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13. ABSTRACT (Maximum 200 words)

Further exploration in the [NZP]-family was carried on-in that the systematic crystal chemistry investigation of $M^{1}Zr_2P_3O_{12}$ ($M^{1} \equiv$ Li,Na,K,Rb and Cs) and $M^{11}Zr_4P_6O_{24}$ ($M^{11} \equiv$ Mg, Ca,Sr,Ba) was completed and few more new compositions were synthesized and characterized. An effort was made to grow single crystals of Na, Sr and Ca zirconium phosphates using B_2O_3 as flux in order to obtain more data to confirm the results obtained on powdered samples. $NaGe_2P_3O_{12}$ was studied as a potential candidate for the development of glass-ceramic due to its low melting behavior. It has been established that sol-gel process is superior to powder method for synthesizing [NZP]-compounds and therefore most of the compositions were prepared by this route. Dielectric measurements made on $CaZr_4P_6O_{24}$ showed that in general, [NZP]-materials have low dielectric constant with relatively low loss.

New families such as diborides and Al_2O_3-GeO_2 were investigated for their thermal expansion behavior. $Pb_3MgNb_2O_9$ and related perovskites were also investigated in order to search any new low thermal expansion composition with high dielectric constant, but so far

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July 1986

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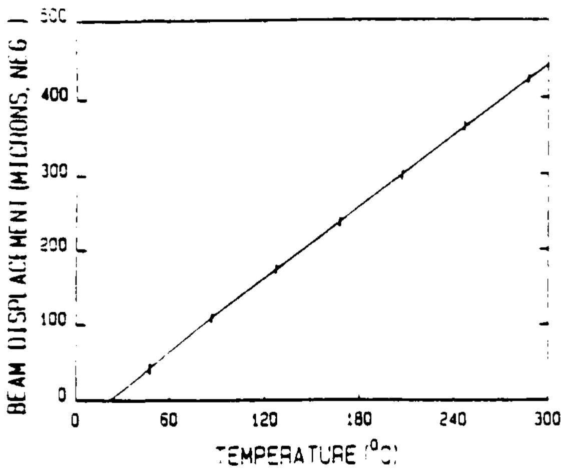

Figure 2. Plot of the laser beam displacement against temperature using the data of Table 1.

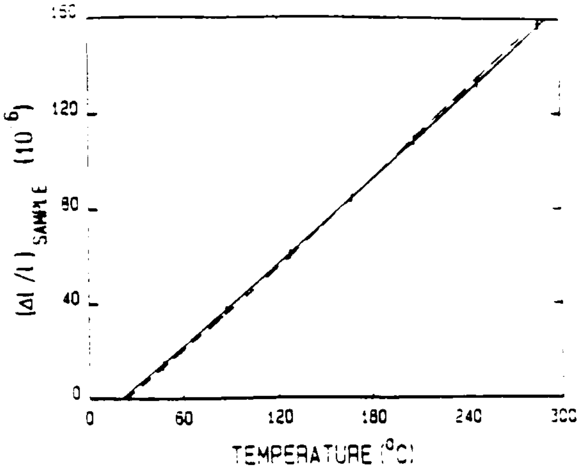

Figure 3. Plot for $(\Delta L/L)_{SAMPLE}$ against temperature determined from the data of Fig. 2. The dashed curve corresponds to the NBS data sheet [9].

DISCUSSION

As we have seen, the photodetector-based method provides a very sensitive approach for thermal expansion measurements. We noticed some signal fluctuations at higher temperatures (above 250°C). The air currents were probably causing vibrations in the freely held sample-reference-probe system. This was confirmed by replacing the sample and reference rods by bigger and heavier ceramic rods resulting in no fluctuations. Our furnace also has an open window for the laser beam. By using a covered window and vacuum furnace these problems can be overcome. Anyway, the prospects for this kind of detector-based measurement should not be underestimated because 0.01μm resolution in the beam position change is possible [11] resulting in phenomenal sensitivity for $(\Delta L/L)$ measurement as 10^{-8} for $D = 1$ cm, $L = 2$ cm, and $\ell = 50$ cm! Obviously, this sensitivity can be realized by very good quality mirror, window, furnace, etc., but this work only shows the potential.

ACKNOWLEDGEMENT

This research work was supported by U.S. Air Force Contract Numbered AFOSR-83-0291.

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19. Abstract (Continued)

much success has not been achieved.

This year also we have continued to develop and modify new techniques to measure ultralow thermal expansion utilizing laser spectroscopy. A simple laser speckle dilatometer was devised based on the technique of direct observation of rotation of the laser speckles on a white paper. Another method was also developed in which change in position of the reflected laser beam from the probe was measured by using a tiny photodetector. Finally, the conventional push rod dilatometer was modified by using a supersensitive dial gage measurement utilizing laser speckles.

The highlight of this year's work is the successful fabrication of low thermal expansion magnetic materials employing composite approach and using YAG and NZP materials as the constituent phases.

PAST ACHIEVEMENTS

Summary:

During the last year on this project the research work covered three following main areas:

1. Further Exploration in the CTP(=NZP) - Family
   a. Systematic crystal chemistry of very low α materials
   b. Growth of single crystals for x-ray structure work
   c. Development of compositions suitable for glass-ceramic
   d. Determination of best processing methods
   e. Studies of dielectric constant of CZP
   f. The crystalline constraints of thermal expansion

2. Exploration for New Families of Zero-Expansion Materials
   a. Axial anisotropy in Diborides (ZrB_2, TiB_2, CrB_2)
   b. Al_2O_3-GeO_2 system
   c. $Pb_3MgNb_2O_9$ and related perovskites

3. New Methods for Measuring Thermal Expansion

As is clear from the reports to follow, we have made substantial progress in these areas.

1. Further Exploration in the CTP(=NZP)-Family

a. Systematic crystal chemistry of very low α materials:

The characterization of $M'Zr_2P_3O_{12}$ (M' = Li,Na,K,Rb,Cs) and $M''Zr_4P_6O_{24}$ (M'' = Mg,Ca,Sr,Ba) was completed and to continue our search for new low thermal expansion materials, we had synthesized and characterized several more new compositions, which are listed in Table 1. In general, they were prepared by powder mixing technique using oxides as precursors, calcining the mixture at 200°-600°C, and finally sintering the pellets made from the calcined powder at temperatures between 1000°-1200°C, depending upon the composition. The x-ray diffraction and thermal expansion results have also been presented in the Table. It is evident from these results that most of these compositions can be easily prepared in single phase and only $CaCrTiP_3O_{12}$ shows negative but low thermal expansion, other compositions were found to have high α.

In order to understand the basic crystal chemistry of anomalously low thermal expansion of [NZP]-family $M'Ti_2P_3O_{12}$ (M' = Li,Na,K,Rb,Cs) and $M''Ti_4P_6O_{24}$ (M'' = Mg,Ca,Sr,Ba) were synthesized by powder method in phase pure form. Most of the compositions sinter quite well and can be produced in low porosity ceramics. The study of thermal expansion behavior by dilatometer and by x-rays is continuing.

b. Growth of single crystals for x-ray structure work:

An effort was made to grow single crystals of Na, Sr and Ca zirconium phosphates by flux method, using B_2O_3 as flux. Robert Hazen at the Geophysical Laboratory, Carnegie Institute, Washington, DC, had obtained and interpreted the x-ray diffraction data for single crystals of $NaZr_2P_3O_{12}$ as a function of temperature. He has done this by means of an NSF grant. The analysis of the data is still in progress. The validity of our proposed model is thus being tested and the anomalous results for XrZP should be explained.

c. Development of compositions suitable for glass-ceramics:

This was carried out with $NaGe_2P_3O_{12}$, which was found to have low congruent melting point. This composition melted around 1130°C, glass obtained at 1200°C was quenched to room temperature and then was heat-treated at 600°, 700°, 800°, and 1000°C for various holding times to investigate the kinetics of recrystallization. After these experiments, the samples were x-rayed and the phases identified were GeO_2, $NaGe_2P_3O_{12}$, and glass. The recrystallization temperature determined by DTA was around 650°C. Further work is in progress in this area.

d. Determination of best processing methods:

It has been established now that sol-gel process is superior to solid state reaction method for synthesizing [NZP]-compounds by sol-gel technique only. In order to improve further the sintered product made by sol-gel route, a new step is being introduced to the conventional sol-gel method, i.e., seeding the gel. In this method, preformed seeds (submicron size particles suspended in water) are added to the gel of the same composition. So far the results of initial experiments are quite encouraging.

e. Studies of the dielectric constant of CZP:

Dielectric measurements were made on $CaZr_4P_6O_{24}$ ceramics to study their potential use in electro-ceramic applications. For this purpose measurements were made on four samples of CZP + 3% MgO, 5% MgO, 1% ZnO, and 5% ZnO compositions. The results are presented in Table 2, from which it is noted that these are, in general, low dielectric constant materials with relatively low loss.

f. The crystalline constraints of thermal expansion:

In order to study the effect of crystalline constraints on thermal expansion, a powdered and a sintered sample of $NaZr_2P_3O_{12}$ were fabricated and their thermal expansions were determined by high temperature x-ray diffractometry. The lattice constants of NZP were not altered in the sintered body with about 30% porosity, however, a sample with 8±3% porosity showed a slight alteration and a less porous sample has not yet been prepared.

2. Explorations for New Families of Zero-Expansion Materials

a. Axial anisotropy in diborides:

Three diborides, namely ZrB_2, TiB_2, and CrB_2, were studied. The anisotropy of the thermal expansion of diborides had been observed earlier by R.V. Sara (Union Carbide, Cleveland; private communication) and crystal chemical parameters of diborides had been studied by K.E. Spear (Materials Research Lab., University Park). We have measured here axial expansivities for Zr, Ti, and Cr diborides, and their chemical bonding character is directly correlated with the ellipicity of the deformation of the metal ion.

b. Al_2O_3-GeO_2 system:

It is known that the system Al_2O_3-TiO_2 contains a low α composition, namely Al_2O_3-TiO_2; one could expect same in an analogous system such as Al_2O_3-GeO_2, and therefore the GeO_2 rich region of this system was explored for any low α composition. Four compositions (Table 3) were prepared by mixing Al_2O_3 and GeO_2 powders in appropriate amounts and sintered at 1100°-1200°C for 20 hr. It was noted that no 1:1 compound exists in this system, the only intermediate compound which was found was Ge-mullite ($Al_6Ge_2O_{13}$). The thermal expansion of these four compositions fall in intermediate range, however, they exhibit temperature ranges where α is almost zero (similar to Al_2TiO_5), this has been shown in the last column of the table.

c. $Pb_3MgNb_2O_9$ and related perovskites:

As outlined in our original proposal, this year we had started an investigation in known ferroelectric perovskite families to examine their thermal expansion behavior. First, we examined the compositions based on PMN [$Pb(Mg_{1/3}Nb_{2/3})O_3$-$A(B'B'')O_3$] which is known to have near-zero thermal expansion between -200°C and 100°C and is a well known perovskite relaxor. Several ionic substitutions were incorporated at B-site, the fabrication of these ceramics was carried out following the technique described in the literature [1,2]. About 10 mole percent substitution was made of thirteen ions listed in Table 4. The sintering temperature for all composition kept at 1250°C for one hour. The thermal expansion measurements were made on rectangular bars cut from the sintered discs. It is clear from the thermal expansion data (Table 3) that all these compositions have quite high α's and show practically no effect on the average α with ionic substitution.

Another family of perovskite structure we had examined was PZT ($PbZr_{1-x}Ti_xO_3$) in which the contents of Zr and Ti were varied and four compositions as listed in Table 5 were fabricated. The thermal expansions of these compositions were measured on Harrop Dilatometer and it was found that $\alpha_{av.}$ for PZT ceramics ($0.44 \leq x \leq 0.54$) does not seem to change very much with the change in composition. More work in this family is in progress.

3. New Methods for Measuring Ultra Low Thermal Expansion

A simple laser speckle dilatometer for thermal expansion measurements was devised and tested. The technique was based on the direct observation of rotation of the laser speckles on white paper, wall, etc. and required inexpensive low power lasers. A schematic diagram of the technique is presented in Figure 1. For 5 cm long sample and reference rods kept 5 mm apart, a measurement sensitivity of 5×10^{-6} for $\Delta L/L$ can easily be obtained.

Another method was also developed that required the measurement of the change in position of the reflected laser beam from the probe using a tiny photodetector. If the size of the photodetector is very small as compared to the laser beam cross section, then the Baussian beam cross section gives the significant changes in the photodetector signal against small changes in the beam position. The change in the beam position ultimately gives the thermal expansion of the sample material. The schematic diagram of the experimental set up is presented in Figure 2.

An attempt was made to improve the sensitivity of the conventional push rod dilatometers by using a supersensitive dial gage measurement utilizing laser speckles (3) or a mirror attached to the push rod. Movement of speckles created in space by the laser beam incident on an aluminum foil attached to the needle of the gage are observed for the measurements. The experimental set up is presented in Figure 3.

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14. "Thermal Expansion Measurements by Photodetector Based Laser Beam Position Change Determination," C.S. Vikram, D.K. Agrawal, R. Roy, and H.A. McKinstry, Mat. Res. Soc. Symp. (in press).

15. "Synthesis and Thermal Expansion of $NaGe_2P_3O_{12}$," D.K. Agrawal, K.R. Kanak, and H.A. McKinstry, Mat. Res. Bull. (submitted).

PAPERS PRESENTED IN SCIENTIFIC MEETINGS

1. 21st University Conference on Ceramic Science held at the Penn State University, July 1985, Agrawal and Roy.

2. 1985 Fall Meeting of Materials Research Society held in Boston, Dec. 1-5, 1985, Agrawal, Roy, and Vikram.

3. 88th Annual Meeting of American Ceramic Society held in Chicago, April 27-May 2, 1986, Agrawal, Vikram, Patankar, and Roy.

The Following Papers were Presented:

i Application of dial-gage and laser speckles for ultralow thermal expansion measurements using push-rod dilatometers

ii study of lattice parameters of sintered ceramic and powdered samples of sodium zirconium phosphate

iii Structural model for thermal expansion of alkali zirconium phosphates

iv Thermal expansion of B-site modifications of bad magnesium niobate

PATENTS

A U.S. Patent application on "New Low Thermal Expansion Solid Solution Compositions" is being processed.

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3. C.S. Vikram and K. Vedam, Experimental Techniques 9, 16 (1985).

PERSONNEL

Dr. D.K. Agrawal has worked on the project full time. Dr. C.S. Vikram has been associated on a part-time basis with project in area of developing new thermal expansion measurements techniques. Mr. Anil Patankar has worked as a graduate student for one year. Professor H.A. McKinstry is the principal investigator for the project.

Manuscripts/reprints of the following papers are enclosed with the report.

1. Thermal Expansion of $NH_4Zr_2(PO_4)_3$

2. New Low Expansion Magnetic Materials - a Composite Approach

3. Thermal Expansion Measurements by Photodetector Based Laser Beam Position Change Determination

4. Synthesis and Thermal Expansion of $NaGe_2P_3O_{12}$

TABLE 1. [NZP]-Composition

COMPOSITIONS	SINTERING TEMP. (°C)	XRD	$\alpha \times 10^6 (°C^{-1})$
1. $NaSn_2P_3O_{12}$	1200	trace of SnO_2	9.2
2. $Na_3Cr_2P_3O_{12}$	1190	single phase	5.3
3. $Na_3Al_2P_3O_{12}$	850	single phase	13.6
4. $CaCrTiP_3O_{12}$	1200	single phase	-1.0
5. $CuTi_2P_3O_{12}$	1000	almost single phase	--

TABLE 2. Dielectric Properties of $CaZr_4P_6O_{24}$

	Samples			
PROPERTIES	CZP Mg_3 1250°C/1h	CZP Mg_5 1250°C/1h	CZP Zn_1 1250°C/1h	CZP Zn_5 1250°C/1h
Thickness (mm)	3.45	3.54	2.98	4.06
Diameter (cm)	1.118	1.122	1.207	1.125
Area (cm^2)	0.982	0.989	1.144	0.994
CAPACITANCE (pf)				
100 Hz	2.2	2.10	2.2	1.90
1 kHz	2.15	2.04	2.15	1.86
100 kHz	2.16	2.06	2.163	1.87
DIELECTRIC CONT.				
100 Hz	8.73	8.49	6.47	8.77
1 kHz	8.53	8.25	6.33	8.58
100 kHz	8.57	8.33	6.36	8.63
TEN				
100 Hz	0.01	0.01	0.01	0.01
1 kHz	0.001	0.001	0.003	0.001
100 kHz	0.02	0.02	0.02	0.01

TABLE 3. Al_2O_3-GeO_2 System

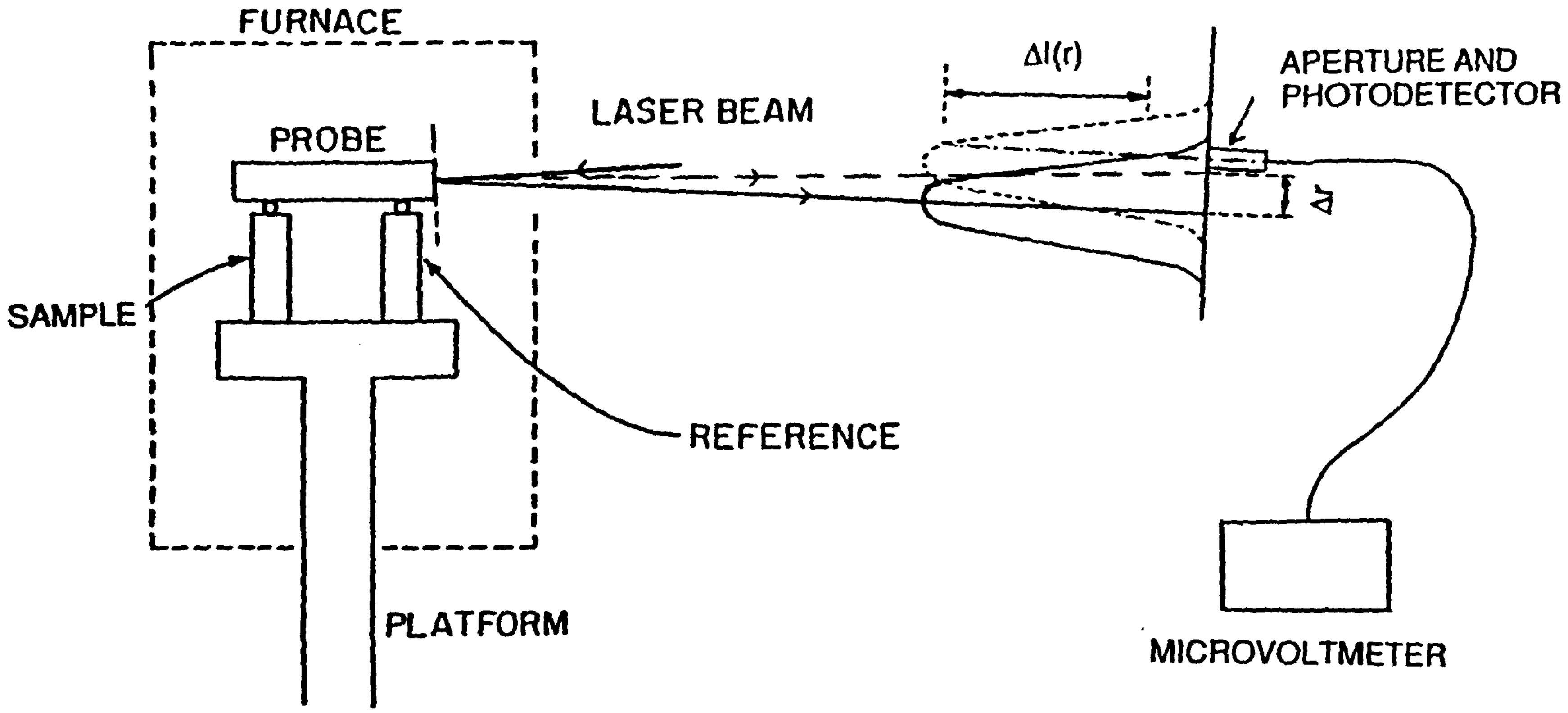
	COMPOSITIONS	XRD	$\alpha \times 10^6$ (°C^{-1})	TEMP. REGION for $\alpha \simeq 0$
1.	$.5Al_2O_3$-$.5GeO_2$	$Al_6Ge_2O_{13}$+GeO_2	5.6	30 - 90
2.	$.4Al_2O_3$-$.6GeO_2$	$Al_6Ge_2O_{13}$+GeO_2 + glass	4.5	30 - 100
3.	$.3Al_2O_3$-$.7GeO_2$	$Al_6Ge_2O_{13}$+GeO_2 + glass	5.8	30 - 70
4.	$.2Al_2O_3$-$.8GeO_2$	GeO_2 + glass + $Al_6Ge_2O_{13}$	5.4	-------

TABLE 4. $Pb(Mg_{1/3}Nb_{2/3})O_3$

SUBSTITUTING ION	$\alpha \times 10^6 (°C^{-1})$
Pure PMN	10.0
Ni^{+2}	9.6
Mg^{+2}	8.7
Co^{+2}	9.7
Zn^{+2}	9.5
Mn^{+2}	10.6
Fe^{+3}	10.1
Sc^{+3}	9.0
Ti^{+4}	9.8
Sn^{+4}	9.7
Hf^{+4}	9.3
Zr^{+4}	9.1
W^{+6}	11.5

TABLE 5. $Pb(Zr_{1-x}Ti_x)O_3$

COMPOSITION	$\alpha \times 10^6 (°C)^{-1}$
x = 0.52	5.8
x = 0.50	6.0
x = 0.54	5.9
x = 0.44	5.3


FURNACE
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LASER BEAM
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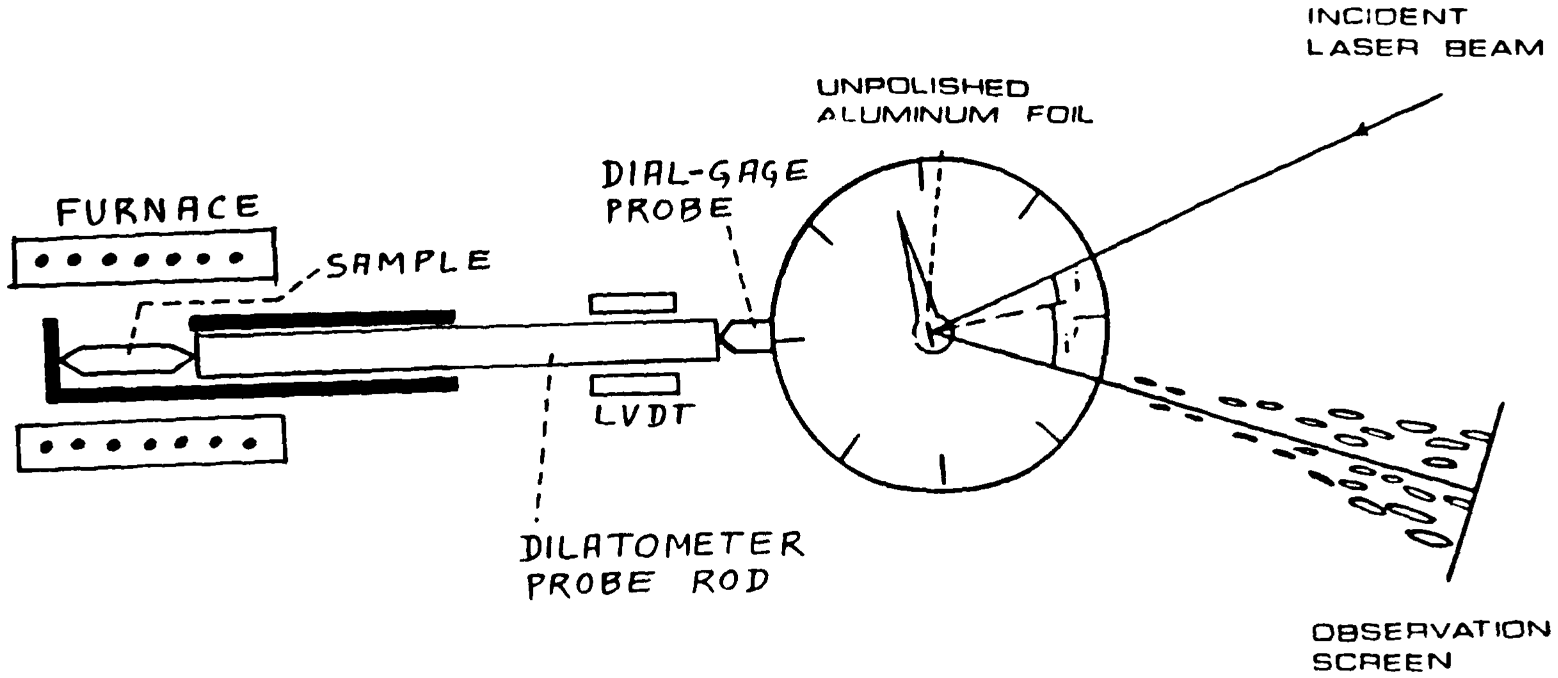
FIGURE 2.


INCIDENT
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UNPOLISHED
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SAMPLE
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OBSERVATION
SCREEN

FIGURE 3.

Experimental

$NaGe_2P_3O_{12}$ was synthesized by solid state reaction method using dry powders of Na_2CO_3 (J.T. Baker Chemical Co., Flux Grade), GeO_2 (Midwest Research Institute) and $NH_4H_2PO_4$ (J.T. Baker Chemical Co.) as precursors. In this method, the stoichiometric amounts of oxides were hand mixed, homogenized in acetone and calcined first at 260°C/16h and then at 900°C/16h to remove the volatiles such as NH_3 and CO_2. The mixture thus obtained was carefully ground, pelletized at 15000 psi, and finally heat-treated between 1000 and 1200°C to study the thermal behavior of $NaGe_2P_3O_{12}$.

The phase-identification of crystalline and melted material was carried out by X-ray diffraction techniques using a GE X-ray diffractometer. A DTA (Differential Thermal Analysis) of $NaGe_2P_3O_{12}$-glass was made on Dupont-900 Thermal Analyzer in order to determine the crystallization temperature. The average bulk thermal expansion measurements were made on small rectangular bars of sintered and glass samples of $NaGe_2P_3O_{12}$ using a Harrop Dilatometer. The glass samples were prepared by melting $NaGe_2P_3O_{12}$ pellets in Pt-crucibles at a suitable temperature.

Results and Discussion

One-inch pellets of calcined $NaGe_2P_3O_{12}$ powder were subjected to heat-treatment at temperatures between 1000°C to 1200°C for 18 hours. It was found that the lowest temperature to form single phase $NaGe_2P_3O_{12}$ was about 1000°C, below that temperature some free GeO_2 remains unreacted. All the samples fired above 1130°C were found to have transformed into colorless transparent glass phase; the melting point of $NaGe_2P_3O_{12}$ was determined to be 1125±5°C. It is known (6) that most of the Zr analogues of [NZP] materials melt at moderately high temperatures between 1600 and 1900°C; however, as in the present case, $NaGe_2P_3O_{12}$ melts at 1125°C which should be attributed to the complete substitution of refractory ZrO_2 by low melting GeO_2 (m.p. $\simeq$ 1100°C). This low melting behavior of this material encouraged us to investigate if a glass-ceramic could be developed with high density by low temperature heat-treatment of glass samples of $NaGe_2P_3O_{12}$. To achieve this goal, first a DTA run on a powdered sample of $NaGe_2P_3O_{12}$-glass was obtained (not shown here), which indicated one broad exothermic crystallization peak at approximately 650°C. Therefore, several samples of $NaGe_2P_3O_{12}$-glass were subjected to heat-treatments at 600°, 700°, and 800°C for the time periods varying from 1 hour to 24 hours. The x-ray study after the heat-treatment showed simultaneous crystallization of both $NaGe_2P_3O_{12}$ and GeO_2 (Hexagonal) in the samples heated at 700° and 800°C, there was not much crystallinity in the samples heated at 800°C as was evident from the absence of well defined lines in their X-ray diffraction patterns. This suggests that a highly stable form of GeO_2 is difficult to prevent from crystallizing with $NaGe_2P_3O_{12}$ and therefore, glass-ceramic containing one single crystalline phase of $NaGe_2P_3O_{12}$ could not be formed.

Figure 1 illustrates the thermal expansion characteristics of sintered and glass samples of $NaGe_2P_3O_{12}$ from room temperature to 400°C, the respective coefficients of thermal expansion were found to be 9.3 and 7.0 x 10^{-6}/°C. These values are quite high in comparison of other members of the [NZP] family (2) and therefore this particular material cannot be considered as low expansion material. However, a composite approach between $NaGe_2P_3O_{12}$

and $NaZr_2P_3O_{12}$ (which has negative coefficient of thermal expansion) may result into the development of a low- or near-zero expansion ceramic.

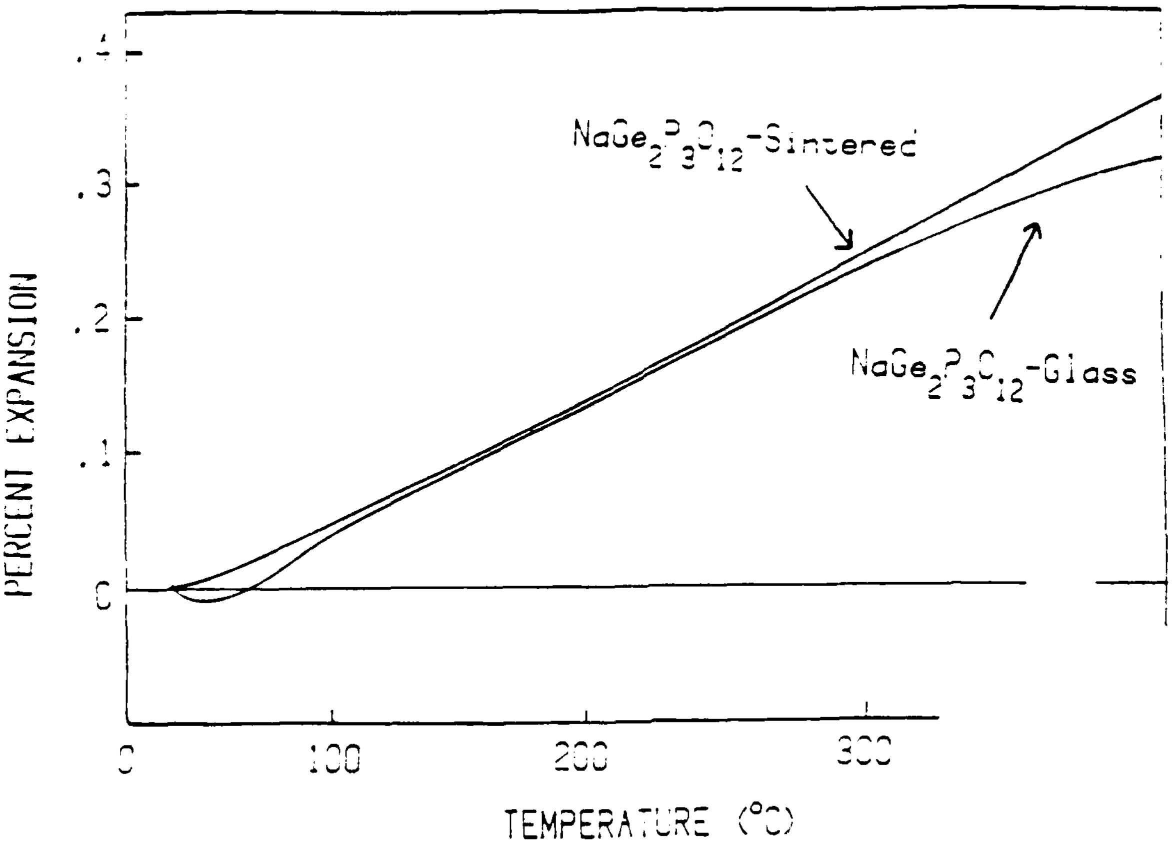

Figure 1: Thermal expansion behavior of sintered and glass samples of $NaGe_2P_3O_{12}$.

Acknowledgement

This work was supported by the U.S. Air Force under the contract number AFOSR-83-0291.

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Thermal expansion of $NH_4Zr_2(PO_4)_3$

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A new structural family of near-zero expansion ceramics has been recently discovered [1–5]. This family is based on the sodium dizirconium triphosphate, $NaZr_2(PO_4)_3$ (referred to hereafter as NZP), structure which has been extensively investigated as a fast ion conductor [6, 7]. Because of the enormous substitutions possible in this structure [8–12], the NZP phase was proposed as the one versatile structure that is capable of immobilizing all the elements in nuclear wastes [13–15]. Thus, there is enormous interest in this NZP phase for several different applications.

The advantages of near-zero thermal-expansion materials from housewares to space structures is well recognized by the materials community. The low thermal expansion of alkali end members of zirconium phosphate has been reported [5]. However, the thermal expansion behaviour of ammonium dizirconium triphosphate is not known because this phase was not synthesized until very recently [16, 17]. Since it has now become possible to synthesize the $NH_4Zr_2(PO_4)_3$, our objective here is to investigate the thermal expansion properties of this phase and compare them with those of the various alkali zirconium phosphates.

The ammonium dizirconium triphosphate (henceforth referred to as AZP) phase was synthesized from solutions under hydrothermal conditions [17] in a Parr bomb with a teflon cup. Appropriate volumes of 2.2 M $ZrOCl_2 \cdot 8H_2O$ solution and 1 M $NH_4H_2PO_4$ solution were mixed in the teflon cup of a Parr bomb and the bomb was heated in an oven at 220° C for six days. A slight excess of $NH_4H_2PO_4$ was helpful in obtaining a single phase of AZP. Phase characterization was accomplished by powder X-ray diffraction (XRD) using a Philips X-ray diffractometer with graphite monochromated CuKα radiation. Morphology of the AZP phase was determined by scanning electron microscopy using an ISI-DS 130 instrument. Differential thermal analysis (DTA) was carried out with a high-temperature Harrop (Model TA 700) analyser.

Thermal-expansion measurements were made with high-temperature X-ray diffractometry only. Dilatometry measurements of thermal expansion were not possible on this sample because sintered AZP pellets could not be obtained without phase decomposition. Above 500° C, the AZP phase decomposed to triclinic hydrogen dizirconium triphosphate as has been observed earlier by Clearfield *et al.* [17]. High-temperature X-ray diffraction measurements were made between room temperature and 400° C using a GE diffractometer with nickel-filtered CuKα radiation. Since the AZP shows strong peak intensities between 100 and 164° 2θ, several of these peaks were indexed and precise lattice parameters were calculated using the method of Cohen as given by Cullity [18]. A scanning speed of 0.2° min^{-1} (2θ) was used to determine precisely the peak positions. Any change in peak position due to thermal expansion could be easily seen at the high angles used in this study and, therefore, unambiguous results are expected for the thermal expansion measurements.

Phase-pure $NH_4Zr_2(PO_4)_3$ was synthesized by the hydrothermal method at a low temperature (220° C). This NZP phase can only be synthesized by the hydrothermal methods because the high temperatures (~ 1000° C) needed for the synthesis of alkali analogues of this family by firing in air would volatilize ammonia. The highly crystalline nature of this phase can be deduced from the X-ray diffractogram (not shown here) at high angles. Scanning electron microscopy showed rhombohedral crystals with well developed faces (Fig. 1). Differential thermal analysis of this phase (Fig. 2) showed the decomposition by NH_3 loss to occur between 600° and 700° C under the dynamic conditions of the DTA experiment resulting in the $HZr_2(PO_4)_3$ phase. The differential thermal analysis curve (Fig. 2) also showed several exotherms. The nature of these transformations has not been characterized so far.

The *a* and *c* lattice parameters of AZP are plotted against ionic radius along with the alkali members of the NZP family (Fig. 3). The NH_4^+ ion end member follows the same trend as the alkali ion end members of the NZP family in exhibiting a variation of cell dimensions in opposite directions with their ionic radii, i.e., the *a* parameter decreases and the *c* parameter increases when the size of the monovalent ion

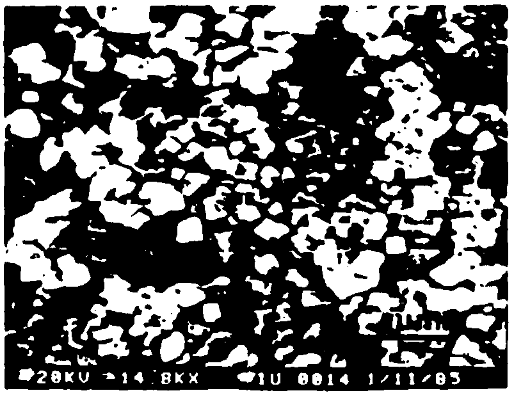

Figure 1 Scanning electron micrograph of the $NH_4Zr_2(PO_4)_3$ phase

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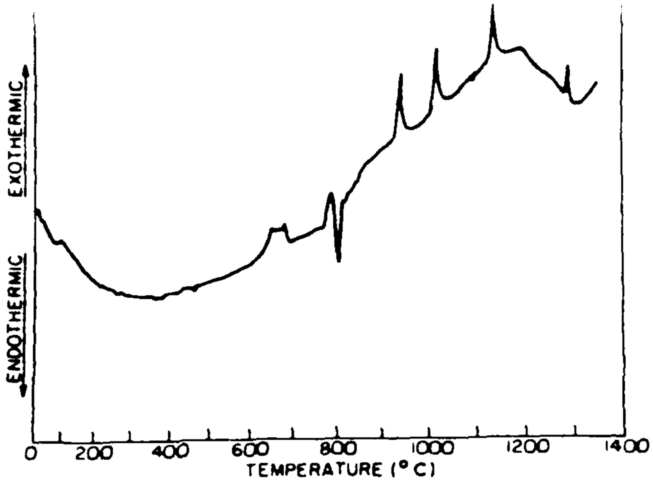

$NH_4Zr_2(PO_4)_3$ phase

of the NZP phase increases. This type of behaviour for alkali ion members of the NZP family was first noted by Sljukic *et al.* [8] and confirmed by Lenain *et al.* [5]. It is interesting that the monovalent NH_4^+ end member perfectly fits in with the behaviour of monovalent alkali members of the NZP family which was reported elsewhere [5]. The cell parameters of the $NH_4Zr_2(PO_4)_3$ phase are the same as those for the $RbZr_2(PO_4)_3$ (Fig. 3) as can be expected from their ionic radii.

The temperature dependence of the *a* and *c* cell parameters of the AZP along with those already reported [5] for the alkali end members of the NZP family are plotted in Fig. 4 and presented in Table I.

From the slopes of the curves $a = f(T)$ and $c = f(T)$, the axial thermal-expansion coefficients $\bar{\alpha}_a$ and $\bar{\alpha}_c$ were calculated. The overall linear thermal-expansion coefficient $\bar{\alpha}_l$ was calculated using the following relationship:

$$\bar{\alpha}_l = 2/3\bar{\alpha}_a + 1/3\bar{\alpha}_c \qquad (1)$$

The plots of the coefficients of thermal expansion against ionic radius for the AZP and the different members of the alkali zirconium phosphate family are shown in Fig. 5. Again, it can be seen from the figure that both the axial thermal-expansion coefficients as well as the overall linear thermal-expansion coefficient of AZP are very similar to those of $RbZr_2(PO_4)_3$. The rubidium and ammonium zirconium phosphates have negative overall thermal-expansion values whereas the other monovalent analogues have positive values. The thermal-expansion values of the rubidium and ammonium analogues are -0.76×10^{-6} and -1.9×10^{-6}, respectively.

The thermal-expansion property of $NH_4Zr_2(PO_4)_3$ is similar to that of $RbZr_2(PO_4)_3$. Both these show the negative overall thermal-expansion values unlike the Li, Na, K and Cs analogues. All these analogues, however, show very low thermal-expansion properties.

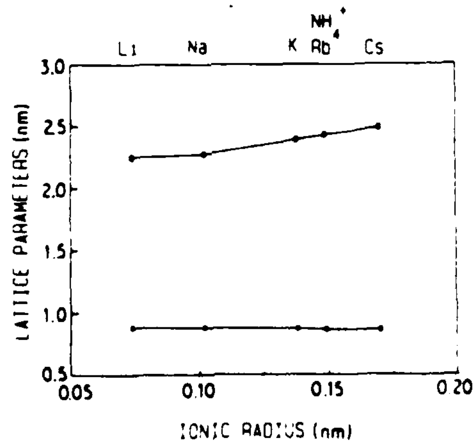

Figure 3 Plot of lattice parameters as a function of ionic radius for the $NH_4Zr_2(PO_4)_3$ and for the alkali members of the NZP family • *a* axis, O, *c* axis

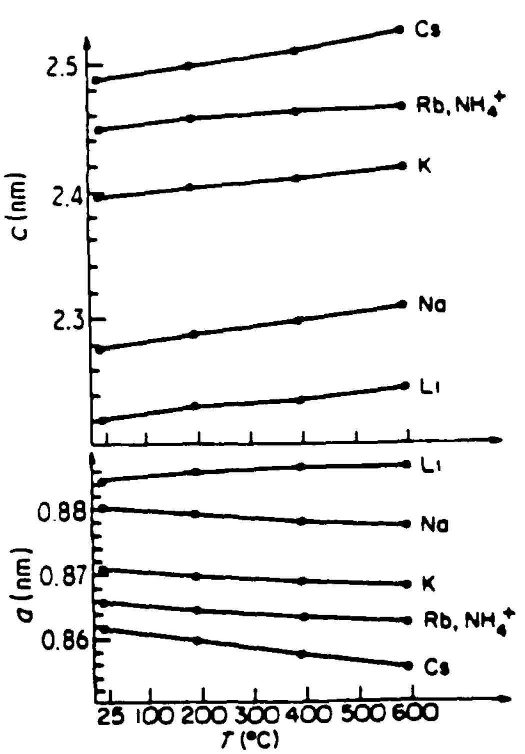

Figure 4 Lattice parameters as a function of temperature for the $NH_4Zr_2(PO_4)_3$ phase in comparison with the alkali members of the NZP family

tion of temperature for $NH_4Zr_2(PO_4)_3$

Temperature	Lattice parameters (nm)	
	a	*c*
25	0 868 076	2 428 208
100	0 867 372	2 430 820
201	0 866 770	2 432 776
301	0 866 211	2 434 545
402	0 865 745	2 435 989

The $\bar{\alpha}_a$ and $\bar{\alpha}_c$ axial coefficients of expansion are -7×10^{-6} and $8\ 24 \times 10^{-6}$, respectively, whereas the overall linear thermal-expansion coefficient, $\bar{\alpha}_l$, is $-1\ 9 \times 10^{-6}$

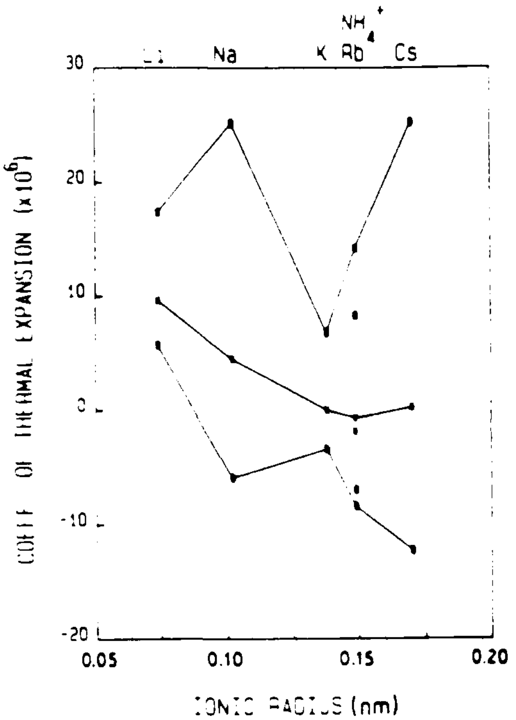

Figure 5 Coefficients of thermal expansion for the $NH_4Zr_2(PO_4)_3$ phase in comparison with the alkali members of the NZP family ○ (lower), $\bar{\alpha}_a$; •, $\bar{\alpha}_l$; ○ (upper), $\bar{\alpha}_c$.

Acknowledgements

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NEW LOW EXPANSION MAGNETIC MATERIALS-A COMPOSITE APPROACH

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INTRODUCTION

A composite ceramic is fabricated by mixing and processing two or more phases which are supposed to be thermodynamically compatible with each other and thus controlling or tailoring a desired property in the composite by varying the amount of each component or by modifying the processing technique. The di/multiphasic concept permits the selection of both materials - both in terms of any special property each phase might have and quantity of each phase. While this concept opens the door wide for tailoring a special property, there are several problems that one may encounter - the intimacy of mixing, the strength of the sintered body, the reactivity of the constituents and the interplay of the elastic forces all combine to determine the effectiveness of the composite material.

In earlier work, the authors have first produced a new family of negative and 'zero' expansion ceramics and then successfully adopted this diphasic approach[1,2] to produce near zero thermal expansion composite ceramics. The strategy was to mix two thermodynamically compatible ceramic phases - one with negative coefficient of thermal expansion (α) and the second one with positive α - and process the mixture by a standard ceramic technique. The negative α phase was chosen from a new structural family of materials now known as [NZP] or [CTP] - discovered recently for low α applications[3,4]. The positive α phase can be selected from several compositions such as $GdPO_4$, Nb_2O_5, $ZrSiO_4$, $Mg_3(PO_4)_2$ and $Zn_3(PO_4)_2$ etc. Figures 1 and 2 demonstrate some of the thermal expansion data of some compositions belonging to $CaZr_4P_6O_{24}$ + Nb_2O_5, $ZrSiO_4$ and MgO systems. It is evident from these results that several compositions exhibit near zero expansion profiles over wide temperature ranges.

In order to fabricate new low thermal expansion magnetic materials the same diphasic strategy was adopted in which Yttrium Iron Garnet (YIG-$Y_3Fe_5O_{12}$) was chosen as a magnetic material with positive α and $Na_4Zr_2Si_3C_{12}$ (another member of NZP-family) as primary phase to control the thermal expansion of the composite ceramic produced. Here in this paper, we present the results of the thermal expansion behavior of various compositions in $Na_4Zr_2Si_3O_{12}$ + YIG system.

treated and sintered at 1000°C/16 hrs and 1200°C/2 days to form single phases of NZP, CZP and NZS. The phase identification of the sintered material was carried out on a GE x-ray diffractometer using a graphite monochromator and CuKα radiation. These sintered pellets were ground to a fine powder (-60 mesh). The diphasic compositions were prepared by adding preformed $Y_3Fe_5O_{12}$ (YIG) powder to NZP, CZP or NZS, in various proportions. The mixture was homogenized in acetone and pelletized again and heat treated at different temperatures. Dilatometric measurements were made on small rectangular bars ($\sim .5 \times 1 \times 1$ cm^3) cut out from the sintered samples in a Harrop Dilatometric Analyzer. The dilatometer was first calibrated using a fused silica standard and adjusting the heating rate to about 1°/minute in the programmer.

RESULTS AND DISCUSSION

The various compositions which were examined in this investigation are listed in the following Table; the sintering temperature and time are also given. The phase composition of the sintered materials was determined by x-rays and is presented in the last column of the Table.

It was observed that only $Na_4Zr_2Si_3O_{12}$ is thermodynamically compatible with $Y_3Fe_5O_{12}$ to form a composite material; NZP and CZP had reacted with YIG to produce Yttrium and Iron phosphates. The composition #3 when sintered at 1200°C produced a partially melted material in which YIG had reacted with NZS but when the same composition was sintered at lower temperature (1040°C) there was no reaction.

The thermal expansion curves of the NZS + YIG system are presented in Figure 3. $\Delta L/L$ (or percent expansion) was measured from room temperature to 500°C at a heating rate of 1°/min. All the three compositions show near 'zero' average thermal expansion between 30° and ~150°C, and up to 500°C α is approximately $3.4 \times 10^{-6}\,{}^\circ C^{-1}$. It is

TABLE: Compositions Studied, Firing Temperature, Time and Phases Present after Sintering

Composition	Temperature (°C)	Time (hrs.)	Phases Present
1. $NaZr_2P_3O_{12} + Y_3Fe_5O_{12}$ (2:1)	1200	18	NZP + YPO_4 + $FePO_4$
2. $CaZr_4P_6O_{24} + Y_3Fe_5O_{12}$ (2:1)	1200	18	CZP + YPO_4 + $FePO_4$
3. $Na_4Zr_2Si_3O_{12} + Y_3Fe_5O_{12}$ (3:1)	1200	16	NZS + YPO_4 + glass (partially melted)
4. $Na_4Zr_2Si_3O_{12} + Y_3Fe_5O_{12}$ (3:1)	1040	15	NZS + YIG
5. $Na_4Zr_2Si_3O_{12} + Y_3Fe_5O_{12}$ (3:2)	1000	15	NZS + YIG
6. $Na_4Zr_2Si_3O_{12} + Y_3Fe_5O_{12}$ (0.85:0.15)	1000	15	NZS + YIG

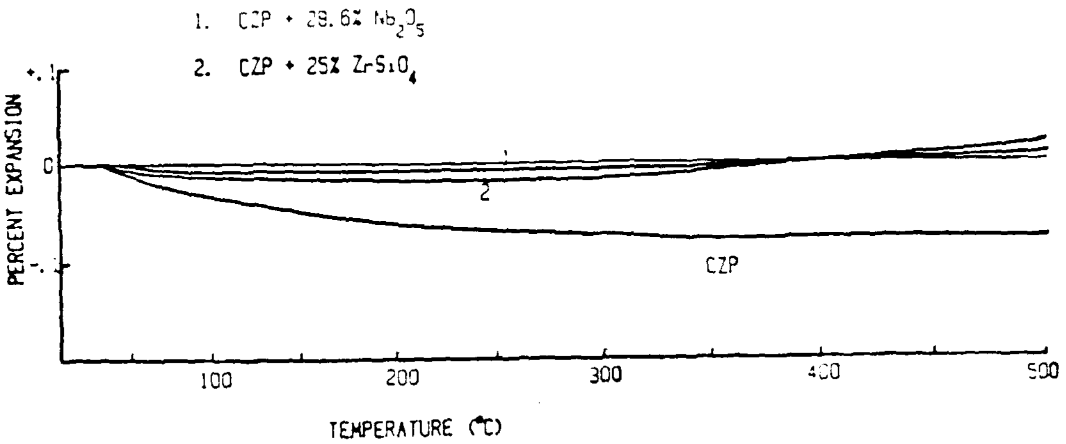

Fig. 1. Thermal Expansion of CZP + Nb_2O_5 and $ZrSiO_4$ systems.

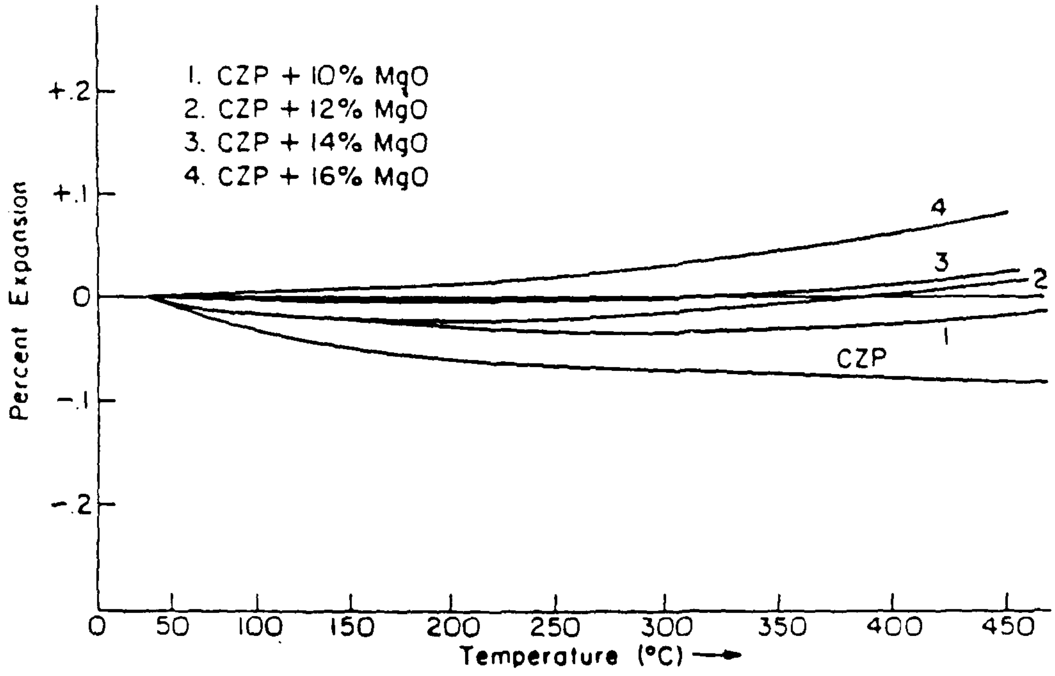

Fig. 2. Thermal Expansions of CZP + MgO System.

EXPERIMENTAL

Single phases of $NaZr_2P_3O_{12}$, $CaZr_4P_6O_{24}$ and $Na_4Zr_2Si_3O_{12}$ (called NZP, CZP and NZS respectively henceforth) were synthesized by solid state reaction using oxide powders as precursors. The stoichiometric amounts of reagent grade $CaCO_3$, Na_2CO_3 (both Fisher Scientific Company), ZrO_2 (Alfa Products) SiO_2 powder (Fisher Scientific Co.) and $NH_4H_2PO_4$ (J.T. Baker Chemical Company) were mixed and homogenized in acetone by hand mixing or ball milling and then air dried. The dry powder was calcined at 200°, 600° and finally at 900°C to drive off the volatiles. The calcined powder was consolidated into 1 inch pellets by cold

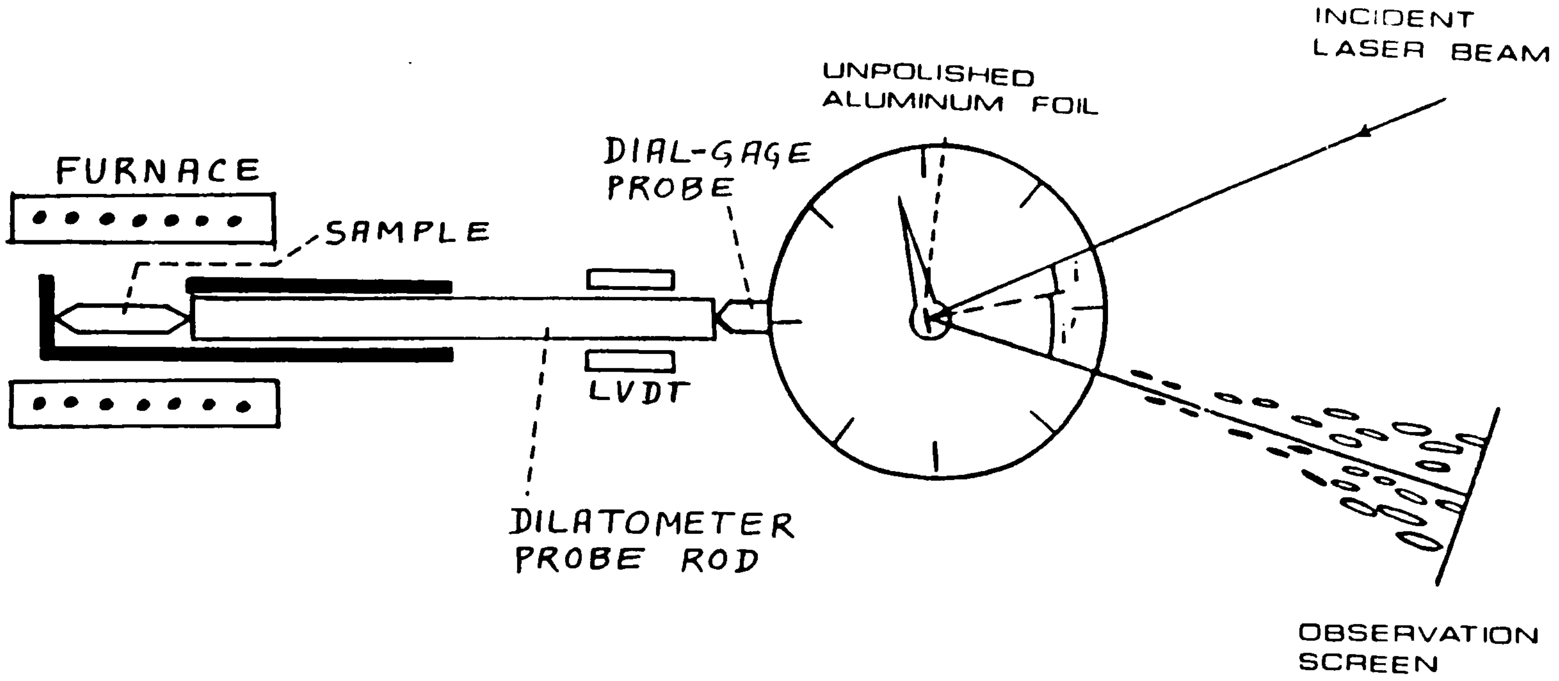
INCIDENT
LASER BEAM
UNPOLISHED
ALUMINUM FOIL
FURNACE
DIAL-GAGE
PROBE
SAMPLE
LVDT
DILATOMETER
PROBE ROD
OBSERVATION
SCREEN

FIGURE 3.

SYNTHESIS AND THERMAL EXPANSION OF $NaGe_2P_3O_{12}$

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ABSTRACT

$NaGe_2P_3O_{12}$ was synthesized by solid state reaction method and its thermal behavior was determined. Due to its low melting behavior, an attempt was made to produce glass-ceramic of $NaGe_2P_3O_{12}$. Bulk thermal expansions of sintered and glass samples of $NaGe_2P_3O_{12}$ were also measured.

MATERIALS INDEX: Thermal Expansion, $NaGe_2P_3O_{12}$, [NZP], Glass-Ceramic

Introduction

$NaGe_2P_3O_{12}$ belongs to [NZP] or [CTP] family of materials which have recently emerged as future candidates for ultra-low thermal expansion applications (1-3). Earlier, Hagman and Kierkegaard (4) had synthesized $NaGe_2P_3O_{12}$ and determined its crystal structure by using a single crystal. They had found that it is iso-structural with $NaZr_2P_3O_{12}$--the parent phase of the [NZP] family--which belongs to R$\bar{3}$C space group and hexagonal lattice. The crystal structure consists of PO_4 tetrahedra and Zr/GeO_6 octahedra linked together through corner sharing in such a manner as to produce a stable and rigid three-dimensional framework structure with a three-dimensionally interconnected network of structural-holes in which Na or any other substituting ion sits. An important feature of the structure is that one can make enormous ionic substitutions (5) at various lattice sites, developing a large number of new compositions.

In the present study, we have synthesized and sintered $NaGe_2P_3O_{12}$ by the traditional ceramic method of powder mixing, formed its glass, and measured the thermal expansion of sintered as well as glass samples. Due to the low melting behavior of $NaGe_2P_3O_{12}$, an attempt was made to produce a glass-ceramic of this compound.

THERMAL EXPANSION MEASUREMENTS BY PHOTODETECTOR BASED LASER BEAM POSITION CHANGE DETERMINATION

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ABSTRACT

A new method for thermal expansion measurements is described. The technique is based on rotation of a laser beam reflected from a probe bar caused by uneven thermal expansions of sample and reference rods. At a distance, the reflected gaussian laser beam is observed with a small photodetector (much smaller than the beam cross-section). The measurement of minute beam position change thus results in related low thermal expansion measurement capability. Experimental arrangement and the sensitivity are described. Some results are also reported.

INTRODUCTION

Many new materials are now being developed with ultra low thermal expansion. These materials cannot be characterized by push-rod dilatometers with desired accuracy particularly when the thermal expansion is nonlinear and the changes over small temperature variations are to be observed. Consequently, many dilatometers based on modern optical interferometry have been developed [1]. The problems with these methods are that they are too complex in terms of instrumentation [2-4], require very long samples [5], etc. A simpler Michelson type of arrangement [6] requires strict conditions on unwanted optical path changes thus requiring vacuum furnaces, etc.

A new optical but non-interferometric approach [7,8] attempts to keep the instrumentation simple still with reasonably good sensitivity. The method utilizes the rotation of a probe bar kept on sample and reference rods on a platform. Uneven thermal expansions of the sample and reference rods will rotate the probe bar. If a laser beam is reflected by a mirror on the probe surface, the beam will be rotated as a result of the thermal expansion of the system. This rotation can be determined by measuring the rotation of laser speckles created by a thin ground glass kept in the path of the reflected laser beam. The ultimate sensitivity of this approach depends on the magnification of the speckles and hence on the laser intensity, TV camera-monitor sensitivity, etc. However, due to the commercial availability of very sensitive photodetectors, the rotation of the laser beam can be measured rather more simply. We explore here the possibility of this approach.

METHOD

The schematic diagram of the experimental arrangement is shown in Fig. 1. A tiny aperture (a 6μm diameter pinhole) is kept on the reflected beam cross section. The usual HeNe lasers are slightly divergent and a typical beam diameter at the laser output is of the order of one mm. This means that after passing the distance to the probe mirror and back to the detector plane, the beam cross-section diameter is more than one mm. The intensity passed by the aperture will thus correspond to its position in the Gaussian profile. A slight rotation in the beam will change its position and hence the intensity on the aperture.

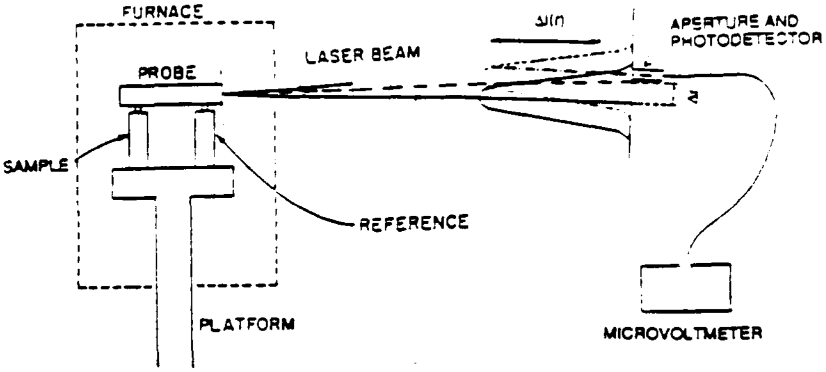

Figure 1. Schematic diagram (not to scale) of the experimental arrangement. Aperture-photodetector combination is supported on a x-y-z translation stage. Signal can also be preamplified and CRT can be used in place of microvoltmeter.

For simplicity, consider the Gaussian intensity distribution of the following form:

$$I(r) = I(o)\exp[-(r^2/2s^2)], \tag{1}$$

where I(o) is the peak intensity at the center (r=0), and s gives the beam radius. The rate of change of the intensity with position r is therefore

$$\Delta I(r)/\Delta r = -(r/s^2)I(r) \tag{2}$$

This rate is somewhat maximum around the middle of the beam radius. However, for the exact measurement of the quantity s, one has to precisely measure the beam profile. Therefore, it is more convenient to calibrate the intensity against the position. This can easily be done by keeping the aperture on a micrometer stage. The relative intensity from the pinhole-photodetector can be measured with a CRT or a microvoltmeter; a DC preamplifier can also be used if needed. However, with our 15mW HeNe laser and a microvoltmeter, we did not require any signal preamplification.

The position change Δr with respect to the temperature change can be related by [7,8]

$$\Delta r = 2\ell L(\alpha_{REF} - \alpha_{SAMPLE})\Delta T/D \tag{3}$$

where L is the common length of the sample and reference rods, α_{REF} and α_{SAMPLE} are the coefficients of thermal expansion of the reference and sample materials respectively, ΔT is the temperature change, D is the effective separation between the sample and the reference, and ℓ is the distance between the probe mirror and the pinhole aperture plane. In terms of the relative length changes of the sample and reference rods, Eq. (3) can be written in the form

$$\left(\frac{\Delta L}{L}\right)_{REF} - \left(\frac{\Delta L}{L}\right)_{SAMPLE} = \frac{\Delta r D}{2\ell L} \tag{4}$$

Thus, for a given D, ℓ and L, the sensitivity is related to the measurement sensitivity of Δr.

In our experimental study, the reference was zerodur rod. The sample was NBS Standard Reference Material 739 Fused-silica whose thermal expansion data is known [9]. The values of ℓ, L and D were 50 cm, 3.111 cm and 1 cm, respectively. The laser beam radius at the aperture plane was about 1.5 mm, i.e. 1500μm. The above data also gives that for a 300°C temperature change, the laser spot should move about 400μm. Since this movement is a considerable part of the beam radius, the beam intensity vs. the position has to be calibrated. The other approach is the null method, i.e. moving the micrometer stage in the vertical direction to get back to the original signal. The micrometer stage has the resolution of about 1μm and at our starting point around the laser beam radius center, the microvoltmeter signal was 481μV ± 1μV with 1μV change per μm position change. This means that the accuracy of measurement of the beam position change is about 1μm. However, since our detector diameter is 5μm, this means the sensitivity of partial relative detector position change exists. For better signal averaging against local defects on the mirror, etc., we are considering here our least count as a conservative value of 6μm for the calculation of errors. For our experimental situation, Eq. (4) gives ($\Delta L/L$) measurement capability of about 2×10^{-6} or for 50°C temperature change, α measurement capability of about 0.4×10^{-7}°C^{-1}.

$$\frac{\delta(\Delta L/L)_{SAMPLE}}{(\Delta L/L)_{SAMPLE}} = \frac{\delta(\Delta r)}{\Delta r} + \frac{\delta D}{D} + \frac{\delta \ell}{\ell} + \frac{\delta L}{L} \qquad (5)$$

The effect of the measurement error $\delta(\Delta T)$ in temperature comes into the picture when the coefficient of thermal expansion is to be determined [8]. Then $-\delta\alpha_{SAMPLE}/\alpha_{SAMPLE}$ is the right-hand side of Eq. (5) added by $\delta(\Delta T)/\Delta T$. Obviously, all the terms except the first one on the right-hand side of Eq. (5) are very small and can be omitted. Then Eqs. (4) and (5) give

$$\delta(\Delta L/L)_{SAMPLE} = -\frac{D\delta(\Delta r)}{2\ell L}, \qquad (6)$$

which is about 2×10^{-6} for our experimental values.

Table 1 shows a typical raw data from such an experiment presented in graphical form in Fig. 2. The calculated values of $(\Delta L/L)_{SAMPLE}$ are plotted in Fig. 3 as the solid curve. The dashed curve represents known values [9]. For zerodur, the values of $(\Delta L/L)_{REF}$ are determined from the curve available for that material [10]. The values are 1, 2, 5, 3, 12, 16 and 21 in terms of 10^{-6}, respectively, at 47°C, 87°C, 127°C, 167°C, 207°C, 247°C and 287°C. These particular temperatures were selected here for the experiment because the sample data at these temperatures is available for comparison [9]. We find a good agreement between determined and available values of $(\Delta L/L)_{SAMPLE}$ as shown in Fig. 3.

Table 1. A typical raw data and some calculated values. The sample was fused silica NBS standard material 739 and the reference was zerodur. L = 3.111 cm, l = 50 cm and D = 1 were used.

Temperature (°C)	Δr (μm)	$\Delta L/L \times 10^6$		
		Reference (Zerodur)	Sample (NBS-Data)	Sample (Determined)
47	42	1	13.5	14.5
87	110	2	36.0	37.4
127	175	5	59.5	61.3
167	237	8	85.0	84.2
207	300	12	110.0	108.5
247	365	16	135.0	133.3
287	424	21	159.0	157.3

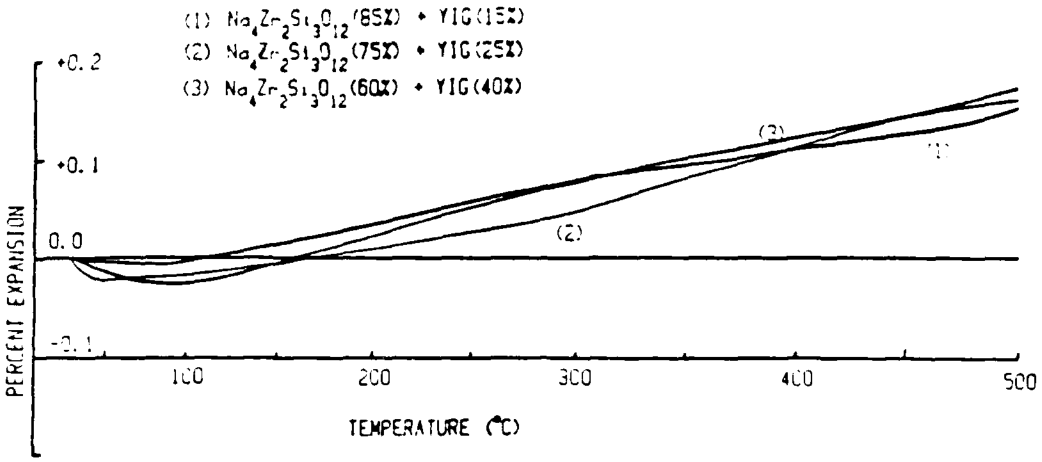

Fig. 3. Thermal Expansion of NZS + $Y_3Fe_5O_{12}$ System.

interesting to note that up to 100°C these compositions demonstrate slightly negative expansion.

It is concluded that by adopting a diphasic approach one can control and tailor a special property in the composite ceramic by varying the amounts of individual components and modifying the processing parameters. In the system $Na_4Zr_2Si_3O_{12}$ + $Y_3Fe_5O_{12}$, some compositions were found to exhibit low thermal expansion behaviour up to 150°C.

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