

Thermal behavior of some germanates with non-olivine structure

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Dedicated to Acad. Bogdan Kurtev on the occasion of his 100th birth anniversary

Single phase germanates LiAlGeO_4 , LiGaGeO_4 and Zn_2GeO_4 with hexagonal structure (space group, S. G., R3), $\text{Li}_2\text{CaGeO}_4$ with tetragonal structure (S. G. I-42m), $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ with monoclinic structure (S. G. C1) and $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$ with cubic structure were obtained by solid-state synthesis. The thermal behavior of these germanates was studied with a view to finding out the most appropriate method and conditions for growing single crystals from them, which, after doping with Cr^{4+} , can be used as matrices for lasers with a broad emission spectrum in the range from 1.0 to 1.6 μm . By means of powder X-ray diffraction and DTA/TG analysis, the melting temperatures, the type of melting (with or without decomposition), the type of the phases crystallizing after decomposition, as well as the presence (or lack) of polymorphic transitions in the vicinity of the melting temperature, were studied. Most of the data on the thermal behavior of these germanates are reported here for the first time. It is found that four of the synthesized germanates (LiAlGeO_4 , Zn_2GeO_4 , $\text{Ca}_5\text{Ge}_3\text{O}_{11}$, and $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$) are melting congruently (without decomposition) and do not display phase transitions. Unlike the germanates with olivine structure, which are examined in more details for the same purpose, single crystals from non-olivine germanates could be directly grown from their own solutions (by the methods of Czochralski, Bridgman-Stockbarger or Kyropoulos) instead of using the flux method, which is characterized by a considerably lower rate of growing and a limited crystal size.

Key words: germanates, melting temperature, phase transitions, X-ray diffraction analysis, DTA analysis

INTRODUCTION

Single crystals of complex oxides doped with ions of transition 3d elements with different oxidation states are of particular interest as laser media. These single crystals display a broad emission range as tunable lasers [1, 2] and may also be used as media for femtosecond lasers [3, 4]. Of particular importance are the Cr^{4+} doped media emitting in the range from 1.1 to 1.6 μm . Lasers emitting in this range find increasing application in medicine, ecology and telecommunications [5, 6]. The most popular Cr^{4+} doped single crystals are those of Mg_2SiO_4 (forsterite) and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (garnet). Both of these single crystals have, however, several drawbacks. For example, a severe problem is caused by nonradiative transitions, as a result of which the quantum efficiency amounts to about 9% for forsterite and 14-22% for YAG [7, 8]. Another problem is the undesired presence of Cr^{3+} along with Cr^{4+} . As a rule, only a small percentage of chromium is in the desired Cr^{4+} state [8]. Owing to the issues mentioned, novel Cr^{4+} doped laser matrices are still looked for. Most promising among

the novel crystal matrices studied so far seem to be the Cr^{4+} doped germanates having Ge^{4+} in the tetrahedral environment preferred by Cr^{4+} as the ionic radii of Ge^{4+} and Cr^{4+} are very close – 0.41 and 0.39 Å [9], respectively. From this point of view, substitution of Ge^{4+} by Cr^{4+} is significantly facilitated up to high concentrations of Cr^{4+} . Favorable fact is that the existence of chromium as Cr^{3+} or Cr^{2+} in these germanates is highly improbable.

Suitable class of single crystal matrices is that of germanates with olivine structure (S. G. Pnma) with the general formulas: Me_2GeO_4 (Me=Mg, Ca); $\text{Li}_2\text{MeGeO}_4$ (Me=Mg, Zn); LiMeGeO_4 (Me= Sc, In, Y), as well as the compound Li_4GeO_4 . Our study of the thermal behavior of these germanates revealed that most of them are melting with decomposition (incongruently) or display phase transitions. The only exception is Mg_2GeO_4 . Its melting temperature is, however, too high (1885 °C) and considerable amounts of GeO_2 evaporate. Hence, the flux method from high-temperature solutions is the only option of growing crystals from these compounds. The crystal growth should be performed below the decomposition temperature or the temperature of phase transition. A major drawback of this method compared with the growth from the own melt

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(methods of Czochralski, Bridgman-Stockbarger or Kyropoulos) is the considerably lower rate of growing. This explains the search for other germanates which possess the advantages of the olivine-group ones (tetrahedral environment of germanium, close ionic radii of Ge^{4+} and Cr^{4+}) and melt with no decomposition or phase transitions.

According to the literature data, LiAlGeO_4 , LiGaGeO_4 and Zn_2GeO_4 are isostructural and belong to the same structural group (S. G. R3) [10-15]. Germanium participates in this structure in two tetrahedra differing by size and deformation degree; lithium and aluminium (lithium and gallium), as well as zinc in Zn_2GeO_4 are also in tetrahedral positions. The structural differences between these three compounds are due to the different Ge-O and Me-Ge distances, where Me is Li, Al, Ga or Zn. There is no information on their thermal behavior before melting (presence or lack of transitions).

$\text{Li}_2\text{CaGeO}_4$ has tetragonal structure (S. G. I-42m), in which germanium and lithium are in tetrahedral environment, while calcium is in dodecahedral coordination [16]. Although this compound, doped with rare earth elements (Er, Tb, Dy), has been examined as a phosphorescent substance, there are no data about its thermal behavior. The phase $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ has monoclinic structure in which germanium participates in three tetrahedra differing by size and deformation degree, while calcium is in a dodecahedral occupation [17, 18]. There is no data about the thermal behavior of this compound either.

According to the pseudobinary diagram of $\text{LiAlGeO}_4\text{-Zn}_2\text{GeO}_4$ [19], the compound $5\text{LiAlGeO}_4\text{:}4\text{Zn}_2\text{GeO}_4$ ($\text{Li}_5\text{Al}_5\text{Zn}_8\text{Ge}_4\text{O}_{36}$) exists and has a temperature of congruent decomposition about 1080°C with no polymorphic transitions up to this temperature.

All the above mentioned six germanates possess Ge^{4+} in a tetrahedral position, therefore they are suitable for Cr^{4+} doping as the already investigated germanates with olivine structure.

The main purpose of this work was to study the thermal behavior (melting temperatures, type of phases obtained by eventual decomposition, presence or lack of polymorphic transitions) of the above mentioned six germanates. The thermal behavior strongly determines the method and conditions of single crystals growth.

EXPERIMENTAL

The studied germanates were obtained by solid-state synthesis using the following reagents: CaCO_3

(99.9), Li_2CO_3 (99.99), ZnO (99.0), Al_2O_3 (99.99), Ga_2O_3 (99.9) and GeO_2 (99.999). Stoichiometric amounts of the starting reagents for the corresponding germanate were weighed with a precision of ± 0.01 g and were mixed and ground in an agate mortar. The reaction mixtures were thermally pretreated at 900°C for 2 h for decomposition of the carbonates present. After a further homogenization, the mixture was heated for 16 h, with two intermediate grindings, at different temperatures until the minimal temperature was established, which was sufficient for obtaining a well-crystallized pure germanate product with no admixtures of unreacted reagents or side compounds. After synthesis at different temperatures the following optimal temperatures for solid-state synthesis were found: 1050°C for LiAlGeO_4 , 1100°C for LiGaGeO_4 , 1150°C for Zn_2GeO_4 , 1050°C for $\text{Li}_2\text{CaGeO}_4$, 1200°C for $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ and 1050°C for $5\text{LiAlGeO}_4\text{:}4\text{Zn}_2\text{GeO}_4$.

Structural characterization was carried out by powder X-ray diffraction (XRD) using a Bruker D8 Advance powder diffractometer with Cu K α radiation and SolX detector. XRD spectra were recorded at room temperature. Data were collected in the 2θ range from 10 to $80^\circ 2\theta$ with a step of $0.048 2\theta$ and counting time of 1 s/step. XRD spectra were identified using the Diffractplus EVA program.

Differential thermal analysis was carried out on a DTA-TG analyzer SETSYS Evolution 2400, SETARAM in static air atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$ and 15-20 mg sample weight.

Additional experiments were performed in order to establish the melting type (congruent or incongruent). For this purpose a sample of about 2 g was placed in a platinum crucible and was heated in a furnace with a MoSi_2 heater with controllable temperature ($\pm 1^\circ\text{C}$) up to a temperature by 20-30 $^\circ\text{C}$ above the melting temperature established by DTA. After holding for 30 min, the sample was withdrawn from the hot area and was briskly cooled on a cold copper plate. The sample cooled down to room temperature for 10-15 s. The briskly crystallized sample was subjected to XRD analysis for identification of the crystallized phases.

RESULTS AND DISCUSSION

Figs. 1 and 2 present the powder XRD patterns of germanates obtained by solid-state synthesis, compared to the corresponding PDF data. No additional phases can be distinguished and the patterns are consistent with the literature data.

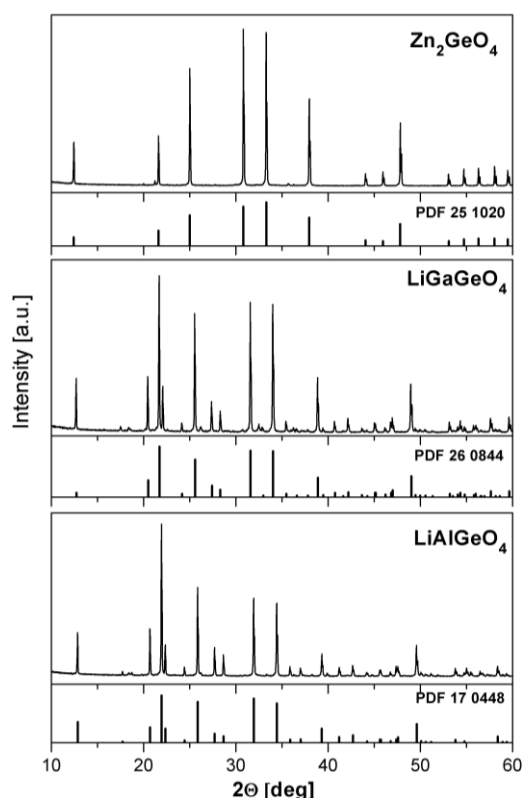


Fig. 1. Powder XRD patterns of the LiAlGeO_4 , LiGaGeO_4 and Zn_2GeO_4 obtained by solid-state synthesis, compared to the corresponding PDF data.

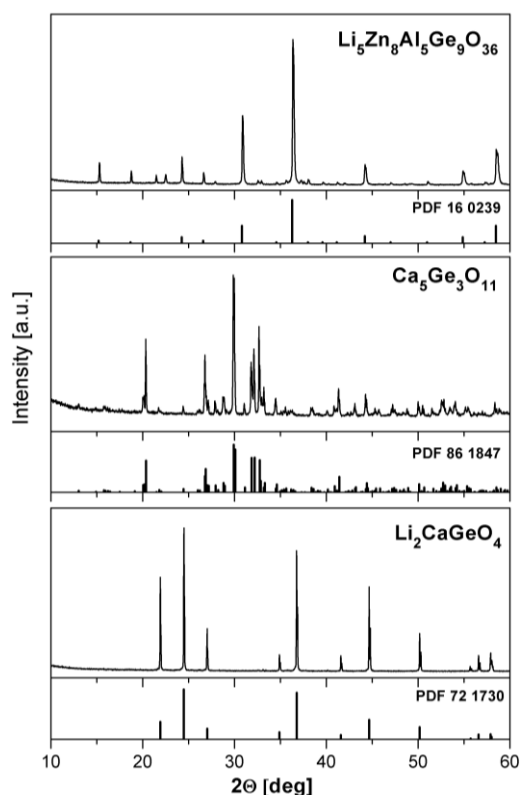


Fig. 2. Powder XRD patterns of the $\text{Li}_2\text{CaGeO}_4$, $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ and $\text{Li}_5\text{Zn}_8\text{Al}_5\text{Ge}_9\text{O}_{36}$ obtained by solid-state synthesis, compared to the corresponding PDF data.

The DTA/TG curves of the samples are shown in Fig. 3. As can be seen, none of the germanates displays phase transitions in the vicinity of the melting temperature. The established melting temperatures are: 1190 °C for LiAlGeO_4 , 1147 °C for LiGaGeO_4 , 1505 °C for Zn_2GeO_4 , 1120 °C for $\text{Li}_2\text{CaGeO}_4$, 1560 °C for $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ and 1160 °C for $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$. Except for the melting temperature of Zn_2GeO_4 , these data differ from those given in the literature. Thus, for LiAlGeO_4 the temperature 1150 °C is given in [13] (1190 °C in this work); for LiGaGeO_4 -1200 °C [20] (1147 °C in this work); for Zn_2GeO_4 -1502 °C [12] (1505 °C in this work); no data are available for $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ and $\text{Li}_2\text{CaGeO}_4$; while the temperature 1080 °C is given for $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$ according to the phase diagram [19], (1160 °C in this work).

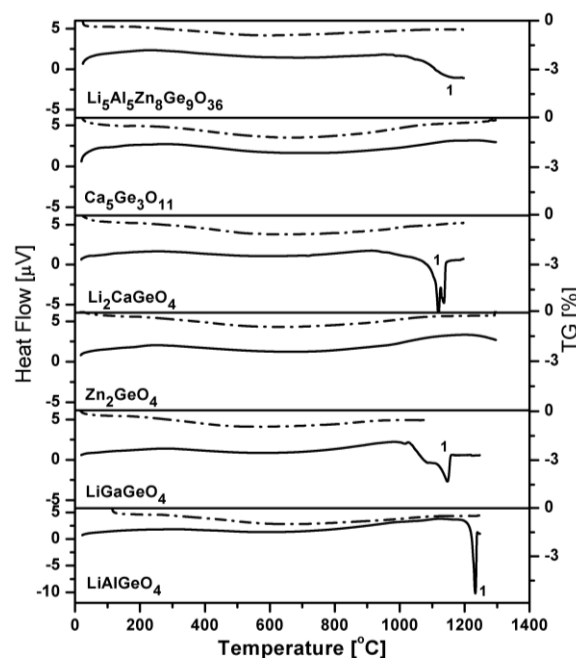


Fig. 3. DTA/TG curves of LiAlGeO_4 , LiGaGeO_4 , Zn_2GeO_4 , $\text{Li}_2\text{CaGeO}_4$, $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ and $\text{Li}_5\text{Zn}_8\text{Al}_5\text{Ge}_9\text{O}_{36}$ up to the melting temperature. 1 – melting temperature.

The results of the experimental study of the type of melting of the germanates and the phases crystallizing from the melts are presented in Fig. 4. As can be seen, the XRD pattern of the products after melting of LiAlGeO_4 and subsequent brisk cooling, does not contain any peaks different from those of LiAlGeO_4 and matches very well the one given in the literature (PDF-270289), *i.e.* LiAlGeO_4 is melting congruently at 1160 °C. Similar behavior is displayed by Zn_2GeO_4 , $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ and $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$. The congruent melting of these four germanates (LiAlGeO_4 , Zn_2GeO_4 , $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ and $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$) is of great

significance as crystal growth is concerned, because single crystals of these germanates could be grown from their own melts by methods characterized by technological simplicity and high growing rate.

Fig. 4 illustrates the thermal behavior of LiGaGeO_4 after melting. Differently from the published assertion [10] that this compound melts congruently, our studies revealed that it melts at 1147°C with decomposition, the main decomposition product being Li_2GeO_3 . Fig. 4 also presents the thermal behavior of $\text{Li}_2\text{CaGeO}_4$ which melts with decomposition to Ca_2GeO_4 and Li_2GeO_3 .

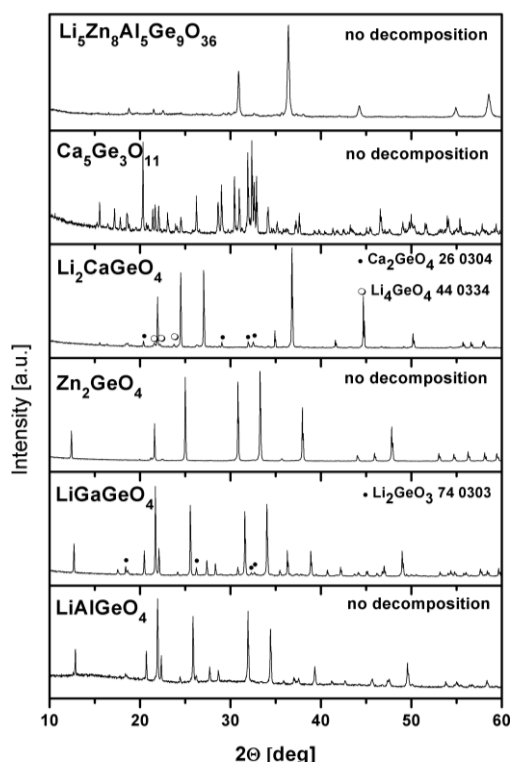


Fig. 4. Powder XRD patterns of the products after melting of LiAlGeO_4 , LiGaGeO_4 , Zn_2GeO_4 , $\text{Li}_2\text{CaGeO}_4$, $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ and $\text{Li}_5\text{Zn}_8\text{Al}_5\text{Ge}_9\text{O}_{36}$. Additional phases in the cases of incongruent melting are marked.

As was already said, none of the examined germanates displays phase transitions.

CONCLUSION

The germanates examined in the present study are considerably more appropriate for crystal growth than the germanates with olivine structure. Our former studies revealed that out of nine germanates with olivine structure, none could be directly grown from its own melt. Unlike the olivine-type germanates, four of the germanates in the present study (LiAlGeO_4 , Zn_2GeO_4 , $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ and $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$) are melting congruently without phase transitions. Hence, methods for

single crystal growth from the own melt can be applied (Czochralski, Bridgman-Stockbarger and Kyropoulos). It should be kept in mind, however, that two of these germanates (Zn_2GeO_4 and $\text{Ca}_5\text{Ge}_3\text{O}_{11}$) are melting at relatively high temperatures (1505°C and 1560°C , respectively), which would hamper the crystal growth due to some evaporation of GeO_2 . The thermal behavior of the other two germanates (LiAlGeO_4 and $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$) is perfectly suited for single crystal growth from their own melts. The compounds LiGaGeO_4 and $\text{Li}_2\text{CaGeO}_4$ are melting with decomposition and crystal growth from them could be realized only by the flux method, as in the case of the germanates of the olivine group.

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ТЕРМИЧНО ПОВЕДЕНИЕ НА НЯКОИ ГЕРМАНАТИ С НЕОЛИВИНОВА СТРУКТУРА

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(Резюме)

Чрез твърдофазен синтез бяха получени монофазни германати от съединенията с хексагонална структура LiAlGeO_4 , LiGaGeO_4 и Zn_2GeO_4 (S.G. R3), от съединението с тетрагонална структура $\text{Li}_2\text{CaGeO}_4$ (S.G. I-42m), от съединението с моноклинна структура $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ (S.G. C1') и от съединението с кубична структура $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$. Беше изследвано термичното поведение на тези германати от гледна точка да се намерят най-подходящия метод и условия за израстване от тях на монокристали, които след дотиране с Cr^{4+} , могат да бъдат използвани като лазерни матрици за лазери с широк спектър на излъчване в областта от 1.0 до 1.6 μm . Температурите на топене, вида на стапяне (с разлагане или без разлагане), вида на кристализиращите фази след разлагане, както и наличието или липсата на полиморфно превръщане близко до температурата на топене бяха изследвани чрез рентгенов фазов анализ и диференциален термичен анализ. Голяма част от данните за термичното поведение на тези германати се публикуват за първи път. Установено е, че четири от синтезираните германати (LiAlGeO_4 , Zn_2GeO_4 , $\text{Ca}_5\text{Ge}_3\text{O}_{11}$, и $5\text{LiAlGeO}_4 \cdot 4\text{Zn}_2\text{GeO}_4$) се топят конгруентно (без разлагане) и не показват наличие на фазов преход. За разлика от германатите с оливинова структура, които бяха изследвани по-детайлно за същите цели, монокристали от неоливиновите германати могат да бъдат израствани директно от тяхната собствена стопилка (по методите на Чохралски, Бриджман-Стокбаргер или Киропулос) вместо да се използва флакс метода, който се характеризира със значително по-малка скорост на израстване и ограничение за размера на израствания кристал.