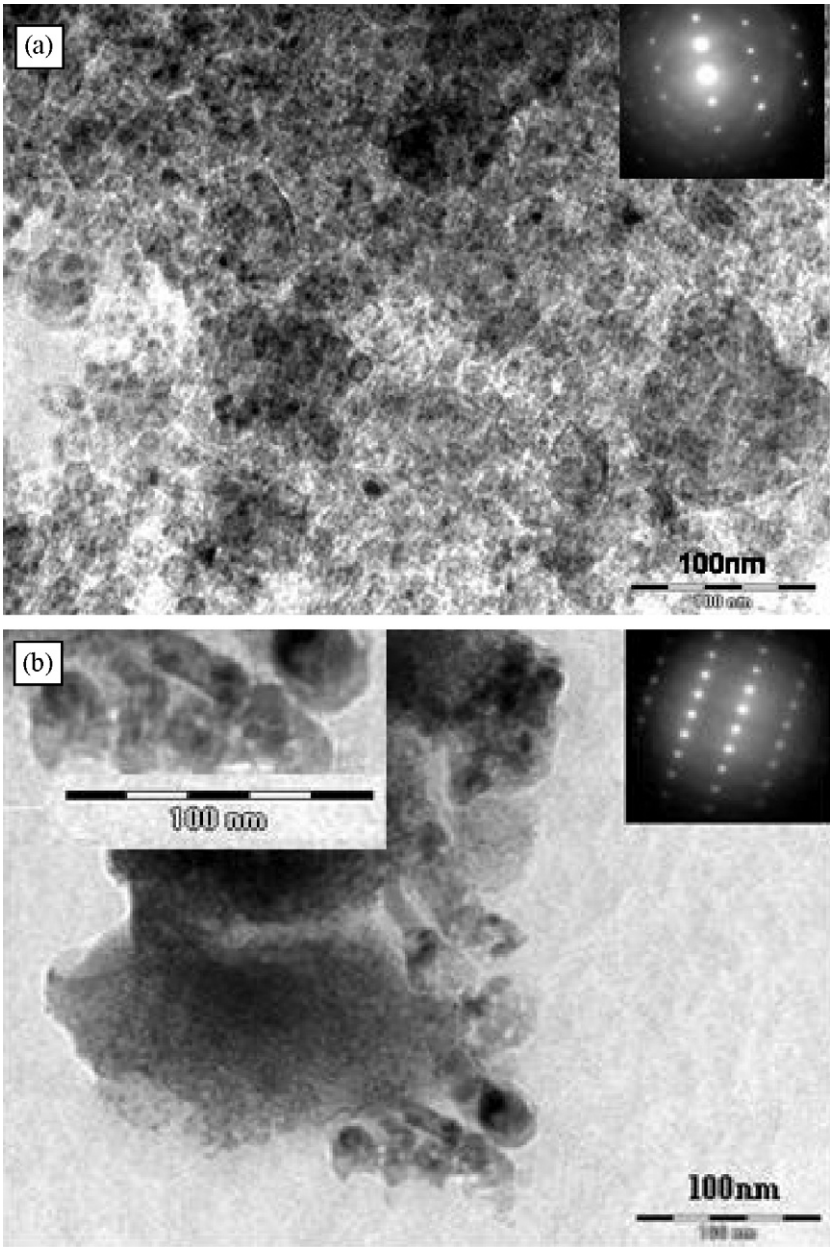

Fig. 4. HRTEM micrograph taken from Mn:LTB (a) annealed at 490 °C and (b) annealed at 570 °C. Inset shows the corresponding selected area diffraction patterns.

micrographs taken from the crushed sample annealed at 450 °C shows the larger size lump with grains which are indicative of glassy phase. The crystallite sizes in Fig. 3(b) observed were varying few tens of nm dispersed in glass matrix. High-resolution transmission electron microscopy (HRTEM) is a good tool to know the local structure, structural transformation and microstructural morphology of the polycrystalline material. HRTEM studies were conducted to investigate the microstructure and the crystalline size of the sample. Fig. 4(a) and (b) shows the representative HRTEM bright field micrographs for the glass samples annealed at 490 °C and 570 °C respectively. The micrograph shown in Fig. 4(a) is a clear indication of the transformation of the glass phase into polycrystalline phase. Inset in Fig. 4(a) shows the corresponding selected area diffraction (SAD) pattern. The faint diffuse scattering along with the main diffraction spots in SAD pattern indicates that the crystallite sizes are of few nanometres. On the other hand the samples annealed at higher temperatures increases in crystallite size have clear diffractions spots (Fig. 4(b)). Inset in Fig. 4(b) shows the magnified images of the nanoparticles and the corresponding selected area diffraction (SAD) pattern. The nanoparticles are clearly seen in the micrograph. The crystalline particle sizes were measured about 20–30 nm. The clear spots in SAD pattern along with the diffuse rings are clear indication of nanosize crystalline particles with single phase.

The samples were evaluated for their optical homogeneity. Transmission spectra of polished glass samples were taken in UV–vis–NIR region. Fig. 5 shows the representative transmission spectrum for Mn:LTB glass sample annealed at 490 °C. The transmittance of 80% was observed which is comparable to the single crystal sample. Significant dip in the absorption spectra at about 465 nm is due to the presence of Mn in the glass. It has been reported that the doping of Mn in $Li_2B_4O_7$ single crystals is not easy and homogeneous [4]. However, it seems that in case of glass it is easier and even higher concentration of Mn could also be incorporated. Since Mn doped LTB crystal has good thermoluminescence (TL) efficiency, therefore these nanoparticles can also be used for dosimeter

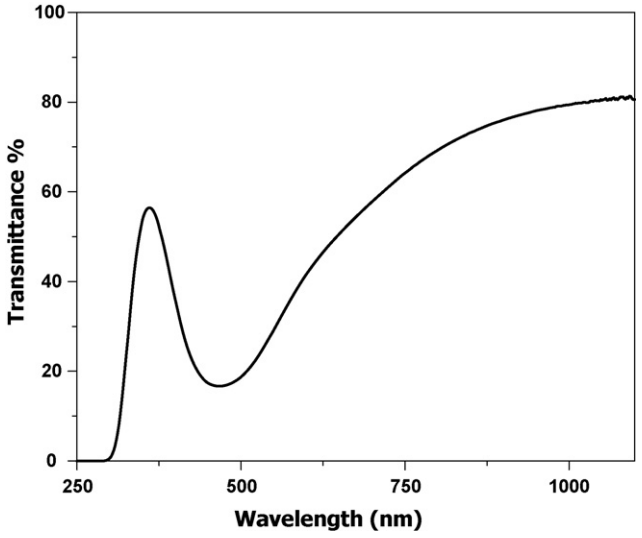

Fig. 5. Representative transmission spectrum for as quenched Mn:LTB sample.

applications. The detailed studies on their TL performances and comparison with the bulk single crystals are under progress.

4. Conclusions

Transparent Mn doped $Li_2B_4O_7$ glass was successfully prepared by simple glass quenching method. The evolution of the crystalline structure by annealing of the glass at different temperatures was monitored by powder XRD. The glass transition temperature (T_g) and crystallization temperature (T_c) were observed as 491 °C and 545 °C respectively. The transmittance of 80% was observed for the annealed sample. The sizes of the particles were measured from FWHM of the highly intense XRD peak was ~20–30 nm. Similar results were obtained from SEM and HRTEM. The particle sizes which are crucial and technologically important could be controlled by optimizing the annealing temperature and time duration during the crystallization.

References

[1] A.E. Aliev, I.N. Kholmanov, P.K. Khabibullaev, Solid State Ionics 118 (1999) 111–115.
[2] R. Komatsu, H. Iizuka, S. Uda, Jpn. J. Appl. Phys. 35 (1996) 5042–5045.
[3] T. Sato, H. Abe, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 45 (1998) 1506–1516.
[4] S. Kar, S. Verma, K.S. Bartwal, Cryst. Res. Technol. 44 (2009) 305–308.
[5] S.J. Kim, J.E. Kim, Y.H. Rim, Y.S. Yang, Solid State Commun. 131 (2004) 129–133.
[6] R. Komatsu, T. Sugawara, K. Sassa, Appl. Phys. Lett. 70 (1997) 3492–3494.
[7] V.T. Adamiv, Ya.V. Burak, I.V. Kityk, J. Kasperczyk, R. Smok, M. Czerwihki, Opt. Mater. 8 (1997) 207–213.
[8] A. Majchrowski, I.V. Kityk, E. Mandowska, A. Mandowski, J. Ebothe, T. Lukasiewicz, J. Appl. Phys. 100 (2006) 53101–53104.
[9] M. Ono, M. Sakai, Y. Fujiwara, N. Wakatsuki, Proc. IEEE Ultrason. Symp. (1997) 1047–1051.
[10] S.J. Kim, J.E. Kim, H.W. Choi, Y.H. Rim, Y.S. Yang, Mater. Sci. Eng. B 113 (2004) 149–153.
[11] C. Furetta, P.S. Weng, Operation Thermoluminescent Dosimetry, World Scientific, London, 1998.
[12] K. Mahesh, P.S. Weng, C. Furetta, Thermoluminescence in Solids and its Applications New Technology, Ashford, Kent, UK, 1989.
[13] C.A. Jayachandran, Phys. Med. Biol. 16 (1971) 617–623.
[14] K.-S. Park, J.K. Ahn, D.J. Kim, H.K. Kim, Y.H. Hwang, J. Cryst. Growth 249 (2003) 483–486.