

# The solid state transformations in the system $\text{Sr}_2\text{GeO}_4\text{—Sr}_3(\text{PO}_4)_2$

<sup>a</sup>I. A. BONDAR, <sup>a</sup>A. K. SHIRVINSKAYA,  
<sup>b</sup>E. KANCLÍŘ, <sup>b</sup>I. KAPRÁLIK, and <sup>b</sup>Z. PÁNEK

<sup>a</sup>*Institute of Silicate Chemistry, Academy of Sciences of the USSR,  
199 164 Leningrad*

<sup>b</sup>*Institute of Inorganic Chemistry, Slovak Academy of Sciences,  
809 34 Bratislava*

Received 22 January 1975

The transformations of the title system was investigated by means of X-ray diffraction, DTA, and optical analyses. It was found that at intermediate compositions one phase which can be derived from the ternary compound  $\text{Sr}_5(\text{GeO}_4)(\text{PO}_4)_2$  is present in the system. This phase crystallizes in an apatite-like structure and forms extensive solid solutions. Its X-ray and optical characteristics are given.

On the basis of end members of the system ( $\text{Sr}_2\text{GeO}_4$ ,  $x\text{-Sr}_3(\text{PO}_4)_2$ ) only limited solid solutions are formed.

At higher temperatures (approaching solidus temperature) the high temperature phase is present within the region of homogeneity in a broad concentration interval.

Рентгенографическим, дифференциально-термическим и микроскопическим методами анализа были изучены превращения в твердом состоянии в системе  $\text{Sr}_2(\text{GeO}_4)\text{—Sr}_3(\text{PO}_4)_2$ . Для промежуточных составов установлено образование фазы на основе тройного соединения  $\text{Sr}_5(\text{GeO}_4)(\text{PO}_4)_2$  со структурой апатита, которая образует твердые растворы в широких пределах. Приводятся рентгенографические и оптические характеристики.

На основе  $\text{Sr}_2\text{GeO}_4$  и  $\alpha\text{-Sr}_3(\text{PO}_4)_2$  образуются только ограниченные поля твердых растворов.

При повышенных температурах (в под-solidusной части системы) образуется раствор с обширной областью гомогенности.

The study of the system  $\text{Sr}_2\text{GeO}_4\text{—Sr}_3(\text{PO}_4)_2$  is a part of the investigation of ortho-phosphato-germanates of calcium, strontium, and barium which is being carried out at the Institute of Silicate Chemistry of the Academy of Sciences of the USSR. In the present investigation also the Institute of Inorganic Chemistry of the Slovak Academy of Sciences took part.

This investigation furnished important information on stable and metastable phases in the system, their transformation, and structural types. Many compositions of this system are exploited in the industry of luminescent and ceramic materials.

## Experimental

The interaction of strontium germanate and strontium phosphate was studied at temperatures between 1000 and 1700°C. The phase composition of the reaction products was determined by X-ray powder diffraction and optical analyses. The powder patterns were taken on Dron-1 (room temperature) and Rigaku-Denki (high temperature) diffractometers using  $\text{CuK}_\alpha$  radiation.

Individual mixtures were prepared at 5 mole % increments (in some parts of the system even at a more finely divided scale) from  $\text{SrCO}_3$  (extra pure) and  $\text{Sr}_3(\text{PO}_4)_2$ .  $\text{Sr}_3(\text{PO}_4)_2$  of the final composition  $2.99\text{SrO} \cdot \text{P}_2\text{O}_5$  in  $\alpha$  modification was prepared from  $\text{SrCO}_3$  and  $\text{SrHPO}_4$  (anal. grade) by heating at 1350°C.

The mixtures were wet-homogenized using water, dried, pelletized, and sintered in the glow-bar and Pt-winding furnaces.

Samples quenched from temperatures 1600–1700°C were heated for 15–20 min using the furnace with Mo winding [1].

The equilibrium at temperatures above 1000°C was reached by one- or twofold heating of samples for 2 or 3 hrs.

## Results and discussion

The obtained results show that three series of solid solutions are present in the system.

At the side of strontium germanate a solid solution is formed with a boundary at 16 mole % of  $\text{Sr}_3(\text{PO}_4)_2$  at 1300°C. For the samples quenched from temperatures above 1300°C the boundary is shifted to about 25 mole % of  $\text{Sr}_3(\text{PO}_4)_2$ . However, this solid solution should be considered as a metastable phase since  $\text{Sr}_2\text{GeO}_4$  containing more than 16 mole % of  $\text{Sr}_3(\text{PO}_4)_2$  decomposes into two phases at temperatures below 1300°C.

$\text{Sr}_2\text{GeO}_4$  is known in one crystallographical modification of the  $\beta\text{-K}_2\text{SO}_4$  type [2–4] stable up to 1550°C (according to the limit of a temperature reached). In the present case we have confirmed by the DTA and powder diffraction that no transition occurs up to 1550°C.

The samples of pure  $\text{Sr}_2\text{GeO}_4$  and of its solid solutions quenched from the temperatures between 1600–1700°C did not reveal any transformation either and, as said above, the metastable solid solution was formed.

At concentrations of  $\text{Sr}_3(\text{PO}_4)_2$  exceeding 16 mole % and temperatures up to 1300°C, besides the solid solution of  $\text{Sr}_2\text{GeO}_4$  a new phase is present which is formed in its pure form at the components ratio 1 : 1 and corresponds to the ternary compound  $\text{Sr}_5(\text{GeO}_4)(\text{PO}_4)_2$ .

The synthesis of this compound is accomplished most preferably by heating the equimolar mixture of  $\text{Sr}_2\text{GeO}_4$  and  $\text{Sr}_3(\text{PO}_4)_2$  at 1250°C (not higher than 1300°C) and subsequent annealing at lower temperatures.

X-Ray powder diffraction data of  $\text{Sr}_5(\text{GeO}_4)(\text{PO}_4)_2$  are shown in Table 1. A comparison of the powder patterns of  $\text{Sr}_5(\text{GeO}_4)(\text{PO}_4)_2$  and Sr-hydroxyapatite (Table 1) shows their resemblance and indicates that both these compounds belong to the same structural type.

In this connection the powder pattern of  $\text{Sr}_5(\text{GeO}_4)(\text{PO}_4)_2$  was indexed on the basis of a hexagonal cell. Unit cell constants derived from [004] and [300] diffractions are as follows:  $a = 9.84$  Å,  $c = 7.36$  Å. The indices of refraction are:  $n_\alpha = 1.666$ ,  $n_\gamma = 1.662$ .

Table 1

Experimental and calculated interplanar spacings for  $\text{Sr}_5(\text{GeO}_4)(\text{PO}_4)_2$  compared with interplanar spacings of  $\text{Sr}_5(\text{PO}_4)_3\text{OH}$

$\text{Sr}_5(\text{PO}_4)_3\text{OH}$ [5]			$\text{Sr}_5(\text{GeO}_4)(\text{PO}_4)_2$				
$d_{hkl}$	$I/I_0$	$hkl$	$d_{hkl}$	$I/I_0$	$1/d_{\text{exp}}^2$	$1/d_{\text{calc}}^2$	$d_{hkl \text{ calc}}$
4.22	16	200	4.27	13	0.054846	0.055124	4.26
4.05	8	111	4.09	2	0.059692	0.059780	4.09
3.63	18	201; 002	3.68	20	0.0740	0.0737	3.68
3.34	18	102	3.37	15	0.0877	0.0875	3.38
3.19	20	210	3.22	21	0.0964	0.0964	3.22
2.92	90	211	2.95	100	0.1150	{0.1150 0.1149}	{2.95 2.95}
2.91	100	112	—	—	—	—	—
2.81	60	300	2.84	60	0.1240	0.1240	2.84
2.75	8	202	2.79	7	0.1287	0.1289	2.79
2.46	6	220?	—	—	—	—	—
2.32	8	103	2.36	10	0.1788	0.1797	2.35
2.29	6	—	—	—	—	—	—
2.22	10	302; 311	2.25	2	0.1970	{0.1976 0.1978}	{2.25 2.25}
2.17	8	113	2.20	5	0.2074	0.2073	2.19
2.10	6	203	2.13	2	0.2208	0.2210	2.12
2.02	20	222; 401	2.045	27	0.2391	{0.2389 0.2391}	{2.046 2.045}
1.97	14	312	1.988	13	0.2530	0.2529	1.985
1.93	20	213	1.952	20	0.2624	0.2624	1.945
1.87	14	321	1.890	13	0.2799	0.2803	1.889
1.84	14	410	1.859	7	0.2894	0.2894	1.860
1.83	14	303	—	—	—	—	—
1.82	12	402; 004	1.841	18	0.2950	{0.2942 0.2950}	{1.843 1.841}

$\text{Sr}_5(\text{GeO}_4)(\text{PO}_4)_2$  exists in one modification which is stable up to  $1300^\circ\text{C}$ . There is a region of homogeneity based on this compound covering the range of compositions from 44 to 62 mole % of  $\text{Sr}_3(\text{PO}_4)_2$ . The phase stable in this interval will be denoted in the next as the phase *C*, by an analogy to an apatite-like phase in the system  $\text{Ca}_2\text{GeO}_4\text{—Ca}_3(\text{PO}_4)_2$  [6]. The samples of the phase *C* can be prepared in a way analogous to the preparation of a pure ternary compound.

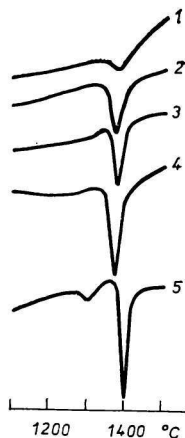
The upper limit of the stability of this phase lies in the temperature interval between  $1300\text{—}1500^\circ\text{C}$  in which a congruent transition of the phase *C* into a high temperature phase of another crystal structure takes place. The rather broad temperature interval of the transformation is a consequence of the small rate of the transformation owing to the stability of an apatite-like structure at high temperatures. Therefore on the DTA curves this transition appears as a small, shallow maximum or it is not revealed at all.

There is probably a maximum of the thermal stability of the phase *C* which corresponds to the temperature of  $1500^\circ\text{C}$  and is shifted in the direction of a higher phosphate content.

The part of the system over 62 mole % of  $\text{Sr}_3(\text{PO}_4)_2$  is a two phase region where the phase *C* coexists with a solid solution of  $\text{Sr}_3(\text{PO}_4)_2$ . The solubility of  $\text{Sr}_2\text{GeO}_4$

Fig. 1. DTA curves for the samples:

1. 40 mole %  $\text{Sr}_2\text{GeO}_4$  — 60 mole %  $\text{Sr}_3(\text{PO}_4)_2$ ; 2. 30 mole %  $\text{Sr}_2\text{GeO}_4$  — 70 mole %  $\text{Sr}_3(\text{PO}_4)_2$ ; 3. 20 mole %  $\text{Sr}_2\text{GeO}_4$  — 80 mole %  $\text{Sr}_3(\text{PO}_4)_2$ ; 4. 10 mole %  $\text{Sr}_2\text{GeO}_4$  — 90 mole %  $\text{Sr}_3(\text{PO}_4)_2$ ; 5.  $\text{Sr}_3(\text{PO}_4)_2$ .

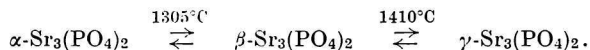


in  $\text{Sr}_3(\text{PO}_4)_2$  is limited and does not exceed 5 mole % at  $1400^\circ\text{C}$ . At lower temperatures the solubility (if any) decreases to 1–2 mole %.

Besides the X-ray diffraction, the solubility of orthogermanate in  $\text{Sr}_3(\text{PO}_4)_2$  was also disproved by microscopic analysis of samples of pure  $\text{Sr}_3(\text{PO}_4)_2$  and of  $\text{Sr}_3(\text{PO}_4)_2$  heated with additions of  $\text{Sr}_2\text{GeO}_4$ . This investigation did not show any change in the magnitude of refractive indices of mixtures in comparison to  $\text{Sr}_3(\text{PO}_4)_2$ . The refractive indices were:  $n_x = 1.708$ ,  $n_y = 1.702$ .

In the interval between 62–95 mole % of  $\text{Sr}_3(\text{PO}_4)_2$  the DTA curves show the presence of one pronounced endothermic effect at  $1370^\circ\text{C}$ . The DTA curve of pure strontium orthophosphate (Fig. 1) contains two signals: a small one at  $1300^\circ\text{C}$  and a deep one at  $1400^\circ\text{C}$ . The signals at 1400 and  $1370^\circ\text{C}$  are reversible and they correspond to the transitions of  $\text{Sr}_3(\text{PO}_4)_2$  and of its solid solutions.

The available literature data on the polymorphism of  $\text{Sr}_3(\text{PO}_4)_2$  based on DTA results [7–9] concur on the existence of the two endothermic signals comparable in their size at 1305 and  $1410^\circ\text{C}$ . On the basis of recent literature data the following scheme of the polymorphism is proposed



According to our estimation, the X-ray data for the  $\beta$  form listed in [7] are identical with those of the  $\alpha$  form. Our high-temperature X-ray investigation did not reveal any changes in the powder diffraction pattern of the  $\alpha$  form up to the temperature of  $1350^\circ\text{C}$ . It can be assumed that the nature of the endo-signal at  $1350^\circ\text{C}$  is not related to the transition of  $\text{Sr}_3(\text{PO}_4)_2$  and is caused by some parallel transitions in connection to the presence of admixtures or a deviation from the stoichiometry.

The results show that for  $\text{Sr}_3(\text{PO}_4)_2$  the only transition takes place at  $1400^\circ\text{C}$ .

The high-temperature form of  $\text{Sr}_3(\text{PO}_4)_2$  is not stable below  $1400^\circ\text{C}$  and owing

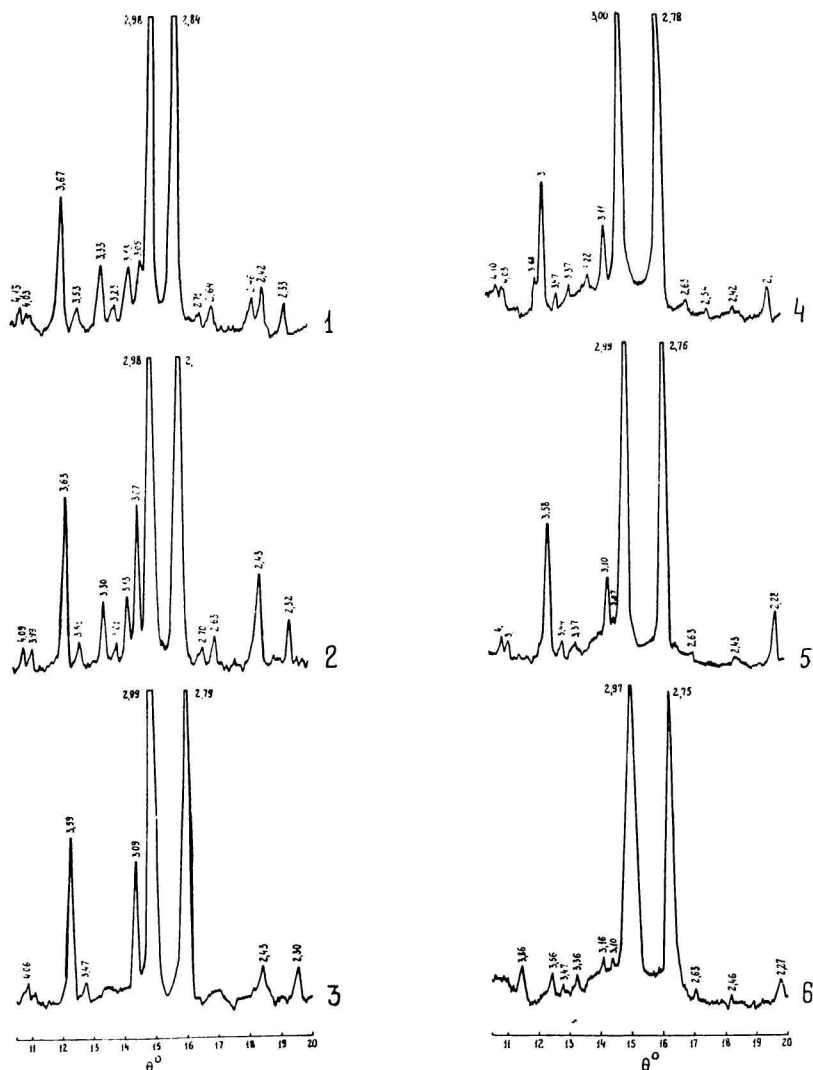


Fig. 2. X-Ray powder diffraction patterns of a metastable solid solution obtained by quenching from 1700°C.

1. 70 mole %  $\text{Sr}_2\text{GeO}_4$  — 30 mole %  $\text{Sr}_3(\text{PO}_4)_2$ ; 2. 60 mole %  $\text{Sr}_2\text{GeO}_4$  — 40 mole %  $\text{Sr}_3(\text{PO}_4)_2$ ; 3. 50 mole %  $\text{Sr}_2\text{GeO}_4$  — 50 mole %  $\text{Sr}_3(\text{PO}_4)_2$ ; 4. 40 mole %  $\text{Sr}_2\text{GeO}_4$  — 60 mole %  $\text{Sr}_3(\text{PO}_4)_2$ ; 5. 30 mole %  $\text{Sr}_2\text{GeO}_4$  — 70 mole %  $\text{Sr}_3(\text{PO}_4)_2$ ; 6. 20 mole %  $\text{Sr}_2\text{GeO}_4$  — 80 mole %  $\text{Sr}_3(\text{PO}_4)_2$ .

to the reversibility of the transformation cannot be preserved by quenching, even from temperatures 1600–1700°C, *i.e.* from the melt (the melting point of  $\text{Sr}_3(\text{PO}_4)_2$  is 1620°C [8]).

The phase relationship in the system at temperatures above 1300°C is characterized by a high-temperature transition resulting in the region of homogeneity (one phase region) in the broad range of concentrations. This transition takes place in the temperature range between 1300–1500°C and is demonstrated by the appearance of new lines on powder diffraction patterns.

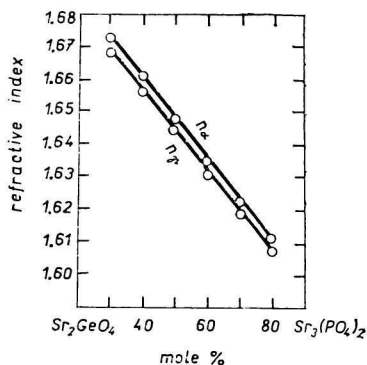


Fig. 3. The dependence of the refractive index on the composition.

The samples containing 30 mole % of  $\text{Sr}_3(\text{PO}_4)_2$  exhibit the lowest temperature of transformation and above 1350°C they already represent new phases. In the concentration range from 30 to 60 mole % of  $\text{Sr}_3(\text{PO}_4)_2$  the complete transformation to the high-temperature phase is observed after 1 to 2 hr thermal treatment at 1500–1550°C. The samples quenched from the temperature 1600 and 1700°C represent single phases in the concentration limits from 30 to 80 mole % of  $\text{Sr}_3(\text{PO}_4)_2$ . At higher or lower phosphate content the quenched samples had the composition of original mixtures.

Powder patterns representing the phase composition of samples heated at 1600–1700°C are shown in Fig. 2. It is evident that they have the same character; they represent the phases of variable composition but of the same structural type. However, regardless the structural type, the powder patterns of samples in the range from 60 to 70 mole % of  $\text{Sr}_3(\text{PO}_4)_2$  are characterized by an enlarged set of diffraction lines in comparison with samples of other composition.

At normal conditions the considered phase of variable composition appears to be a metastable phase. For this reason the superstructure diffraction lines appear in patterns 1, 2 (Fig. 2) which indicates the ordering of the structure of the high-temperature phase in the process of cooling and a possibility to form the metastable intermediate compound of approximate composition  $2\text{Sr}_2\text{GeO}_4 \cdot \text{Sr}_3(\text{PO}_4)_2$ ; this composition represents one of the end members of the metastable solid solution series. The formation of the solid solution is confirmed also by the diagram shown in Fig. 3 where the dependence of the linear change of the refractive index on the composition is presented.

The results of quenching experiments and of the DTA study of the high-temperature phase transitions of pure  $\text{Sr}_3(\text{PO}_4)_2$  and of its solid solutions at 1400°C indicate the formation of a continuous series of solid solutions at temperatures close to sub-solidus temperature of the system.

## References

1. Pánek, Z. and Pluhár, E., *Patent pending*, No. PV 8270—72.
2. Grebenshchikov, P. G., Shirvinskaya, A. K., and Shitova, V. I., *Zh. Neorg. Khim.* **12**, 3399 (1967).
3. Grebenshchikov, P. G. and Shitova, V. I., *Izv. Akad. Nauk SSSR, Ser. Neorg. Mat.* **6**, 773 (1970).
4. Pieper, J., Eysel, W., and Hahn, T., *J. Amer. Ceram. Soc.* **55**, 619 (1972).
5. Ropp, R. C., Ala, M. A., Hoffman, C. W. W., Veleker, T. J., and Mooney, R. W., *Anal. Chem.* **31**, 1163 (1959).
6. Shirvinskaya, A. K. and Bondar, I. A., *Izv. Akad. Nauk SSSR, Ser. Neorg. Mat.*, in press.
7. Sarver, J. F., Hoffman, M. V., and Hummel, F. A., *J. Electrochem. Soc.* **108**, 19 (1961).
8. Sarver, J. F., Katnack, F. L., and Hummel, F. A., *J. Electrochem. Soc.* **106**, 960 (1959).
9. Looney, J. R. and Brown, J. J., *J. Electrochem. Soc.* **118**, 470 (1971).

Translated by J. Majling