

## Structural and dielectric properties of $\text{Pb}_5(\text{Ge}, \text{Si})\text{O}_{11}$

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**Abstract.** The ferroelectric lead germanate ( $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ ) and its isomorphous compounds are important because of their uses as pyroelectric and electro-optic devices. Comparison of inter-planar d-spacings of  $\text{Pb}_5\text{Ge}_{3-x}\text{Si}_x\text{O}_{11}$  ( $x = 0, 0.3, 0.7$  and  $1.00$ ) suggests that there is no change in basic structure of  $\text{Pb}_5\text{Ge}_{3-x}\text{Si}_x\text{O}_{11}$  when Si is substituted for Ge in small quantity ( $x < 1$ ). The dielectric properties of the Si-substituted compounds have been studied as a function of temperature (30 to 200°C). The ferroelectric-paraelectric phase transition has been observed at 185°C. The Si doping causes (a) Curie point to shift towards low temperature, (b) peak value of the dielectric constant to decrease and (c) phase transition diffuse. The fast increase in dielectric constant of pure  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  with temperature (beyond transition temperature) may be attributed to the development of space charge polarization in the system.

**Keywords.** Ferroelectrics; pyroelectric; dielectric constants; diffuse phase transitions.

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### 1. Introduction

Lead germanate ( $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ ) is an attractive ferroelectric material (Nanamatsu *et al* 1971; Eysel *et al* 1973) and has many industrial applications (Srinivasan 1984). Its space group is P3 (trigonal) below Curie temperature ( $T_c = 177^\circ\text{C}$ ) and  $\text{P}\bar{6}$  (hexagonal) above it (Iwasaki *et al* 1971). It is considered as a most favourable pyroelectric sensor material because of its (a) reasonably high pyroelectric coefficient in wide temperature range (Watton *et al* 1976), (b) small dielectric constant (Mansing *et al* 1979; Goto 1981) and (c) high pyroelectric figure of merit. The possibility of inexpensive synthesis of the material has attracted industrial users (Lang 1974). By substituting alkali and alkaline earth ions at Pb site and tetrahedrally coordinated ions (like  $\text{W}^{6+}$ ,  $\text{Te}^{6+}$ ,  $\text{Cr}^{6+}$ ,  $\text{V}^{5+}$  and  $\text{Si}^{4+}$ ) at germanium sites, it is possible to prepare a large number of isomorphous compounds. It has been observed that among these, only silicon substituted lead germanate compounds show the dielectric anomaly (Iwasaki *et al* 1972). Though some studies of dielectric and structural properties on single crystal and thin film of lead germanate have been done in the past, not much information is available on ceramic samples of the compound. Results of a comprehensive study of dielectric and structural properties of  $\text{Pb}_5\text{Ge}_{3-x}\text{Si}_x\text{O}_{11}$  ( $0 \leq x \leq 1$ ) ceramics are reported here.

## 2. Experimental procedure

The polycrystalline lead germanate silicate  $\text{Pb}_5\text{Ge}_{3-x}\text{Si}_x\text{O}_{11}$  ( $x = 0, 0.3, 0.7, 1$ ) were prepared from high purity (AR grade)  $\text{PbO}$  (Sarabhai Chemicals),  $\text{GeO}_2$  (BARC, Bombay) and  $\text{SiO}_2$  (Jyoti Chemicals) by high-temperature solid-state reaction technique. These oxides are mixed in a agate-mortar for an hour and calcined at  $600^\circ\text{C}$  in a platinum crucible. The calcined powder was again grounded to make fine and homogeneous powder and screened through 38 micron screen (sieve). Then the powder was uniaxially cold pressed into pellets (dia = 1.12 cm, thickness = 1 ~ 2 mm) at a pressure of  $5 \times 10^6 \text{ kg/m}^2$ . The pellet samples were then sintered at  $670^\circ\text{C}$  for 12 h. Silver paste was used as an electrode on either side of the pellet samples.

X-ray diffractogram of all the samples was recorded at room temperature by Rigaku diffractometer (miniflex) with  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in wide  $2\theta$  range ( $10 \leq 2\theta \leq 70^\circ$ ). d-spacings of many planes and cell parameters of the samples were calculated and compared with the standard data. The surface morphology of the samples were studied using a scanning electron microscope (CAMSCAN).

Measurements of dielectric constant ( $\epsilon$ ) and loss ( $\tan \delta$ ) were carried out by GR 1620 capacitance measuring assembly as a function of temperature (room temperature to  $200^\circ\text{C}$ ).

## 3. Results and discussion

The sharp-single X-ray profiles of all the reflections of the samples suggest the formation of single phase compounds. Using d values of 25 reflections, cell parameters of  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  have been determined which are found to be consistent with the reported values (Iwasaki *et al* 1971). These are:  $a = 10.251 \text{ \AA}$ ,  $c = 10.685 \text{ \AA}$  at room temperature. Experimentally observed ( $d_{\text{obs}}$ ) and calculated d spacings ( $d_{\text{cal}}$ ) of some reflections with their intensities for all samples with  $x = 0, 0.3, 0.7$  and 1 have been summarized in tables 1 and 2. It is clear that the positions (i.e.  $2\theta$ ) and d-spacings of the diffraction lines of  $\text{Pb}_5\text{Ge}_{3-x}\text{Si}_x\text{O}_{11}$  with varying composition of Si (i.e.  $x$ ) are essentially invariant. A reasonably good agreement of calculated and observed d-values of all the diffraction lines of different compositions of lead germanate clearly suggests that at room temperature there is no change in crystal structure of  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$  by substituting Si up to  $x = 1$ . However, slight difference in the d values could be explained due to variation of ionic sizes and amount of the substituted ions. The change in the intensity of the observed reflections with different  $x$ -values may be due to (i) variation of particle size and (ii) the presence of Si in  $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ . The linear particle size ( $P$ ) has been calculated from some strong reflections in the wide  $2\theta$  range ( $10 \leq 2\theta \leq 70$ ) using the Scherrer's equation  $P = 0.89 \lambda / (\beta_{1/2} \cos \theta)$  where  $\beta_{1/2}$  is the halfwidth. The average particle size of the samples was found to be about  $330 \text{ \AA}$ .

The SEM photographs of lead germanate of different compositions (i.e.,  $x = 0, 0.3, 0.7, 1.0$ ) are shown in figures 1(a) to 1(d). In figures 1(b) and 1(d), we do not see much island or holes. Some holes and island can be seen in figures 1(a) and 1(c) which suggest that densities of the compound with  $x = 0$  and  $x = 0.7$  are less compared to those of  $x = 0.3$  and  $x = 1$ . The grain shape is almost spherical. The average grain size is approximately  $2.3 \mu\text{m}$ .

The variation of the dielectric constant and loss with temperature for various

**Table 1.** Comparison of some observed d-values of lead germanate  $Pb_5Ge_{3-x}Si_xO_{11}$  ( $x = 0, 0.3, 0.7, 1$ ). a = observed and b = calculated (from cell parameters given in the text) d values for  $x = 0$ . [in Å].

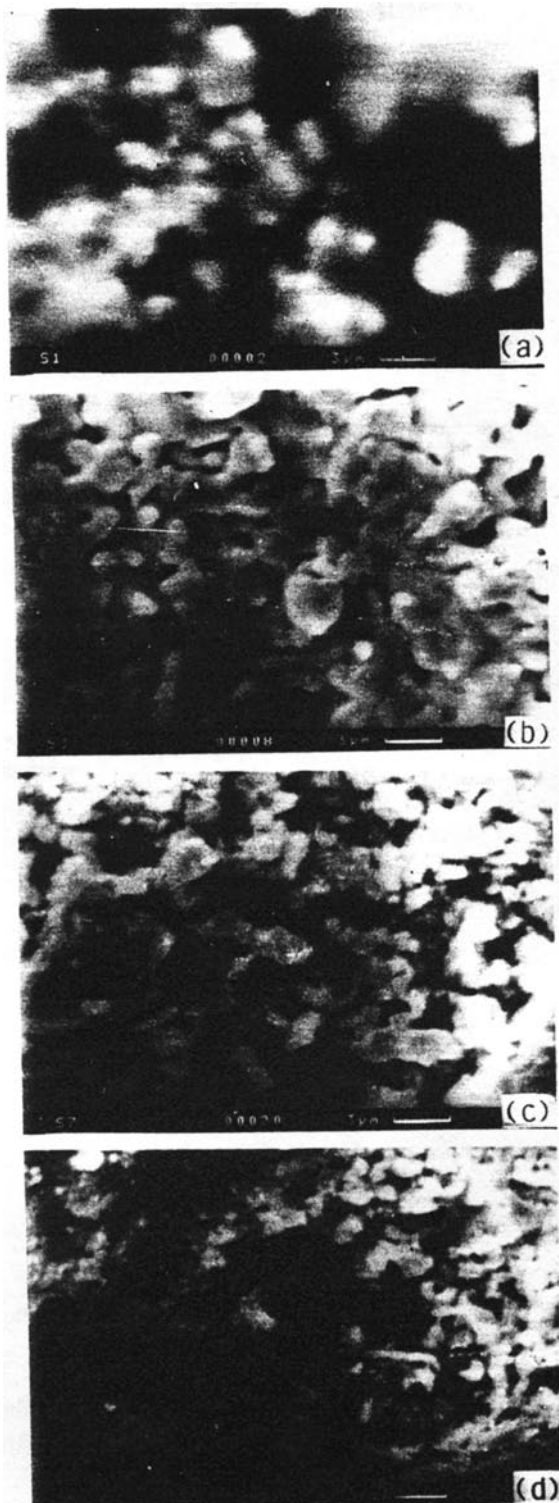
<i>hkl</i>	$x = 0$	$x = 0.3$	$x = 0.7$	$x = 1$
002	a) 5.3470 b) 5.3425	—	—	5.2727
110	a) 5.1253 b) 5.1255	—	—	5.0620
111	a) 4.6263 b) 4.6213	4.6263	4.6141	4.5670
200	a) 4.4394 b) 4.4388	4.4394	4.4284	4.3909
112	a) 3.6978 b) 3.6986	3.6978	3.681	3.6651
003	a) 3.5658 b) 3.5617	3.5587	3.5447	3.5209
210	a) 3.3584 b) 3.3554	3.3522	3.3505	3.3103
103	a) 3.3093 b) 3.3056	3.3093	3.2972	3.2725
211	a) 3.2040 b) 3.2013	3.2040	3.1871	3.1594
300	a) 2.9590 b) 2.9542	2.9590	2.9494	2.9261
113	a) 2.9241 b) 2.9248	2.9241	2.9148	2.8930
212	a) 2.8468 b) 2.8415	2.8468	2.8380	2.8096
203	a) 2.7860 b) 2.7780	2.7778	2.7365	2.7303
312	a) 2.2395 b) 2.2362	2.2368	—	—
400	a) 2.2210 b) 2.2194	2.2210	2.2205	2.1910
223	a) 2.0806 b) 2.0802	2.0708	2.0700	2.0556
320	a) 2.0357 b) 2.0367	2.0357	2.0313	2.0121
313	a) 2.0272 b) 2.0254	2.0272	2.0187	2.0039
321	a) 2.0018 b) 2.0006	2.0018	1.9976	1.9770
410	a) 1.9391 b) 1.9373	1.9371	1.9352	1.9141
322	a) 1.9027 b) 1.9031	1.9027	1.8916	1.8880
403	a) 1.8842 b) 1.8836	1.8842	1.8787	1.8687
215	a) 1.8022 b) 1.8025	1.8018	1.8000	1.7825
006	a) 1.7808 b) 1.7808	1.7825	1.7776	1.7617
421	a) 1.6556 b) 1.6574	1.6556	1.6584	1.6574

**Table 2.** Comparison of observed intensity ratio of some reflections for  $\text{Pb}_5\text{Ge}_{3-x}\text{Si}_x\text{O}_{11}$  ( $x=0, 0.3, 0.7, 1$ ).

<i>hkl</i>	$x=0$	$x=0.3$	$x=0.7$	$x=1$
002	1	VW	VW	2
110	3	VW	VW	4
111	7	7	5	9
200	25	21	17	24
112	17	15	13	20
003	11	10	6	11
210	47	34	25	40
103	23	20	15	24
211	40	37	25	36
300	77	61	44	56
113	100	76	49	64
212	38	34	25	35
203	5	5	8	15
312	2	2	VW	VW
400	5	4	2	22
223	32	28	12	12
320	10	8	7	9
313	12	18	21	8
321	10	8	6	6
410	10	9	7	17
322	11	10	12	11
403	20	20	14	11
215	11	7	5	7
006	8	7	5	7
421	2	5	3	10

\*VW = Very weak

composition ( $x=0, 0.3, 0.7$  and  $1.0$ ) is shown in figures 2 and 3 respectively. The room temperature dielectric constant of pure compound ( $x=0$ ) is 20, rising to a maximum value of around 100 at curie temperature (i.e.  $185^\circ\text{C}$ ). The slow increase of dielectric constant in lower temperature region (less than  $140^\circ\text{C}$ ) may be due to lattice and ionic polarizability and faster increase at higher temperatures may be due to space charge polarization of thermally generated carrier. The increase in Si doping concentration causes the curie point to shift towards the lower temperature. The peak value of the dielectric constant ( $\epsilon_{\text{max}}$ ) has been decreased and hence the phase transition has become diffused (i.e. broaden). The decrease in the maximum value of dielectric constant with increase in silicon concentration implies that this substitution reduces the dipole moment of the lattice. The region around  $\epsilon_{\text{max}}$  was found to be broadened. This broadness increases as the concentration of Si increases. The broadening of dielectric peaks may be considered due to compositional fluctuation and structural disordered (Lines and Glass 1977) caused by the doping and to the decrease in the grain size with increase in silicon concentration. Detailed studies of the dielectric behaviour of Si doped lead germanate also show a systematic decrease and broadening of the peak at  $T_c$  which very well fits into the microstructural variation from single crystal to the polycrystalline and possibly glassy state. The dielectric loss increases monotonically with temperature for pure sample. The increase of silicon concentration causes the dielectric loss to decrease and the hump of the curve (i.e. dielectric peak) to shift towards lower temperature region. Like dielectric constant,



**Figure 1.** SEM photographs of  $Pb_5Ge_{3-x}Si_xO_{11}$  at 3  $\mu m$  resolution for (a)  $x = 0$ ; (b)  $x = 0.3$ ; (c)  $x = 0.7$ ; (d)  $x = 1$ .

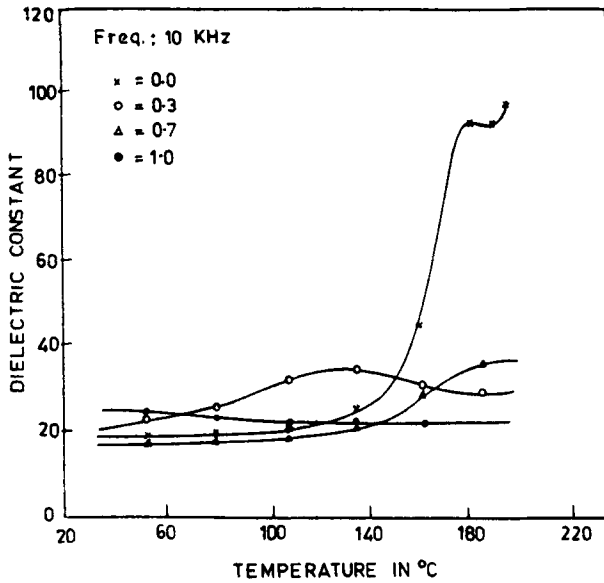


Figure 2. Variation of dielectric constant as a function of temperature in  $Pb_5Ge_{3-x}Si_xO_{11}$  at 10 kHz.

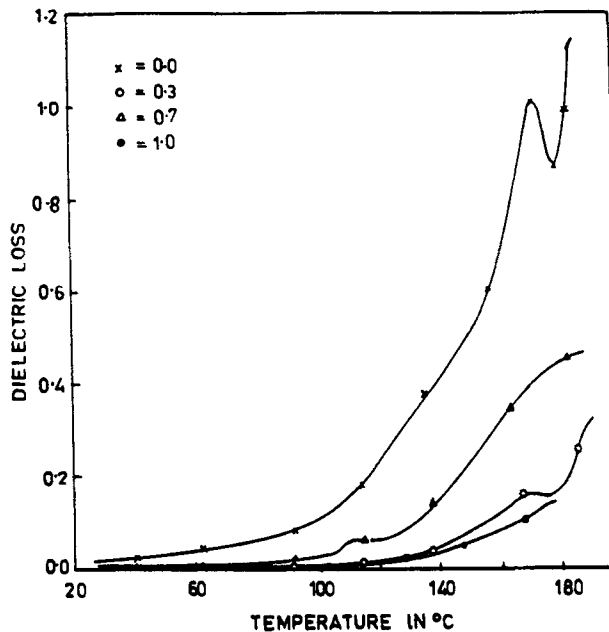


Figure 3. Variation of dielectric loss ( $\tan \delta$ ) as a function of temperature in  $Pb_5Ge_{3-x}Si_xO_{11}$  at 10 kHz.

$\tan \delta$  has been found almost constant up to 100°C. For pyroelectric detector with better performance, it is always required to reduce the dielectric constants and loss with compositional adjustment. It is finally concluded that the  $Pb_5Ge_3O_{11}$  with  $x = 1$  could be suitable for pyroelectric detector and further work has been planned in this direction.

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