



Thermal behavior of germanates with olivine structure



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ABSTRACT

A series of germanates with olivine structure: Me_2GeO_4 (Me = Mg, Ca); $\text{Li}_2\text{MeGeO}_4$ (Me = Mg, Zn); LiMeGeO_4 (Me = Sc, In, Y), and the compound Li_4GeO_4 were obtained by solid-state synthesis. Their thermal behavior was studied from the viewpoint of the possibilities of growing single crystals as matrices doped with Cr^{4+} for lasers. By means of X-ray and DTA/TG analysis data are obtained about the melting temperatures, type of melting (with or without decomposition), the substances during melting with decomposition, as well as the temperatures of the polymorphic transitions for some of the germanates. Most of the data reported in this work are novel. It is found that owing to the rather high melting temperatures and the decomposition or polymorphic transitions during the melting, the germanates with olivine structure do not allow single crystal growth from their own melts, but the flux method from appropriate high-temperature solutions should be applied.

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1. 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 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+} . In addition, 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 fac-

ilitated up to high concentrations of Cr^{4+} . The fact is also favorable that the existence of chromium as Cr^{3+} or Cr^{2+} in these germanates is highly improbable.

Suitable matrices are the germanates with olivine structure (space group Pbmn) 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 . In all these germanates germanium is in tetrahedral environment, appropriate for substitution by Cr^{4+} . These compounds differ, however, in the number of different germanium tetrahedra in the unit cell, the size of these tetrahedra, the degree of their deformation, as well as the local environment of other chemical elements in the compound. As a result of these differences, the crystal field around germanium (chromium) is different, which leads to different optical and laser characteristics of Cr^{4+} as an active ion in these matrices. The systematic study of chromium doped single crystals from these compounds may throw light on the relation between the microstructural features of the compounds and their optical and laser characteristics with a view to prognosing and finding out the most appropriate laser-active medium. Unfortunately, single crystals have been grown only from three of these compounds – Ca_2GeO_4 , LiScGeO_4 and LiInGeO_4 [10–12]. Obviously, there is a need of a broader and more systematic study of the germanate single crystal matrices. Obtaining of single crystals presupposes knowledge of the thermal behavior of the compounds in order to determine the most suitable method for single crystal growth and the thermal conditions of the growth. For the prevailing part of these compounds, no data

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are available about the main thermal characteristics such as melting temperature, melting type (with or without decomposition), presence or lack of polymorphic transitions.

The present study deals with the thermal behavior of the germanates with olivine structure mentioned above, single crystals of which are potential matrices for Cr⁴⁺ doped laser-active media.

2. Materials and methods

All germanates under study were obtained by solid-state synthesis using the following reagents: CaCO₃ (99.9), Li₂CO₃ (99.99), Mg(OH)₂ (99.8), ZnO (99.0), Sc₂O₃ (99.9), In₂O₃ (99.9), Y₂O₃ (99.9) and GeO₂ (99.999). Preweighed (± 0.01 g) stoichiometric amounts of the reagents for the corresponding germanate were mixed and grinded in an agate mortar and were thermally treated at 900 °C for 2 h to decompose carbonates and hydroxides. After homogenization, the reaction mixture was treated for 16 h with two intermediate grindings at a temperature sufficient for preparing the desired germanate without admixtures of unreacted reagents or other side phases. The syntheses carried out at different temperatures revealed that the optimal temperature for obtaining a well crystallized pure product is: 1373 K for Li₂MgGeO₄, Li₂ZnGeO₄ and Li₄GeO₄; 1423 K for LiScGeO₄, LiInGeO₄ and LiYGeO₄; 1473 K for Ca₂GeO₄; 1573 K for CaMgGeO₄ and 1673 K for Mg₂GeO₄. The phase composition of the products synthesized at different temperatures was monitored by powder X-ray analysis.

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 2 θ range from 10 to 80 2 θ with a step of 0.048 2 θ and counting time of 1 s/step. The phases in the XRD spectra were identified using the Diffractplus EVA program.

The thermal behavior of the synthesized germanates (melting temperature, phase transitions) was studied on a DTA-TG analyzer SETSYS Evolution 2400, SETARAM in static air atmosphere with a heating rate of 10 °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 MoSi₂ heater with controllable temperature (± 1 K) up to a temperature by 20–30 K 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 X-ray analysis for identification of the crystallized phases.

The germanates displaying phase transitions (Mg₂GeO₄, Li₂MgGeO₄, Li₂ZnGeO₄ and Li₄GeO₄) were examined for establishing the reversibility of the transitions. For this purpose the germanate samples were heated up to temperatures below and above the corresponding transition temperature (according to DTA data), held for 8 h and cooled down to room temperature by brisk cooling on a copper plate for 5–10 s or by slow cooling in the furnace at a rate of 50 K/h.

3. Results and discussion

3.1. Solid-phase synthesis

Fig. 1 shows the X-ray diffractograms of the products of the solid-phase synthesis of Mg₂GeO₄, CaGeO₄ and CaMgGeO₄, compared with the available PDF data for the corresponding germanates. Fig. 2 presents the data for LiScGeO₄, LiInGeO₄ and LiYGeO₄, and Fig. 3—the data for Li₂MgGeO₄, Li₂ZnGeO₄ and

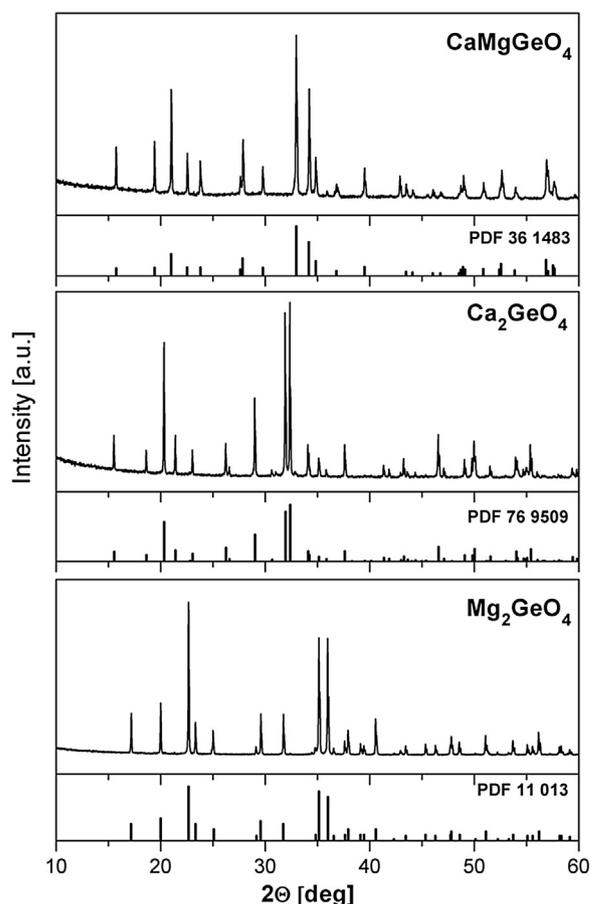


Fig. 1. X-ray diffractograms of the products of the solid-phase synthesis of Mg₂GeO₄, CaGeO₄ and CaMgGeO₄, compared with the available PDF data for the corresponding germanates.

Li₄GeO₄. As can be seen from the Figures, all diffractograms of the synthesized products match well the PDF data without showing additional peaks, i.e., it may be concluded that the synthesis of the germanates was successful. There are no published PDF data on LiYGeO₄. The X-ray pattern of the synthesized LiYGeO₄ matches very well those of LiScGeO₄ and LiInGeO₄ (Fig. 2). Obviously, LiYGeO₄ is also successfully synthesized, all three germanates displaying orthorhombic symmetry and the same structural group Pbnm. There are three diffractograms, which are typical for the orthorhombic symmetry of Li₂MgGeO₄—PDF 240626, PDF 300754 and PDF 702379. It is peculiar that these data considerably differ from one another. There is also a diffractogram typical for the monoclinic symmetry of Li₂MgGeO₄—PDF 240627, which matches very well the diffractogram of the germanate synthesized by us (Fig. 3).

3.2. Melting temperatures. congruently and incongruently melting germanates

As regards the type of melting, the germanates under study can be divided in two groups: (1) germanates that melt without decomposition and the product crystallized after melting is the same germanate; and (2) germanates that melt with decomposition, and the product crystallized after melting displays phases different from those of the germanate before treating. Only three germanates can be designated as congruently melting ones (without decomposition)—Mg₂GeO₄, Ca₂GeO₄ and Li₂ZnGeO₄. According to literature data [13,14], the melting temperatures of Mg₂GeO₄ and Ca₂GeO₄ are 2128 K and 2173 K, respectively, while that of Li₂ZnGeO₄ is

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