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Nonlinear-optical phases in strontium tetraborate–lead tetraborat system

Yu.S.Oseledchik, A.L.Prosvirnin, V.Yu.Lutsenko

Zaporozhye State Engineering Academy,
226 Lenin Ave., 69006 Zaporozhye, Ukraine

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The phase diagram of strontium tetraborate SrB_4O_7 — lead tetraborat PbB_4O_7 system was specified by means of improved DTA technique. Concentration dependence of phases formation, trigonal β or orthorhombic α, by low-temperature crystallization of the glasses $(1-x)\cdot SrB_4O_7-x\cdot PbB_4O_7$ ($0\le x\le 1$) was studied. Only the metastable trigonal phase $\beta-Sr_{1-x}Pb_xB_4O_7$ for concentration $x<0.2$ is crystallized. The both high nonlinear phases of strontium–lead tetraborates (d_{eff} ($\beta-Sr_{0.8}Pb_{0.2}B_4O_7$) ≈ d_{eff} (PbB_4O_7)) are perspective for use as the nonlinear-optical crystals components of glass-ceramic materials on the basis of strontium tetraborate–lead tetraborate system.

Путем улучшенной методики дифференциального температурного анализа уточнена фазовая диаграмма системы тетраборат стронция SrB_4O_7 — тетраборат свинца PbB_4O_7. Изучена концентрационная зависимость образования фаз, тригональной β или орторомбической α в процессе низкотемпературной кристаллизации стекол состава $(1-x)\cdot SrB_4O_7-x\cdot PbB_4O_7$ ($0<x<1$). Для концентраций $x<0{,}2$ кристаллизуется только метастабильная тригональная $\beta-Sr_{1-x}Pb_xB_4O_7$ фаза. Обе фазы тетрабората стронция–свинца обладают высокой нелинейностью (d_{eff} ($\beta-Sr_{0.8}Pb_{0.2}B_4O_7$) ≈ d_{eff} (PbB_4O_7)) и являются перспективными для использования в качестве нелинейно-оптических кристаллических компонент стеклокерамических материалов на основе системы тетраборат стронция–тетраборат свинца.

1. Introduction

Earlier it was shown that the crystals of a high-temperature phase strontium tetraborate SrB_4O_7 (SBO) and the crystals of lead tetraborate PbB_4O_7 (PBO) are isostructural, non centrosymmetrical crystals and have attractive optical and nonlinear-optical properties [1–6]. SrB_4O_7 crystals belong to the orthorhombic space group $Pnm2_1$ and their unit cell parameters are $a = 4.4255$ Å; $b = 10.709$ Å; $C = 4.231$ Å; and $Z = 2$ [1]. The SBO crystals can be grown by Chokhral'ski (Cz) method [4, 7–10] or by Kyropolus method [5]. One of the most serious and common problem in borate crystal growth is a high viscosity of melt resulted in macroscopic opaque defects and cloudy crystals [11]. Application of SBO has been investigated since 1985 [12]. Recently SBO has attracted much attention as a nonlinear optical crystal with the following benefits: a transparency down to 120 nm, high nonlinear coefficients, the highest optical damage threshold and an absence of hygroscopicity [4, 9, 13]. Petrov et al. [13] reported about the wavelength conversion of femtosecond pulses by SHG down to 125 nm using SBO. Komatsu et al. [14] and A.I.Zaitsev et al. [15] demonstrated that this crystal also had the highest SAW velocity among piezoelectric crystals.

Compound SrB_4O_7 lies in a glass-forming range within the $SrO–B_2O_3$ system and can be simply obtained as a glass. The process of glass crystallization occurs through complex mechanisms with a possible formation of other crystalline phases, in particular

metastable phases. I.G.Polyakova and E.O.Litovchik [16] reported that at the temperatures (670–700)°C for crystallization of the glass composition $SrO{\cdot}2B_2O_3$ (SrB_4O_7) a new phase — β–SrB_4O_7 appears. A new phase is metastable and with the increase of temperature up to 900 °C it transfers in known orthorhombic phase — α–SrB_4O_7. According to [17] low-temperature phase strontium tetraborat has non centrosymmetric structure (SG P3, a = 17.145(1) Å; c = 4.2527(5) Å; z = 9).

The crystal of lead tetraborate PbB_4O_7 is isostructural to the high-temperature phase of strontium tetraborate (the $Pnm2_1$ space group and PBO has unit cell parameters a = 4.4255 Å; b = 10.709 Å; C = 4.231 Å; and Z = 2) [1]. The crystal PbB_4O_7 has attractive physical properties [5], however in the presence of high nonlinearity (d_{eff} (PbB_4O_7) = (3–4) d_{eff} (KDP)), but small birefringence, the phase matching is not satisfied as well as for SBO crystal [4]. In paper [18] stimulated Raman's scattering in PbB_4O_7 crystal was investigated, cascade generation $\chi^{(3)} \rightarrow \chi^{(2)}$ and applicability of PbB_4O_7 crystal for nonlinear optics is shown.

Therefore, investigations of SrB_4O_7–PbB_4O_7 system in a view of crystallization of nonlinear optical phases and their properties are urgent. The phase diagram of strontium tetraborate SrB_4O_7 — lead tetraborate PbB_4O_7 system was studied in [19]. In this paper the possibility of solid solutions formation in all range of concentrations of compounds is shown, the dependence of parameters of a crystalline lattice upon concentration of a solid solution is studied. However, experimental results for concentrations of SrB_4O_7 more than 50 mol.% do not match theoretically calculated curve of solidus.

In the present paper formation of nonlinear optical phases at the process of recrystallization glasses in strontium tetraborate — lead tetraborate system was investigated. It was shown that the nonlinear optical phases of strontium — lead tetraborates crystals can be used to form glass-ceramic materials on the basis of this borates system. Comparison of nonlinearities of glass-ceramic materials is represented.

2. Experimental

Compositions for glasses were made from $SrCO_3$ (high pure grade 99.9 %), $PbCO_3$ (analytical grade 98.5 %) and H_3BO_3 (high pure grade 99.9 %). They were taken in corresponding quantities with the excess of the boric acid of 2 mol.%. The composition was prepared by solid-state reaction in the air, melting and then heating up to the temperature of 1030–1050 °C. The melt was mixed by platinum stirring rod. The melt was poured out on a metal plate and rapidly cooled. For reduction of mechanical tension after hardening the glass was annealed at temperature 350–450 °C during 4–5 h.

Differential thermal analysis (DTA) was made on an equipment made in laboratory. The peculiar of DTA equipment is the quartz channel for introduction of the micro seed in a studied sample. It is possible to achieve true relation of concentrations in a solid state only by quasi-stationary crystallization homogenized flux of the given concentration. Considering tendency of system for supercooling, there is the method to satisfy this condition by introducing SrB_4O_7 microcrystal into the sample at temperatures below, but near to the expected temperature of liquidus and crystallization of sample at low-speed cooling. It can be considered that the sample concentration change practically does not occur, because the weight of the melt during DTA was 100–150 mg, and a weight of a microcrystal strontium tetraborate moved by us through the quartz channel was 1–2 mg. The rate of temperature change during the record of DTA curves was 3 °C/min.

The polished glasses plates of 1.5 mm thickness of various composition in SrB_4O_7–PbB_4O_7 system were made for examination of the phase formation process at thermal treatment.

Crystalline phases were determined by X-ray phase analysis method on DRON-1 UM system.

Nonlinear optical properties of crystallized glasses were studied by Kurtz test procedure for powder samples, laser LTI-401 was used (YAG:Nd laser parameters of radiation: wavelength — 1.064 μm; pulse duration — 16 nS; pulse frequency — 6 Hz; an average energy radiation — 60 mJ). Radiation of the second harmonic was separated by the light filter SZS-21 and registered by photomultiplier FEU-106.

3. Results and discussion

3.1 Phase diagram of SrB_4O_7–PbB_4O_7 system. The studied phase diagram of SrB_4O_7–PbB_4O_7 system is show on Fig. 1. The results of Mikhael et al. [19] present by continuous circles — •.

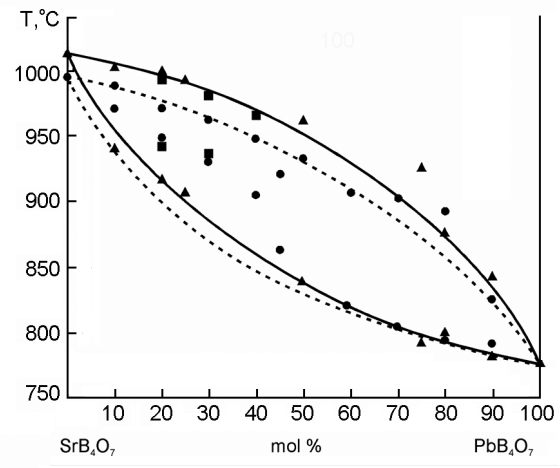

Fig. 1. Phase diagram of the strontium tetraborate SrB_4O_7 — lead tetraborate PbB_4O_7 system: a — experimental data and a theoretical curve agree to work [19]; b — experimental data of present work; — experimental data of present workfor homogenized glass without seed crystal introduction

The temperatures of liquidus, solidus and crystallization temperature of the glasses of compositions $(1-x)\cdot SrB_4O_7-x\cdot PbB_4O_7$ ($0\le x\le 1$ — the molar part lead tetraborate in the glass) were determined by means of DTA method. It can been seen from Fig. 1 that the determined temperatures of solidus and liquidus for the compositions with concentration of $x<0.5$ are above values of the data from paper [19] (these points are presented as continuous triangles — N) and well agree with the solidus curve.

It is possible to explain the difference of our experimental results in comparison with the results of [19] by higher melting temperature strontium tetraborate (1015±5 °C, [20]), and also by difference of the procedure of the phase diagram investigation. In the work [19] initial compositions for DTA were obtained by solid-state reaction and had the fixed concentration. In our opinion, it became the reason of falsification of the differential temperature curve and got the error of measured temperatures of solidus for compositions $(1-x)\cdot SrB_4O_7-x\cdot PbB_4O_7$ ($x<0.5$). We made testing measures in which homogenized glasses of concentration $(1-x)\cdot SrB_4O_7-x\cdot PbB_4O_7$ ($x = 0.2$; 0.3) were used as samples (temperatures of solidus and liquidus in figure are presented by a continuous quadrate — ■). DTA has sown error of measured temperatures of solidus, that agree with the results of [19]. It is

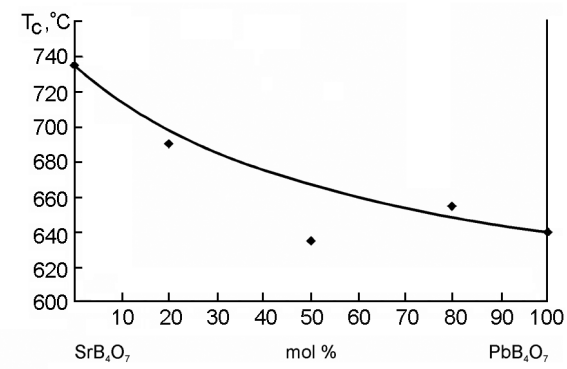

Fig. 2. Crystallization temperature of glasses of the SrB_4O_7–PbB_4O_7 system.

difficult to register temperatures of solidus for compositions $(1-x)\cdot SrB_4O_7-x\cdot PbB_4O_7$ ($0\le x\le 1$) for the cigar-shaped diagram. This is connected with a small value of differential temperature of the sample and temperature of junction control thermocouple. It was not possible to define reliably the temperatures of solidus of compositions $(1-x)\cdot SrB_4O_7-x\cdot PbB_4O_7$ ($x = 0.3$; 0.4) despite of accuracy of measuring.

Thus, investigation of the phase diagram of SrB_4O_7–PbB_4O_7 system has confirmed an opportunity of formation of the solid solutions $Sr_{1-x}Pb_xB_4O_7$ in full range of concentrations ($0\le x\le 1$), and an opportunity of the crystallization of the glass ceramic structure of a various concentration composition.

3.2. Nonlinear optical phases in SrB_4O_7–PbB_4O_7 system. One-stage isothermal crystallization annealing of the glasses plats at certain specified temperatures T_c was carried out. The results are presented on Fig. 2.

As it was suggested, process of crystallization began from the unelaborated surface of butt-end glasses plats, (Fig. 3) and was gradually extended in the central areas. The crystallization was not continuous but extended wavy, forming crystallization blocks. Depending on the glass composition the influence of extracting heat of crystallization at annealing had various characters. Increase of density was taken place during crystallization of pure strontium tetraborate, interblock surface indentation and volumetric hollows were formed. Spreading of crystalline phase from periphery to the central areas, softening of the glass and its extrusion with the subsequent formation of crystallization humps and interior gas hollows were observed for the

Fig. 3. Crystallization of the glass ($0.8{\cdot}SrB_4O_7$–$0.2{\cdot}PbB_4O_7$) an initial stage in isothermal conditions.

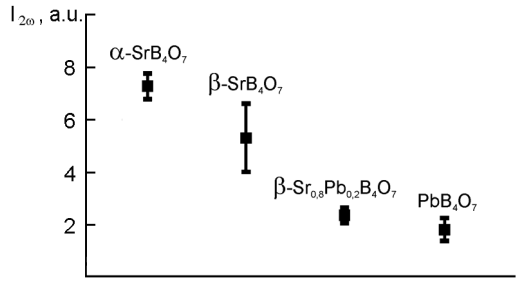

Fig. 4. Relative intensity of the second harmonic generation of YAG:Nd laser radiation by the glass ceramic samples.

glasses with composition $0.8{\cdot}SrB_4O_7$–$0.2{\cdot}PbB_4O_7$.

Crystal phases were detected by an X-ray phase analysis method. On the surface and on perimeter of the plates the tracks of the orthorhombic phases α–$Sr_{1-x}Pb_xB_4O_7$ were revealed. It is possible to remove α-phase completely by polishing the surface of the plates. Thereafter volume of the sample contains only a crystal phase β–$Sr_{1-x}Pb_xB_4O_7$. The crystallization blocks have size 1–3 mm, they are homogeneous and semitransparent. The thermal treatment of the crystallized glasses of the composition $(1-x){\cdot}SrB_4O_7$–$x{\cdot}PbB_4O_7$ ($x \le 0.2$) at temperatures 900–920°C ensure complete transition of β–$Sr_{1-x}Pb_xB_4O$ in α–$Sr_{1-x}Pb_xB_4O_7$ phase. The hard, opaque, homogeneous ceramics are formed.

In volume of the crystallized glass sample of the composition $0.7{\cdot}SrB_4O_7$–$0.3{\cdot}PbB_4O_7$ is found out as α-phase $Sr_{1-x}Pb_xB_4O_7$ as β-phase $Sr_{1-x}Pb_xB_4O_7$ of crystalline. In crystallized glass of the composition $0.6{\cdot}SrB_4O_7$–$0.4{\cdot}PbB_4O_7$ only traces of β-phase $Sr_{1-x}Pb_xB_4O_7$ are found, and at further raising of concentration of lead tetraborat in the glasses up to 50 % and more β–$Sr_{1-x}Pb_xB_4O_7$ is not found, there is only the orthorhombic crystal phase α–$Sr_{1-x}Pb_xB_4O_7$.

Microstructure of the samples was studied with an optical microscope. Sizes of the formed microcrystals are in a range of 1–8 μm, crystals are isomerous, they have no prevailing orientation that is confirmed by the results of X-ray study.

Comparison of the nonlinear optical properties has been made by Kurtz-Perry method because crystallized samples have microcrystalline structure without any primary orientation of the crystals [21]. The samples were irradiated by YAG:Nd laser ($\lambda = 1.064$ μm), pumping radiation was filtered by filter SZS-21 and the radiation of the second harmonic was detected by a photomultiplier FEU-106. Rotation of the sample about an axis of the incident radiation does not change intensity of the second harmonic that also confirms equally probable orientation of microcrystal in crystallized glasses. The results of the test are represented on Fig. 4.

β–Phase SrB_4O_7 possesses high nonlinearity and as well as α–SrB_4O_7 it is interesting for making nonlinear optical glass-ceramic materials (nonlinearity of phases comparable with those for KTP, BBO). Nonlinearity of α–$Sr_{1-x}Pb_xB_4O_7$ and β–$Sr_{1-x}Pb_xB_4O_7$ decreases with an increase of lead tetraborate concentration in the system.

4. Conclusions

The investigation of the phase diagram of strontium tetraborate SrB_4O_7-lead tetraborate PbB_4O_7 system confirmed the main role of DTA method to obtain reliable results. A good agreement with liquidus phase curve is achieved. It was confirmed that strontium tetraborate SrB_4O_7–tetraborate lead PbB_4O_7 form solid solutions for any concentration.

Crystallization of two crystalline nonlinear-optical phases in the system of strontium tetraborate SrB_4O_7–lead tetraborate PbB_4O_7 takes place at crystallization of the glasses. The low-temperature β–$Sr_{1-x}Pb_xB_4O_7$ trigonal phase is detected at low concentrations of PbB_4O_7 ($x < 0.3$). It transforms to orthorhombic α–$Sr_{1-x}Pb_xB_4O_7$ phase in the case of increase of annealing temperature. Only crystallization of orthorhombic α–$Sr_{1-x}Pb_xB_4O_7$ phases is taken place for concentrations PbB_4O_7 ($x > 0.3$).

High nonlinearity of both phases of strontium–lead tetraborates makes it possible to use them as nonlinear optical crystals components of glass-ceramic materials on the basis of the glass-forming strontium tetraborate — lead tetraborate system.

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Нелінійно оптичні фази у системі тетраборат стронцію-тетраборат свинцю

Ю.С.Оселедчик, А.Л.Просвірнін, В.Ю.Луценко

За допомогою покращеної методики диференціального температурного аналізу уточнено фазову діаграму системи тетраборат стронцію SrB_4O_7–тетраборат свинцю PbB_4O_7. Вивчено концентраційну залежність утворення фаз, тригональної β або орторомбічної α у процесі низькотемпературної кристалізації скла складу $(1-x)\cdot SrB_4O_7-x\cdot PbB_4O_7$ ($0<x<1$). Для концентрацій $x<0,2$ кристалізується лише метастабільна тригональна β–$Sr_{1-x}Pb_xB_4O_7$ фаза. Обидві фази тетраборату стронцію–свинцю характеризуються високою нелінійністю (d_{eff} (β–$Sr_{0,8}Pb_{0,2}B_4O_7$) ≈ d_{eff} (PbB_4O_7)) і є перспективними для використання в якості нелінійно-оптичних кристалічних компонент склокерамічних матеріалів на основі системи тетраборат стронцію–тетраборат свинцю.